Glossary

A

Absolute configuration (Section 5.15A): The actual arrangement of groups in a molecule. The absolute configuration of a molecule can be determined by X-ray analysis or by relating the configuration of a molecule, using reactions of known stereochemistry, to another molecule whose absolute configuration is known.

Absorption spectrum (Section 13.9B): A plot of the wavelength (λ) of a region of the spectrum versus the absorbance (A) at each wavelength. The absorbance at a particular wavelength (A_λ) is defined by the equation $A_\lambda = \log(I_R/I_S)$, where I_R is the intensity of the reference beam and I_S is the intensity of the sample beam.

Acetal (Section 16.7B): A functional group, consisting of a carbon bonded to alkoxy groups [i.e., $RCH(OR')_2$ or $R_2C(OR')_2$], derived by adding 2 molar equivalents of an alcohol to an aldehyde or ketone. An acetal synthesized from a ketone is sometimes called a ketal.

Acetoacetic ester synthesis (Section 18.6): A sequence of reactions involving removal of the α-hydrogen of ethyl 3-oxobutanoate (ethyl acetoacetate, also called "acetoacetic ester"), creating a resonance-stabilized anion which then can serve as a nucleophile in an S_N2 reaction. The α-carbon can be substituted twice; the ester functionality can be converted into a carboxylic acid which, after decarboxylation, yields a substituted ketone.

Acetonide (Section 22.5E): A cyclic acetal formed from acetone.

Acetylene (Sections 1.14, 7.1, and 7.11): A common name for ethyne.

Acetylenic hydrogen atom (Sections 3.15, 4.6, and 7.9): A hydrogen atom attached to a carbon atom that is bonded to another carbon atom by a triple bond.

Achiral molecule (Section 5.3): A molecule that is superposable on its mirror image. Achiral molecules lack handedness and are incapable of existing as a pair of enantiomers.

Acid strength (Section 3.6): The strength of an acid is related to its acidity constant, K_a or to its pK_a. The larger the value of its K_a or the smaller the value of its pK_a, the stronger is the acid.

Acidity constant, K_a (Section 3.6A): An equilibrium constant related to the strength of an acid. For the reaction,

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Activating group (Sections 15.10, 15.10D, and 15.11A): A group that when present on a benzene ring causes the ring to be more reactive in electrophilic substitution than benzene itself.

Activation energy, E_{act} (See **Energy of activation** and Section 10.5B)

Active hydrogen compounds (Section 18.8): Compounds in which two electron-withdrawing groups are attached to the same carbon atom (a methylene or methane carbon). The electron-withdrawing groups enhance the acidity of the hydrogens on carbon; these hydrogens are easily removed, creating a resonance-stabilized nucleophilic anion.

Active site (Section 24.9): The location in an enzyme where a substrate binds.

Acyl compounds (Section 17.1): A compound containing the group $(R\text{—}C{=}O)\text{—}$, usually derived from a carboxylic acid, such as an ester, acid halide (acyl halide), amide, or carboxylic acid anhydride.

Acyl group (Section 15.7): The general name for groups with the structure $RCO\text{—}$ or $ArCO\text{—}$.

Acyl halide (Section 15.7): Also called an *acid halide*. A general name for compounds with the structure $RCOX$ or $ArCOX$.

Acyl transfer reactions (Section 17.4): A reaction in which a new acyl compound is formed by a nucleophilic addition-elimination reaction at a carbonyl carbon bearing a leaving group.

Acylation (Section 15.7): The introduction of an acyl group into a molecule.

Acylium ion (Sections 9.16C and 15.7): The resonance-stabilized cation:

$$R\text{—}\overset{+}{C}{=}\ddot{O}: \longleftrightarrow R\text{—}C{\equiv}\overset{+}{O}:$$

Addition polymer (Section 10.10 and Special Topic A): A polymer that results from a stepwise addition of monomers to a chain (usually through a chain reaction) with no loss of other atoms or molecules in the process. Also called a chain-growth polymer.

Addition reaction (Sections 3.1, 8.1–8.9, 8.12, 8.13, 12.1A, 16.6, and 17.4): A reaction that results in an increase in the number of groups attached to a pair of atoms joined by a double or triple bond. An addition reaction is the opposite of an elimination reaction.

Adduct (Section 13.11): The product formed by a Diels-Alder [4+2] cycloaddition reaction, so called because two compounds (a *diene* and a *dienophile*) are added together to form the product.

Aglycone (Section 22.4): The alcohol obtained by hydrolysis of a glycoside.

Aldaric acid (Section 22.6C): An α,ω-dicarboxylic acid that results from oxidation of the aldehyde group and the terminal 1° alcohol group of an aldose.

Alditol (Section 22.7): The alcohol that results from the reduction of the aldehyde or keto group of an aldose or ketose.

Aldol (Section 19.4): A common name for 3-hydoxybutanal, which contains both *ald*ehyde and an alcoh*ol* functional groups. Aldol is formed from the *aldol reaction* (see below) of ethanal (acetaldehyde) with itself.

Aldol additions (Section 19.4): See Aldol reaction and aldol condensation.

Aldol condensation (Section 19.1, Section 19.4C): An aldol reaction that forms an α,β-unsaturated product by dehydration of the β-hydroxy aldehyde or ketone aldol product.

Aldol reactions (Sections 19.4–19.6): Reactions in which the enol or enolate ion of an aldehyde or ketone reacts with the carbonyl group of the same or a different aldehyde or ketone, creating a β-hydroxy aldehyde or ketone and a new carbon-carbon σ-bond.

Aldonic acid (Section 22.6B): A monocarboxylic acid that results from oxidation of the aldehyde group of an aldose.

Aliphatic compound (Section 14.1): A nonaromatic compound such as an alkane, cycloalkane, alkene, or alkyne.

Alkaloid (Special Topic E): A naturally occurring basic compound that contains an amino group. Most alkaloids have profound physiological effects.

Alkanes (Sections 2.2, 4.1–4.3, 4.7, and 4.16): Hydrocarbons having only single (σ) bonds between carbon atoms. Acyclic alkanes have the general formula C_nH_{2n+2}. Monocyclic alkanes have the general formula of C_nH_{2n}. Alkanes are said to be "saturated" because $C—C$ single bonds cannot react to add hydrogen to the molecule.

Alkanide (Section 7.8A): An alkyl anion, $R:^-$, or alkyl species that reacts as though it were an alkyl anion.

Alkenes (Sections 2.2, 4.1, and 4.5): Hydrocarbons having at least one double bond between carbon atoms. Acyclic alkenes have the general formula C_nH_{2n}. Monocyclic alkenes have the general formula of C_nH_{2n-2}. Alkenes are said to be "unsaturated" because their $C{=}C$ double bonds can react to add hydrogen to the molecule, yielding an alkane.

Alkyl group (See **R**): (Sections 2.5A and 4.3A) The designation given to a fragment of a molecule hypothetically derived from an alkane by removing a hydrogen atom. Alkyl group names end in "yl." Example: the methyl group, $CH_3—$, is derived from methane, CH_4.

Alkylation (Sections 7.12, 15.6, and 18.4C): The introduction of an alkyl group into a molecule.

Alkynes (Sections 2.2, 4.1, and 4.6): Hydrocarbons having at least one triple bond between carbon atoms. Acyclic alkynes have the general formula C_nH_{2n-2}. Monocyclic alkynes have the general formula of C_nH_{2n-4}. Alkynes are said to be "unsaturated" because $C{\equiv}C$ triple bonds can react to add two molecules of hydrogen to the molecule, yielding an alkane.

Allyl group (Section 4.5): The $CH_2{=}CHCH_2—$ group.

Allyl (propenyl cation): (Section 13.4) The carbocation formally related to propene by removal of a proton from its methyl group. The two contributing resonance structures of the delocalized carbocation each include a positive charge on a carbon adjacent to the double bond, such that a *p* orbital on each of the three carbons overlaps to delocalize positive charge to each end of the allyl system.

Allyl radical (Sections 13.2A and 13.3): The radical formally related to propene by removal of a hydrogen atom from its methyl group. The two contributing resonance structures of the delocalized radical each include an unpaired electron on a carbon adjacent to the double bond, such that a *p* orbital on each of the three carbons overlaps to delocalize the radical to each end of the allyl system. in which the radical carbon is adjacent to a carbon-carbon double bond.

Allylic carbocation (Sections 13.4, 13.10, and 15.15): A substructure involving a three-carbon delocalized carbocation in which the positively charged carbon is adjacent to a carbon-carbon double bond in each of two contributing resonance structures.

Allylic substituent (Section 13.2): Refers to a substituent on a carbon atom adjacent to a carbon–carbon double bond.

Alpha (α) anomer (Section 22.2C): In the standard Haworth formula representation for a D-hexopyranose, the α anomer has the hemiacetal hydroxyl or acetal alkoxyl group trans to C6. Similar usage applies to other carbohydrate forms regarding the stereochemical relationship of the anomeric hydroxyl or alkoxyl group and the configuration at the carbon bearing the ring oxygen that forms the hemiacetal or acetal.

Alpha (α) carbon (Section 18.1): A carbon adjacent to a carbonyl ($C{=}O$) group.

Alpha (α) helix (Section 24.8A): A secondary structure in proteins where the polypeptide chain is coiled in a right-handed helix.

Alpha (α) hydrogens (Sections 18.1, 18.5C, 18.5D): A hydrogen atom bonded to an α carbon. These hydrogens are significantly more acidic than the typical alkane hydrogen.

Aminium salt (Section 20.3D): The product of the reaction of an amine, acting as a Bronsted-Lowry base, with an acid. The amine can be primary, secondary, or tertiary. The positively charged nitrogen in an aminium salt is attached to at least one hydrogen atom. (An ammonium salt has no hydrogen atoms bonded directly to the nitrogen.)

Amino acid residue (Section 24.4): An amino acid that is part of a peptide.

Angle strain (Section 4.10): The increased potential energy of a molecule (usually a cyclic one) caused by deformation of a bond angle away from its lowest energy value.

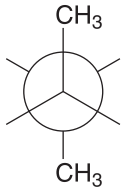
Annulene (Section 14.7B): Monocyclic hydrocarbon that can be represented by a structure having alternating single and double bonds. The ring size of an annulene is represented by a number in brackets, e.g., benzene is [6]annulene and cyclooctatetraene is [8]annulene.

Anomeric carbon (Section 22.2E): The hemiacetal or acetal carbon in the cyclic form of a carbohydrate. The anomeric carbon can have either the α or β stereochemical configuration (using carbohydrate nomenclature), resulting in diastereomeric forms of the carbohydrate called anomers (α-anomers and β-anomers). Anomers differ *only* in the stereochemistry at the anomeric carbon.

Anomers (Section 22.2C): A term used in carbohydrate chemistry. Anomers are diastereomers that differ only in configuration at the acetal or hemiacetal carbon of a sugar in its cyclic form.

Anti addition (Sections 7.14A, 7.15B, and 8.13): An addition that places the parts of the adding reagent on opposite faces of the reactant.

Anti conformation (Section 4.9): An anti conformation of butane, for example, has the methyl groups at an angle of 180° to each other:



Anti conformation of butane

Antiaromatic compound (Section 14.7E): A cyclic conjugated system whose π electron energy is greater than that of the corresponding open-chain compound.

Antibonding molecular orbital (antibonding MO) (Sections 1.11, 1.13, and 1.15): A molecular orbital whose energy is higher than that of the isolated atomic orbitals from which it is constructed. Electrons in an antibonding molecular orbital destabilize the bond between the atoms that the orbital encompasses.

Anticodon (Section 25.5C): A sequence of three bases on transfer RNA (tRNA) that associates with a codon of messenger RNA (mRNA).

anti-Markovnikov addition (Sections 8.2D, 8.7, 8.19, and 10.9): An addition reaction where the hydrogen atom of a reagent becomes bonded to an alkene or alkyne at the carbon having the fewer hydrogen atoms initially. This orientation is the opposite of that predicted by Markovnikov's rule.

Aprotic solvent (Section 6.13C): A solvent whose molecules do not have a hydrogen atom attached to a strongly electronegative element (such as oxygen). For most purposes, this means that an aprotic solvent is one whose molecules lack an —OH group.

Arenium ion (Section 15.2): A general name for the cyclohexadienyl carbocations that form as intermediates in electrophilic aromatic substitution reactions.

Aromatic compound (Sections 2.1, 2.1D, 14.1–14.8, and 14.11): A cyclic conjugated unsaturated molecule or ion that is stabilized by π electron delocalization. Aromatic compounds are characterized by having large resonance energies, by reacting by substitution rather than addition, and by deshielding of protons exterior to the ring in their ^{1}H NMR spectra caused by the presence of an induced ring current.

Aromatic ions (Section 14.7D): Cations and anions that fulfill the criteria for aromaticity (planarity, electron delocalization, and a Hückel number of π-electrons) and thus have additional (aromatic) stability.

Aryl amines (Section 20.1A): A compound in which the carbon of an aromatic ring bears the amine nitrogen atom. Aryl amines can be primary, secondary, or tertiary.

Aryl group (Section 6.1): The general name for a group obtained (on paper) by the removal of a hydrogen from a ring position of an aromatic hydrocarbon. Abbreviated Ar—.

Aryl halide (Section 6.1): An organic halide in which the halogen atom is attached to an aromatic ring, such as a benzene ring.

Atactic polymer (Special Topic B.1): A polymer in which the configuration at the stereogenic centers along the chain is random.

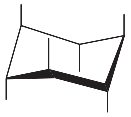
Atomic orbital (AO) (Sections 1.10, 1.11, and 1.15): A volume of space about the nucleus of an atom where there is a high probability of finding an electron. An atomic orbital can be described mathematically by its wave function. Atomic orbitals have characteristic quantum numbers; the *principal quantum number, n*, is related to the energy of the electron in an atomic orbital and can have the values 1, 2, 3, ... The *azimuthal quantum number, l*, determines the angular momentum of the electron that results from its motion around the nucleus, and can have the values 0, 1, 2, . . . , $(n - 1)$. The *magnetic quantum number, m*, determines the orientation in space of the angular momentum and can have values from $+l$ to $-l$. The *spin quantum number, s*, specifies the intrinsic angular momentum of an electron and can have the values of $+{}^1/_2$ and $-{}^1/_2$ only.

Atropisomers (Section 5.18): Conformational isomers that are stable, isolable compounds.

Aufbau principle (Section 1.10A): A principle that guides us in assigning electrons to orbitals of an atom or molecule in its lowest energy state or ground state. The aufbau principle states that electrons are added so that orbitals of lowest energy are filled first.

Autoxidation (Section 10.11D): The reaction of an organic compound with oxygen to form a hydroperoxide.

Axial bond (Section 4.12): The six bonds of a cyclohexane ring (below) that are perpendicular to the general plane of the ring, and that alternate up and down around the ring.



B

Base peak (Section 9.13): The most intense peak in a mass spectrum.

Base strength (Sections 3.6C and 20.3): The strength of a base is inversely related to the strength of its conjugate acid; the weaker the conjugate acid, the stronger is the base. In other words, if the conjugate acid has a large pK_a, the base will be strong.

Benzene (Section 2.2D): The prototypical aromatic compound having the formula C_6H_6. Aromatic compounds are planar, cyclic, and contain 4n + 2 π electrons *delocalized* in contiguous fashion about a ring of electron density in the molecule. Electron delocalization gives aromatic compounds a high degree of stability.

Benzenoid aromatic compound (Section 14.8A): An aromatic compound whose molecules have one or more benzene rings.

Benzyl group (Section 2.4B): The $C_6H_5CH_2$— group.

Benzylic cation (Section 15.12A): A carbocation where the positive charge is on a carbon bonded to a benzene ring. The positive charge is delocalized into the benzene ring through conjugation, resulting in a relatively stable carbocation.

Benzylic radical (Section 15.12): The radical comprised of a methylene (CH_2) group bonded to a benzene ring, wherein the unpaired electron is *delocalized* over the methylene group and the ring. As a highly *conjugated* system, the benzylic radical has greatly enhanced stability.

Benzylic substituent (Sections 15.15): Refers to a substituent on a carbon atom adjacent to a benzene ring.

Benzyne (Section 21.11B): An unstable, highly reactive intermediate consisting of a benzene ring with an additional bond resulting from sideways overlap of sp^2 orbitals on adjacent atoms of the ring.

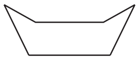
Beta (*β*) anomer (Section 22.2C): In the standard Haworth formula representation for a D-hexopyranose, the β anomer has the hemiacetal hydroxyl or acetal alkoxyl group cis to C6. Similar usage applies to other carbohydrate forms regarding the stereochemical relationship of the anomeric hydroxyl or alkoxyl group and the configuration at the carbon bearing the ring oxygen that forms the hemiacetal or acetal.

Beta (β)-carbonyl compound (Section 18.4C): A compound having two carbonyl groups separated by an intervening carbon atom.

Bicyclic compounds (Sections 4.4B and 4.14): Compounds with two fused or bridged rings.

Bimolecular reaction (Section 6.5): A reaction whose rate-determining step involves two initially separate species.

Boat conformation (Section 4.11): A conformation of cyclohexane that resembles a boat and that has eclipsed bonds along its two sides:



It is of higher energy than the chair conformation.

Boiling point (Sections 2.14A and 2.14D): The temperature at which the vapor pressure of a liquid is equal to the pressure above the surface of the liquid.

Bond angle (Section 1.12): The angle between two bonds originating at the same atom.

Bond dissociation energy (See **Homolytic bond dissociation energy** and Section 10.2)

Bond length (Sections 1.11 and 1.14A): The equilibrium distance between two bonded atoms or groups.

Bond-line formula (Section 1.17C): A formula that shows the carbon skeleton of a molecule with lines. The number of hydrogen atoms necessary to fulfill each carbon's valence is assumed to be present but not written in. Other atoms (e.g., O, Cl, N) are written in.

Bonding molecular orbital (bonding MO) (Sections 1.11 and 1.15): The energy of a bonding molecular orbital is lower than the energy of the isolated atomic orbitals from which it arises. When electrons occupy a bonding molecular orbital they help hold together the atoms that the molecular orbital encompasses.

Broadband (BB) proton decoupling (see **Proton decoupling**) (Section 9.11B): A method of eliminating carbon-proton coupling by irradiating the sample with a wide-frequency ("broadband") energy input in the frequencies in which protons absorb energy. This energy input causes the protons to remain in the high energy state, eliminating coupling with carbon nuclei.

Bromination (Sections 8.12, 10.5C, and 10.6A): A reaction in which one or more bromine atoms are introduced into a molecule.

Bromohydrin (Section 8.14): A compound bearing a bromine atom and a hydroxyl group on adjacent (vicinal) carbons.

Bromonium ion (Section 8.12A): An ion containing a positive bromine atom bonded to two carbon atoms.

Brønsted–Lowry theory of acids and bases (Section 3.2A): An acid is a substance that can donate (or lose) a proton; a base is a substance that can accept (or remove) a proton. The **conjugate acid** of a base is the molecule or ion that forms when a base accepts a proton. The **conjugate base** of an acid is the molecule or ion that forms when an acid loses its proton.

C

Carbanion (Sections 3.4 and 12.1A): A chemical species in which a carbon atom bears a formal negative charge.

Carbene (Section 8.15): An uncharged species in which a carbon atom is divalent. The species :CH_2, called methylene, is a carbene.

Carbenoid (Section 8.15C): A carbene-like species. A species such as the reagent formed when diiodomethane reacts with a zinc–copper couple. This reagent, called the Simmons–Smith reagent, reacts with alkenes to add methylene to the double bond in a stereospecific way.

Carbocation (Sections 3.4, 6.11, and 6.12): A chemical species in which a trivalent carbon atom bears a formal positive charge.

Carbohydrate (Section 22.1A): A group of naturally occurring compounds that are usually defined as polyhydroxyaldehydes or polyhydroxyketones, or as substances that undergo hydrolysis to yield such compounds. In actuality, the aldehyde and ketone groups of carbohydrates are often present as hemiacetals and acetals. The name comes from the fact that many carbohydrates possess the empirical formula $C_x(H_2O)_y$.

Carbon-13 NMR spectroscopy (Section 9.11): NMR spectroscopy applied to carbon. Carbon-13 is NMR active, whereas carbon-12 is not and therefore cannot be studied by NMR. Only 1.1% of all naturally occurring carbon is carbon-13.

Carbonyl group (Section 16.1): A functional group consisting of a carbon atom doubly bonded to an oxygen atom. The carbonyl group is found in aldehydes, ketones, esters, anhydrides, amides, acyl halides, and so on. Collectively these compounds are referred to as carbonyl compounds.

Carboxylic acid derivatives (Section 17.1): Acyl compounds that can be synthesized from a carboxylic acid or another carboxylic acid derivative. Examples include esters, amides, acid halides, anhydrides, etc.

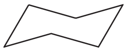
CFC (see **Freon**): A chlorofluorocarbon.

Chain-growth polymer (see **Addition polymer** and Special Topic B): Polymers (macromolecules with repeating units) formed by adding subunits (called *monomers*) repeatedly to form a chain.

Chain reaction (Sections 10.4–10.6, 10.10, and 10.11): A reaction that proceeds by a sequential, stepwise mechanism, in which each step generates the reactive intermediate that causes the next step to occur. Chain reactions have *chain-initiating steps, chain-propagating steps*, and *chain-terminating steps*.

Chain-terminating (dideoxynucleotide) method (Section 25.6): A method of sequencing DNA that involves replicating DNA in a way that generates a family of partial copies, each differing in length by one base pair and containing a nucleotide-specific fluorescent tag on the terminal base. The partial copies of the parent DNA are separated by length, usually using capillary electrophoresis, and the terminal base on each strand is identified by the covalently attached fluorescent marker.

Chair conformation (Section 4.11): The all-staggered conformation of cyclohexane that has no angle strain or torsional strain and is, therefore, the lowest energy conformation:



Chemical shift, δ (Sections 9.2A, 9.7, and 9.11C): The position in an NMR spectrum, relative to a reference compound, at which a nucleus absorbs. The reference compound most often used is tetramethylsilane (TMS), and its absorption point is arbitrarily designated zero. The chemical shift of a given nucleus is proportional to the strength of the magnetic field of the spectrometer. The chemical shift in delta units, δ, is determined by dividing the observed shift from TMS in hertz multiplied by 10^6 by the operating frequency of the spectrometer in hertz.

Chiral auxiliary (Section 13.11C): A group, *present in one enantiomeric form only*, that is appended by a functional group to a reactant so as to provide a chiral influence on the course of the reaction. The chiral auxiliary is removed once the reaction has been completed.

Chiral molecule (Sections 5.3 and 5.12): A molecule that is not superposable on its mirror image. Chiral molecules have handedness and are capable of existing as a pair of enantiomers.

Chirality (Sections 5.1, 5.4, and 5.6): The property of having handedness.

Chirality center (Sections 5.2, 5.4, and 5.17): An atom bearing groups of such nature that an interchange of any two groups will produce a stereoisomer.

Chiron (Section 13.11C): A starting material for a reaction in which a chirality center, *in a single enantiomeric form*, is included. The chiral influence of the chirality center in the chiron leads to enantioselective interactions during the synthesis.

Chlorination (Sections 8.12, 10.3B, 10.4, and 10.5): A reaction in which one or more chlorine atoms are introduced into a molecule.

Chlorohydrin (Section 8.14): A compound bearing a chlorine atom and a hydroxyl group on adjacent (vicinal) carbons.

Cis–trans isomers (Sections 1.13B, 4.13, and 7.2): Diastereomers that differ in their stereochemistry at adjacent atoms of a double bond or on different atoms of a ring. Cis groups are on the same side of a double bond or ring. Trans groups are on opposite sides of a double bond or ring.

Claisen condensation (Section 19.1): A reaction in which an enolate anion from one ester attacks the carbonyl function of another ester, forming a new carbon-carbon σ-bond. A tetrahedral intermediate is involved that, with expulsion of an alkoxyl group, collapses to a β-ketoester. The two esters are said to *"condense"* into a larger product with loss of an alcohol molecule.

Claisen rearrangement (Section 21.9): A [3,3] sigmatropic rearrangement reaction involving an allyl vinyl ether, in which the allyl group of migrates to the other end of the vinyl system, with bond reorganization leading to a γ,δ-unsaturated carbonyl compound.

Codon (Section 25.5C): A sequence of three bases on messenger RNA (mRNA) that contains the genetic information for one amino acid. The codon associates, by hydrogen bonding, with an anticodon of a transfer RNA (tRNA) that carries the particular amino acid for protein synthesis on the ribosome.

Coenzyme (Section 24.9): A small organic molecule that participates in the mechanism of an enzyme and which is bound at the active site of the enzyme.

Cofactor (Section 24.9): A metal ion or organic molecule whose presence is required in order for an enzyme to function.

Concerted reaction (Section 6.6): A reaction where bond forming and bond breaking occur simultaneously (in concert) through a single transition state.

Condensation polymer (see **Step-growth polymer**, Section 17.12, and Special Topic C): A polymer produced when bifunctional monomers (or potentially bifunctional monomers) react with each other through the intermolecular elimination of water or an alcohol. Polyesters, polyamides, and polyurethanes are all condensation polymers.

Condensation reaction (Sections 19.1, 19.2, and 19.4–19.6): A reaction in which molecules become joined through the intermolecular elimination of water or an alcohol.

Configuration (Sections 5.7, 5.15, and 6.8): The particular arrangement of atoms (or groups) in space that is characteristic of a given stereoisomer.

Conformation (Section 4.8): A particular temporary orientation of a molecule that results from rotations about its single bonds.

Conformational analysis (Sections 4.8, 4.9, 4.11, and 4.12): An analysis of the energy changes that a molecule undergoes as its groups undergo rotation (sometimes only partial) about the single bonds that join them.

Conformational stereoisomers (Section 4.9A): Stereoisomers differing in space only due to rotations about single (σ) bonds.

Conformations of cyclohexane (Sections 4.11 and 4.13): Rotations about the carbon-carbon single bonds of cyclohexane can produce different conformations which are interconvertible. The most important are the chair conformation, the boat conformation, and the twist conformation.

Conformer (Section 4.8): A particular staggered conformation of a molecule.

Conjugate acid (Section 3.2A): The molecule or ion that forms when a base accepts a proton.

Conjugate addition (Section 19.7): A form of nucleophilic addition to an α,β-unsaturated carbonyl compound in which the nucleophile adds to the β carbon. Also called Michael addition.

Conjugate base (Section 3.6C): The molecule or ion that forms when an acid loses its proton.

Conjugated protein (Section 24.12): A protein that contains a nonprotein group (called a prosthetic group) as part of its structure.

Conjugated unsaturated system (Section 13.1): Molecules or ions that have an extended π system. A conjugated system has a *p* orbital on an atom adjacent to a multiple bond; the *p* orbital may be that of another multiple bond or that of a radical, carbocation, or carbanion.

Connectivity (Sections 1.3 and 1.17A): The sequence, or order, in which the atoms of a molecule are attached to each other.

Constitutional isomers (Sections 1.3A, 4.2, and 5.2A): Compounds that have the same molecular formula but that differ in their connectivity (i.e., molecules that have the same molecular formula but have their atoms connected in different ways).

Coplanar (Section 7.6D): A conformation in which vicinal groups lie in the same plane.

Copolymer (Special Topic A): A polymer synthesized by polymerizing two monomers.

COSY (Section 9.12) (Correlation Spectroscopy): A two-dimensional NMR method that displays coupling relationships between protons in a molecule.

Coupling (Section 9.2C): In NMR, the splitting of the energy levels of a nucleus under observation by the energy levels of nearby NMR-active nuclei, causing characteristic splitting patterns for the signal of the nucleus being observed. The signal from an NMR-active nucleus will be split into $(2nI + 1)$ peaks, where $n =$ the number of equivalent neighboring magnetic nuclei and I = the spin quantum number. For hydrogen (I = 1/2) this rule devolves to (n + 1), where n = the number of equivalent neighboring hydrogen nuclei.

Coupling constant, J_{ab} (Section 9.9C): The separation in frequency units (hertz) of the peaks of a multiplet caused by spin–spin coupling between atoms a and b.

Covalent bond (Section 1.4B): The type of bond that results when atoms share electrons.

Cracking (Section 4.1A): A process used in the petroleum industry for breaking down the molecules of larger alkanes into smaller ones. Cracking may be accomplished with heat (thermal cracking), or with a catalyst (catalytic cracking).

Crossed-aldol reaction (Section 19.5): An aldol reaction involving two different aldehyde or ketone reactants. If both aldol reactants have α hydrogens, four products can result. Crossed aldol reactions are synthetically useful when one reactant has no α hydrogens, such that it can serve only as an electrophile that is subject to attack by the enolate from the other reactant.

Crown ether (Section 11.16): Cyclic polyethers that have the ability to form complexes with metal ions. Crown ethers are named as *x*-crown-*y* where *x* is the total number of atoms in the ring and *y* is the number of oxygen atoms in the ring.

Curved arrows (Sections 1.8, 3.5, and 10.1): Curved arrows show the direction of electron flow in a reaction mechanism. They point from the source of an electron pair to the atom receiving the pair. Double-barbed curved arrows are used to indicate the movement of a pair of electrons; single-barbed curved arrows are used to indicate the movement of a single electron. Curved arrows are never used to show the movement of atoms.

Cyanohydrin (Sections 16.9 and 17.3): A functional group consisting of a carbon atom bonded to a cyano group and to a hydroxyl group, i.e., $RHC(OH)(CN)$ or $R_2C(OH)(CN)$, derived by adding HCN to an aldehyde or ketone.

Cycloaddition (Section 13.11): A reaction, like the Diels–Alder reaction, in which two connected groups add to the end of a π system to generate a new ring. Also called 1,4-cycloaddition.

Cycloalkanes (Sections 4.1, 4.4, 4.7, 4.10–4.12, 4.15, and 4.16): Alkanes in which some or all of the carbon atoms are arranged in a ring. Saturated cycloalkanes have the general formula C_nH_{2n}.

D

D and L nomenclature (Section 22.2B): A method for designating the configuration of monosaccarides and other compounds in which the reference compound is (+)- or (−)-glyceraldehyde. According to this system, (+)-glyceraldehyde is designated D-(+)-glyceraldehyde and (−)-glyceraldehyde is designated L-(−)-glyceraldehyde. Therefore, a monosaccharide whose highest numbered stereogenic center has the same general configuration as D-(+)-glyceraldehyde is designated a D-sugar; one whose highest numbered stereogenic center has the same general configuration as L-(+)-glyceraldehyde is designated an L-sugar.

Dash structural formulas (Section 1.17A): Structural formulas in which atom symbols are drawn and a line or "dash" represents each pair of electrons (a covalent bond). These formulas show connectivities between atoms but do not represent the true geometries of the species.

Deactivating group (Sections 15.10, 15.10E, 15.10F, and 15.11A): A group that when present on a benzene ring causes the ring to be less reactive in electrophilic substitution than benzene itself.

Debromination (Section 7.10): The elimination of two atoms of bromine from a *vic*-dibromide, or, more generally, the loss of bromine from a molecule.

Debye unit (Section 2.2): The unit in which dipole moments are stated. One debye, D, equals 1×10^{-18} esu cm.

Decarboxylation (Section 17.10): A reaction whereby a carboxylic acid loses CO_2.

Degenerate orbitals (Section 1.10A): Orbitals of equal energy. For example, the three 2*p* orbitals are degenerate.

Dehydration reaction (Sections 7.7 and 7.8): An elimination that involves the loss of a molecule of water from the substrate.

Dehydrohalogenation (Sections 6.15A and 7.6): An elimination reaction that results in the loss of HX from adjacent carbons of the substrate and the formation of a π bond.

Delocalization (Sections 3.11A and 6.11B): The dispersal of electrons (or of electrical charge). Delocalization of charge always stabilizes a system.

Deoxyribonucleic acid (DNA) (Sections 25.1 and 25.4): One of the two molecules (the other is RNA) that carry genetic information in cells. Two molecular strands held together by hydrogen bonds give DNA a "twisted ladder"-like structure, with four types of heterocyclic bases (adenine, cytosine, thymine, and guanine) making up the "rungs" of the ladder.

Dextrorotatory (Section 5.8B): A compound that rotates plane-polarized light clockwise.

Diastereomers (Section 5.2C): Stereoisomers that are not mirror images of each other.

Diastereoselective reaction (See **Stereoselective reaction** and Sections 5.10B and 12.3C)

Diastereotopic hydrogens (or **ligands**) (Section 9.8B): If replacement of each of two hydrogens (or ligands) by the same groups yields compounds that are diastereomers, the two hydrogen atoms (or ligands) are said to be diastereotopic.

1,2-Diaxial interaction (Section 4.12): The interaction between two axial groups that are on adjacent carbon atoms.

Diazonium salts (Sections 20.6A, 20.6B, 20.7, and 20.8): Salts synthesized from the reaction of primary amines with nitrous acid. Diazonium salts have the structure $[R{-}N{\equiv}N]^+\ X^-$. Diazonium salts of primary aliphatic amines are unstable and decompose rapidly; those from primary aromatic amines decompose slowly when cold, and are useful in the synthesis of substituted aromatics and *azo* compounds.

Dieckmann condensation (Section 19.2A): An intramolecular Claisen condensation of a diester; the enolate from one ester group attacks the carbonyl of another ester function in the same molecule, leading to a cyclic product.

Dielectric constant (Section 6.13D): A measure of a solvent's ability to insulate opposite charges from each other. The dielectric constant of a solvent roughly measures its polarity. Solvents with high dielectric constants are better solvents for ions than are solvents with low dielectric constants.

Diels-Alder reaction (Section 13.11): In general terms, a reaction between a conjugated diene (a 4-π-electron system) and a compound containing a double bond (a 2-π-electron system), called a dienophile, to form a cyclohexene ring.

Diene (Section 13.11): A molecule containing two double bonds (*di* = two, *ene* = alk*ene* or double bonds). In a Diels-Alder reaction, a *conjugated* diene in the *s-cis* conformation reacts with a dienophile.

Dienophile (Section 13.11): The diene-seeking component of a Diels–Alder reaction.

Dihedral angle (Sections 4.8 and 9.9D): See Fig. 4.4. The angle between two atoms (or groups) bonded to adjacent atoms, when viewed as a projection down the bond between the adjacent atoms.

Dihydroxylation (Section 8.16): A process by which a starting material is converted into a product containing adjacent alcohol functionalities (called a "1,2-diol" or "glycol").

Dipeptide (Section 24.4): A peptide comprised of two amino acids.

Dipolar ion (Section 24.2C): The charge-separated form of an amino acid that results from the transfer of a proton from a carboxyl group to a basic group.

Dipole moment, μ (Section 2.2): A physical property associated with a polar molecule that can be measured experimentally. It is defined as the product of the charge in electrostatic units (esu) and the distance that separates them in centimeters: $\mu = e \times d$.

Dipole–dipole force (Section 2.13B): An interaction between molecules having permanent dipole moments.

Direct alkylation (Section 18.4C): A synthetic process in which the α-hydrogen of an ester is removed by a strong, bulky base such as LDA, creating a resonance-stabilized anion which will act as a nucleophile in an S_N2 reaction.

Directed aldol reaction (Section 19.5B): A crossed aldol reaction in which the desired enolate anion is generated first and rapidly using a strong base (e.g., LDA) after which the carbonyl reactant to be attacked by the enolate is added. If both a *kinetic enolate anion* and a *thermodynamic enolate anion* are possible, this process favors generation of the kinetic enolate anion.

Disaccharide (Sections 22.1A and 22.12): A carbohydrate that, on a molecular basis, undergoes hydrolytic cleavage to yield two molecules of a monosaccharide.

Dispersion force (or **London force**) (Sections 2.13B, 4.9, and 4.11): Weak forces that act between nonpolar molecules or between parts of the same molecule. Bringing two groups (or molecules) together first results in an attractive force between them because a temporary unsymmetrical distribution of electrons in one group induces an opposite polarity in the other. When groups are brought closer than their *van der Waals radii*, the force between them becomes repulsive because their electron clouds begin to interpenetrate each other.

Distortionless enhanced polarization transfer (DEPT) spectra (Section 9.11E): A technique in ^{13}C NMR spectroscopy by which the number of hydrogens at each carbon, e.g., C, CH, CH_2, and CH_3 can be determined.

Disulfide linkage (Section 24.2A): A sulfur-sulfur single bond in a peptide or protein formed by an oxidative reaction between the thiol groups of two cysteine amino acid residues.

Double bonds (Section 1.2 and 1.13): Bonds composed of four electrons: two electrons in a sigma (σ) bond and two electrons in a pi (π) bond.

Doublet (Section 9.2C): An NMR signal comprised of two peaks with equal intensity, caused by signal splitting from one neighboring NMR-active nucleus.

Downfield (Section 9.2A): Any area or signal in an NMR spectrum that is to the left relative to another. (See "**Upfield**" for comparison.) A signal that is downfield of another occurs at higher frequency (and higher δ and ppm values) than the other signal.

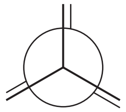
E

(*E*)–(*Z*) system (Section 7.2): A system for designating the stereochemistry of alkene diastereomers based on the priorities of groups in the Cahn–Ingold–Prelog convention. An *E* isomer has the highest priority groups on opposites sides of the double bond, a *Z* isomer has the highest priority groups on the same side of the double bond.

E1 reaction (Sections 6.15C, 6.17, and 6.18B): A unimolecular elimination in which, in a slow, rate-determining step, a leaving group departs from the substrate to form a carbocation. The carbocation then in a fast step loses a proton with the resulting formation of a π bond.

E2 reaction (Sections 6.15C, 6.16, and 6.18B): A bimolecular 1,2 elimination in which, in a single step, a base removes a proton and a leaving group departs from the substrate, resulting in the formation of a π bond.

Eclipsed conformation (Section 4.8A): A temporary orientation of groups around two atoms joined by a single bond such that the groups directly oppose each other.



An eclipsed conformation

Edman degradation (Section 24.5A): A method for determining the *N*-terminal amino acid in a peptide. The peptide is treated with phenylisothiocyanate ($C_6H_5—N{=}C{=}S$), which reacts with the *N*-terminal residue to form a derivative that is then cleaved from the peptide with acid and identified. Automated sequencers use the Edman degradation method.

Electromagnetic spectrum (Section 13.9A): The full range of energies propagated by wave fluctuations in an electromagnetic field.

Electron density surface (Section 1.12B): An electron density surface shows points in space that happen to have the same electron density. An electron density surface can be calculated for any chosen value of electron density. A "high" electron density surface (also called a "bond" electron density surface) shows the *core* of electron density around each atomic nucleus and regions where neighboring atoms share electrons (bonding regions). A "low" electron density surface roughly shows the *outline* of a molecule's electron cloud. This surface gives information about molecular shape and volume, and usually looks the same as a van der Waals or space-filling model of the molecule. (Contributed by Alan Shusterman, Reed College, and Warren Hehre, Wavefunction, Inc.)

Electron impact (EI) (Sections 9.14 and 9.18A): A method of ion formation in mass spectrometry whereby the sample to be analyzed (analyte) is placed in a high vacuum and, when in the gas phase, bombarded with a beam of high-energy electrons. A valence electron is displaced by the impact of the electron beam, yielding a species called the *molecular ion* (if there has been no fragmentation), with a $+1$ charge and an unshared electron (a radical cation).

Electronegativity (Sections 1.4A and 2.2): A measure of the ability of an atom to attract electrons it is sharing with another and thereby polarize the bond.

Electrophile (Sections 3.4A and 8.1A): A Lewis acid, an electron-pair acceptor, an electron-seeking reagent.

Electrophilic aromatic substitutions (Sections 15.1, 15.2, and 21.8): A reaction of aromatic compounds in which an *electrophile* ("electron-seeker" – a positive ion or other electron-deficient species with a full or large partial positive charge) replaces a hydrogen bonded to the carbon of an aromatic ring.

Electrophoresis (Section 25.6A): A technique for separating charged molecules based on their different mobilities in an electric field.

Electrospray ionization (ESI) (Section 9.18A): A method of ion formation in mass spectrometry whereby a solution of the sample to be analyzed (analyte) is sprayed into the vacuum chamber of the mass spectrometer from the tip of a high-voltage needle, imparting charge to the mixture. Evaporation of the solvent in the vacuum chamber yields charged species of the analyte; some of which may have charges greater than $+1$. A family of *m/z* peaks unique to the formula weight of the analyte results, from which the formula weight itself can be calculated by computer.

Electrostatic potential map (maps of electrostatic potential, MEP) (Sections 1.8, 2.2A, and 3.3A): Electrostatic potential maps are models calculated by a computer that show the relative distribution of electron density at some surface of a molecule or ion. They are very useful for understanding interactions between molecules that are based on attraction of opposite charges. Usually we choose the van der Waals surface (approximately the outermost region of electron density) of a molecule to depict the electrostatic potential map because this is where the electron density of one molecule would first interact with another. In an electrostatic potential map, color trending toward red indicates a region with more negative charge, and color trending toward blue indicates a region with less negative charge (or more positive charge). An electrostatic potential map is generated by calculating the extent of charge interaction (electrostatic potential) between an imaginary positive charge and the electron density at a particular point or surface in a molecule. (Contributed by Alan Shusterman, Reed College, and Warren Hehre, Wavefunction, Inc.)

Elimination reaction (Sections 3.1, 6.15–6.17, 7.5, 7.7): A reaction that results in the loss of two groups from the substrate and the formation of a π bond. The most common elimination is a 1,2 elimination or β elimination, in which the two groups are lost from adjacent atoms.

Elimination-addition (via benzyne) (Section 21.11B): A substitution reaction in which a base, under highly forcing conditions, deprotonates an aromatic carbon that is adjacent to a carbon bearing a leaving group. Loss of the leaving group and overlap of the adjacent *p* orbitals creates a species, called *benzyne*, with a π-bond in the plane of the ring (separate from the aromatic π-system). Attack by a nucleophile on this π-bond followed by protonation yields a substituted aromatic compound.

Enamines (Sections 16.8 and 18.9): An *enamine* group consists of an amine function bonded to the sp^2 carbon of an alkene.

Enantiomeric excess or enantiomeric purity (Section 5.9B): A percentage calculated for a mixture of enantiomers by dividing the moles of one enantiomer minus the moles of the other enantiomer by the moles of both enantiomers and multiplying by 100. The enantiomeric excess equals the percentage optical purity.

Enantiomers (Sections 5.2C, 5.3, 5.7, 5.8, and 5.16): Stereisomers that are mirror images of each other.

Enantioselective reaction (See **Stereoselective reaction** and Sections 5.10B and 12.3C)

Enantiotopic hydrogens (or **ligands**) (Section 9.8B): If replacement of each of two hydrogens (or ligands) by the same group yields compounds that are enantiomers, the two hydrogen atoms (or ligands) are said to be enantiotopic.

Endo group (Section 13.11B): A group on a bicyclic compound that is on the same side (syn) as the longest bridge in the compound.

Endergonic reaction (Section 6.7): A reaction that proceeds with a positive free-energy change.

Endothermic reaction (Section 3.9A): A reaction that absorbs heat. For an endothermic reaction ΔH° is positive.

Energy (Section 3.9): Energy is the capacity to do work.

Energy of activation, E_{act} (Section 10.5B): A measure of the difference in potential energy between the reactants and the transition state of a reaction. It is related to, but not the same as, the free energy of activation, $\Delta G^\ddagger$.

Enolate (Sections 18.1, 18.3, and 18.4): The delocalized anion formed when an enol loses its hydroxylic proton or when the carbonyl tautomer that is in equilibrium with the enol loses an α proton.

Enthalpy change (Sections 3.9A and 3.10): Also called the heat of reaction. The *standard enthalpy change*, ΔH°, is the change in enthalpy after a system in its standard state has undergone a transformation to another system, also in its standard state. For a reaction, ΔH° is a measure of the difference in the total bond energy of the reactants and products. It is one way of expressing the change in potential energy of molecules as they undergo reaction. The enthalpy change is related to the free-energy change, ΔG°, and to the entropy change, ΔS°, through the expression:

$$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$$

Entropy change (Section 3.10): The standard entropy change, ΔS°, is the change in entropy between two systems in their standard states. Entropy changes have to do with changes in the relative order of a system. The more random a system is, the greater is its entropy. When a system becomes more disorderly its entropy change is positive.

Enzyme (Section 24.9): A protein or polypeptide that is a catalyst for biochemical reactions.

Enzyme-substrate complex (Section 24.9): The species formed when a substrate (reactant) binds at the active site of an enzyme.

Epimers, epimerization (Sections 18.3A and 22.8): Diastereomers that differ in configuration at only a single tetrahedral chirality center. Epimerization is the interconversion of epimers.

Epoxidation (Section 11.13): The process of synthesizing an expoxide. Peroxycarboxylic acids (RCO_3H) are reagents commonly used for epoxidation.

Epoxide (Sections 11.13 and 11.14): An oxirane. A three-membered ring containing one oxygen and two carbon atoms.

Equatorial bond (Section 4.12): The six bonds of a cyclohexane ring that lie generally around the "equator" of the molecule:

Equilibrium constant, K_{eq} (Section 3.6A): A constant that expresses the position of an equilibrium. The equilibrium constant is calculated by multiplying the molar concentrations of the products together and then dividing this number by the number obtained by multiplying together the molar concentrations of the reactants.

Equilibrium control (See **Thermodynamic control**)

Essential amino acid (Section 24.2B) An amino acid that cannot be synthesized by the body and must be ingested as part of the diet. For adult humans there are eight essential amino acids ($RCH(NH_2)CO_2H$): valine (R = isopropyl), Leucine (R = isobutyl), isoleucine (R = *sec*-butyl), phenylalanine (R = benzyl), threonine (R = 1-hydroxyethyl), methionine (R = 2-(methylthio)ethyl), lysine (R = 4-aminobutyl), and tryptophen (R = 3-methyleneindole).

Essential oil (Section 23.3): A volatile odoriferous compound obtained by steam distillation of plant material.

Esterification (Section 17.7A): The synthesis of an ester, usually involving reactions of carboxylic acids, acid chlorides or acid anhydrides with alcohols.

Exchangeable protons (Section 9.10): Protons that can be transferred rapidly from one molecule to another. These protons are often attached to electronegative elements such as oxygen or nitrogen.

Exergonic reaction (Section 6.7): A reaction that proceeds with a negative free-energy change.

Exo group (Section 13.11B): A group on a bicyclic compound that is on the opposite side (anti) to the longest bridge in the compound.

Exon (Section 25.5A): Short for "expressed sequence," an exon is a segment of DNA that is used when a protein is expressed. (See **Intron**).

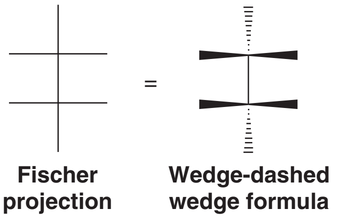
Exothermic reaction (Section 3.9A): A reaction that evolves heat. For an exothermic reaction, ΔH° is negative.

F

Fat (Section 23.2): A triacylglycerol. The triester of glycerol with carboxylic acids.

Fatty acid (Section 23.2): A long-chained carboxylic acid (usually with an even number of carbon atoms) that is isolated by the hydrolysis of a fat.

Fischer projection formula (Sections 5.13 and 22.2C): A two-dimensional formula for representing the configuration of a chiral molecule. By convention, Fischer projection formulas are written with the main carbon chain extending from top to bottom with all groups eclipsed. Vertical lines represent bonds that project behind the plane of the page (or that lie in it). Horizontal lines represent bonds that project out of the plane of the page.



Fluorination (Section 10.5C): A reaction in which fluorine atoms are introduced into a molecule.

Formal charge (Section 1.7): The difference between the number of electrons assigned to an atom in a molecule and the number of electrons it has in its outer shell in its elemental state. Formal charge can be calculated using the formula: $F = Z - S/2 - U$, where F is the formal charge, Z is the group number of the atom (i.e., the number of electrons the atom has in its outer shell in its elemental state), S is the number of electrons the atom is sharing with other atoms, and U is the number of unshared electrons the atom possesses.

Fourier transform NMR (Section 9.5): An NMR method in which a pulse of energy in the radiofrequency region of the electromagnetic spectrum is applied to nuclei whose nuclear magnetic moment is precessing about the axis of a magnetic field. This pulse of energy causes the nuclear magnetic moment to "tip" toward the xy plane. The component of the nuclear magnetic moment in the x–y plane generates ("induces") a radiofrequency signal, which is detected by the instrument. As nuclei relax to their ground states this signal decays over time; this time-dependent signal is called a "Free Induction Decay" (FID) curve. A mathematical operation (a Fourier transform) converts time-dependent data into frequency-dependent data – the NMR signal.

Fragmentation (Section 9.16): Cleavage of a chemical species by the breaking of covalent bonds, as in the formation of fragments during mass spectrometric analysis.

Free energy of activation, $\Delta G^\ddagger$ (Section 6.7): The difference in free energy between the transition state and the reactants.

Free-energy change (Section 3.10): The *standard free-energy change*, ΔG°, is the change in free energy between two systems in their standard states. At constant temperature, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K_{eq}$, where ΔH° is the standard enthalpy change, δS° is the standard entropy change, and K_{eq} is the equilibrium constant. A negative value of ΔG° for a reaction means that the formation of products is favored when the reaction reaches equilibrium.

Free-energy diagram (Section 6.7): A plot of free-energy changes that take place during a reaction versus the reaction coordinate. It displays free-energy changes as a function of changes in bond orders and distances as reactants proceed through the transition state to become products.

Freon (Section 10.11D): A chlorofluorocarbon or CFC.

Frequency, ν (Sections 2.15 and 13.9A): The number of full cycles of a wave that pass a given point in each second.

Fullerenes (Section 14.8C): Cagelike aromatic molecules with the geometry of a truncated icosahedron (or geodesic dome). The structures are composed of a network of pentagons and hexagons.

Each carbon is sp^2 hybridized; the remaining electron at each carbon is delocalized into a system of molecular orbitals that gives the *whole molecule* aromatic character.

Functional class nomenclature (Section 4.3E): A system for naming compounds that uses two or more words to describe the compound. The final word corresponds to the functional group present; the preceding words, usually listed in alphabetical order, describe the remainder of the molecule. Examples are methyl alcohol, ethyl methyl ether, and ethyl bromide.

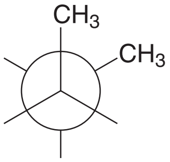
Functional group (Section 2.4): The particular group of atoms in a molecule that primarily determines how the molecule reacts.

Functional group interconversion (Section 6.14): A process that converts one functional group into another.

Furanose (Section 22.2C): A sugar in which the cyclic acetal or hemiacetal ring is five membered.

G

Gauche conformation (Section 4.9): A gauche conformation of butane, for example, has the methyl groups at an angle of 60° to each other:



A gauche conformation of butane

GC/MS analysis (Section 9.19): An analytical method that couples a gas chromatograph (GC) with a mass spectrometer (MS). The GC separates the components of a mixture to be analyzed by sweeping the compounds, in the gas phase, through a column containing an adsorbant called a *stationary phase*. The gaseous molecules will cling to the surface of the stationary phase (be *adsorbed*) with different strengths. Those molecules that cling (adsorb) weakly will pass through the column quickly; those that *adsorb* more strongly will pass through the column more slowly. The separated components of the mixture are then introduced into the mass spectrometer, where they are analyzed.

Geminal (*gem*-) substituents (Section 7.10A): Substituents that are on the same atom.

Gene (Section 25.1): A section of DNA that codes for a given protein.

Genetic code (Sections 25.5C and 25.5D): The correspondence of specific three-base sequences in mRNA (codons) that each code for a specific amino acid. Each codon pairs with the anticodon of a specific tRNA, which in turn carries the corresponding amino acid.

Genome (Sections 25.1 and 25.9): The set of all genetic information coded by DNA in an organism.

Genomics (Section 24.14): The study of the complete set of genetic instructions in an organism.

Glycan (see **Polysaccharide** and Section 22.13): An alternate term for a polysaccharide; monosaccharies joined together by glycosidic linkages.

Glycol (Sections 4.3F and 8.16): A diol.

Glycolipids (Section 22.16): Carbohydrates joined through glycosidic linkages to lipids.

Glycoproteins (Section 22.16): Carbohydrates joined through glycosidic linkages to proteins.

Glycoside (Section 22.4): A cyclic mixed acetal of a sugar with an alcohol.

Grignard reagent (Section 12.6B): An organomagnesium halide, usually written RMgX.

Ground state (Section 1.12): The lowest electronic energy state of an atom or molecule.

H

^1H—^1H correlation spectroscopy (COSY) (Section 9.12): A two-dimensional NMR method used to display the coupling between hydrogen atoms.

Haloform reaction (Section 18.3C): A reaction specific to methyl ketones. In the presence of base multiple halogenations occur at the carbon of the methyl group; excess base leads to acyl substitution of the trihalomethyl group, resulting in a carboxylate anion and a *haloform* (CHX_3).

Halogenation (Sections 10.3–10.6 and 10.8): A reaction in which one or more halogen atoms are introduced into a molecule.

Halohydrin (Section 8.14): A compound bearing a halogen atom and a hydroxyl group on adjacent (vicinal) carbons.

Halonium ion (Section 8.12A): An ion containing a positive halogen atom bonded to two carbon atoms.

Hammond–Leffler postulate (Section 6.13A): A postulate stating that the structure and geometry of the transition state of a given step will show a greater resemblance to the reactants or products of that step depending on which is closer to the transition state in energy. This means that the transition state of an endothermic step will resemble the products of that step more than the reactants, whereas the transition state of an exothermic step will resemble the reactants of that step more than the products.

Heat of hydrogenation (Section 7.3A): The standard enthalpy change that accompanies the hydrogenation of 1 mol of a compound to form a particular product.

Heisenberg uncertainty principle (Section 1.11): A fundamental principle that states that both the position and momentum of an electron (or of any object) cannot be exactly measured simultaneously.

Hemiacetal (Sections 16.7A and 22.2C): A functional group, consisting of an sp^3 carbon atom bearing both an alkoxyl group and a hydroxyl group [i.e., $RCH(OH)(OR')$ or $R_2C(OH)(OR')$].

Hemiketal (See **Hemiacetal** and Section 16.7A)

Henderson-Hasselbalch equation (Section 24.2): The Henderson-Hasselbalch equation ($pK_a = pH + \log[HA]/[A^-]$) shows that when the concentration of an acid and its conjugate base are equal, the pH of the solution equals the pK_a of the acid.

Hertz (Hz) (Sections 9.7A, 9.9C, and 13.9A): The frequency of a wave. Now used instead of the equivalent cycles per second (cps).

Heteroatom (Section 2.3): Atoms such as oxygen, nitrogen, sulfur and the halogens that form bonds to carbon and have unshared pairs of electrons.

Heterocyclic amines (Section 20.1B): A secondary or tertiary amine in which the nitrogen group is part of a carbon-based ring.

Heterocyclic compound (Sections 14.9): A compound whose molecules have a ring containing an element other than carbon.

Heterogeneous catalysis (Sections 7.13 and 7.14): Catalytic reactions in which the catalyst is insoluble in the reaction mixture.

Heterolysis (Section 3.1A): The cleavage of a covalent bond so that one fragment departs with both of the electrons of the covalent bond that joined them. Heterolysis of a bond normally produces positive and negative ions.

Heteronuclear correlation spectroscopy (HETCOR or C-H HETCOR) (Section 9.12): A two-dimensional NMR method used to display the coupling between hydrogens and the carbons to which they are attached.

Heterotopic (chemically nonequivalent atoms) (Section 9.8A): Atoms in a molecule where replacement of one or the other leads to a new compound. Heterotopic atoms are not chemical shift equivalent in NMR spectroscopy.

Hofmann rule (Sections 7.6C and 20.12A): When an elimination yields the alkene with the less substituted double bond, it is said to follow the Hofmann rule.

HOMO (Sections 3.3A and 13.9C): The highest occupied molecular orbital.

Homogeneous catalysis (Sections 7.13 and 7.14A): Catalytic reactions in which the catalyst is soluble in the reaction mixture.

Homologous series (Section 4.7): A series of compounds in which each member differs from the next member by a constant unit.

Homolysis (Sections 3.1A and 10.1): The cleavage of a covalent bond so that each fragment departs with one of the electrons of the covalent bond that joined them.

Homolytic bond dissociation energy, *DH*° (Section 10.2): The enthalpy change that accompanies the homolytic cleavage of a covalent bond.

Homotopic (chemically equivalent) atoms (Section 9.8A): Atoms in a molecule where replacement of one or another results in the same compound. Homotopic atoms are chemical shift equivalent in NMR spectroscopy.

Hückel's rule (Section 14.7): A rule stating that planar monocyclic rings with $(4n + 2)$ delocalized π electrons (i.e., with 2, 6, 10, 14, . . . , delocalized π electrons) will be aromatic.

Hund's rule (Section 1.10A): A rule used in applying the aufbau principle. When orbitals are of equal energy (i.e., when they are degenerate), electrons are added to each orbital with their spins unpaired, until each degenerate orbital contains one electron. Then electrons are added to the orbitals so that the spins are paired.

Hybridization of atomic orbitals (Sections 1.12 and 1.15): A mathematical (and theoretical) mixing of two or more atomic orbitals to give the same number of new orbitals, called *hybrid orbitals*, each of which has some of the character of the original atomic orbitals.

Hydration (Sections 8.5–8.10 and 11.4): The addition of water to a molecule, such as the addition of water to an alkene to form an alcohol.

Hydrazone (Section 16.8B): An imine in which an amino group ($-NH_2$, $-NHR$, $-NR_2$) is bonded to the nitrogen atom.

Hydride (Section 7.8): A hydrogen anion, $H:^-$ Hydrogen with a filled 1s shell (containing two electrons) and negative charge.

Hydroboration (Sections 8.7, 8.8, and 11.4): The addition of a boron hydride (either BH_3 or an alkylborane) to a multiple bond.

Hydrocarbon (Section 2.2): A molecular containing only carbon and hydrogen atoms.

Hydrogen abstraction (Section 10.1B): The process by which a species with an unshared electron (a radical) removes a hydrogen atom from another species, breaking the bond to the hydrogen homolytically.

Hydrogen bond (Sections 2.13B, 2.13E, and 2.13F): A strong dipole–dipole interaction ($4–38\ \text{kJ mol}^{-1}$) that occurs between hydrogen atoms bonded to small strongly electronegative atoms (O, N, or F) and the nonbonding electron pairs on other such electronegative atoms.

Hydrogenation (Sections 4.16A, 7.3A, and 7.13–7.15): A reaction in which hydrogen adds to a double or triple bond. Hydrogenation is often accomplished through the use of a metal catalyst such as platinum, palladium, rhodium, or ruthenium.

Hydrophilic group (Sections 2.13D and 23.2C): A polar group that seeks an aqueous environment.

Hydrophobic group (or **lipophilic group**) (Sections 2.13D and 23.2C): A nonpolar group that avoids an aqueous surrounding and seeks a nonpolar environment.

Hydroxylation (Sections 8.16 and 11.15): The addition of hydroxyl groups to each carbon or atom of a double bond.

Hyperconjugation (Sections 4.8 and 6.11B): Electron delocalization (via orbital overlap) from a filled bonding orbital to an adjacent unfilled orbital. Hyperconjugation generally has a stabilizing effect.

I

Imines (Section 16.8): A structure with a carbon-nitrogen double bond. If the groups bonded to carbon are not the same, (*E*) and (*Z*) isomers are possible.

Index of hydrogen deficiency (Section 4.17): The index of hydrogen deficiency (or IHD) equals the number of pairs of hydrogen atoms that must be subtracted from the molecular formula of the corresponding alkane to give the molecular formula of the compound under consideration.

Induced fit hypothesis (Section 24.9): An hypothesis regarding enzyme reactivity whereby formation of the enzyme-substrate complex causes conformational changes in the enzyme that facilitate conversion of the substrate to product.

Inductive effect (Sections 3.8B, 3.11B, and 15.11B): An intrinsic electron-attracting or -releasing effect that results from a nearby dipole in the molecule and that is transmitted through space and through the bonds of a molecule.

Infrared (IR) spectroscopy (Section 2.15): A type of optical spectroscopy that measures the absorption of infrared radiation. Infrared spectroscopy provides structural information about functional groups present in the compound being analyzed.

Inhibitor (Section 24.9): A compound that can negatively alter the activity of an enzyme.

Integration (Section 9.2B): A numerical value representing the relative area under a signal in an NMR spectrum. In ^1H NMR, the integration value is proportional to the number of hydrogens producing a given signal.

Intermediate (Sections 3.1, 6.10, and 6.11): A transient species that exists between reactants and products in a state corresponding to a local energy minimum on a potential energy diagram.

Intermolecular forces (Sections 2.13B and 2.13F): Also known as van der Waals forces. Forces that act between molecules because of permanent (or temporary) electron distributions. Intermolecular forces can be attractive or repulsive. Dipole-dipole forces (including hydrogen bonds) and dispersion forces (also called London forces), are intermolecular forces of the van der Waal type.

Intron (Section 25.5A): Short for "intervening sequence," an intron is a segments of DNA that is not actually used when a protein is expressed, even though it is transcripted into the initial mRNA.

Inversion of configuration (Sections 6.6 and 6.14): At a tetrahedral atom, the process whereby one group is replaced by another bonded 180° opposite to the original group. The other groups at the tetrahedral atom "turn inside out" (shift) in the same way that an umbrella "turns inside out." When a chirality center undergoes configuration inversion, its (*R*,*S*) designation may switch, depending on the relative Chan-Ingold-Prelog priorities of the groups before and after the reaction.

Iodination (Section 10.5C): A reaction in which one or more iodine atoms are introduced into a molecule.

Ion (Sections 1.4A and 3.1A): A chemical species that bears an electrical charge.

Ion–dipole force (Section 2.13D): The interaction of an ion with a permanent dipole. Such interactions (resulting in solvation) occur between ions and the molecules of polar solvents.

Ion-ion forces (Section 2.14A): Strong electrostatic forces of attraction between ions of opposite charges. These forces hold ions together in a crystal lattice.

Ion sorting (Section 9.18B): Sorting of ions in a mass spectrometer by m/z. Ions are presented on the x-axis of the mass spectrum in order of increasing m/z. If $z = +1$, m/z is equivalent to the molecular mass of the molecule.

Ionic bond (Section 1.4A): A bond formed by the transfer of electrons from one atom to another resulting in the creation of oppositely charged ions.

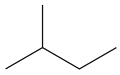
Ionic reaction (Sections 3.1A and 10.1): A reaction involving ions as reactants, intermediates, or products. Ionic reactions occur through the heterolysis of covalent bonds.

Ionization (Section 9.14): Conversion of neutral molecules to ions (charged species).

Isoelectric point (p*I*) (Section 24.2C): The pH at which the number of positive and negative charges on an amino acid or protein are equal.

Isomers (Sections 1.3A and 5.2): Different molecules that have the same molecular formula.

Isoprene unit (Section 23.3): A name for the structural unit found in all terpenes:



Isotactic polymer (Special Topic B.1): A polymer in which the configuration at each stereogenic center along the chain is the same.

Isotopes (Section 1.2A): Atoms that have the same number of protons in their nuclei but have differing atomic masses because their nuclei have different numbers of neutrons.

IUPAC system (Section 4.3): (also called the "systematic nomenclature") A set of nomenclature rules overseen by the International Union of Pure and Applied Chemistry (IUPAC) that allows every compound to be assigned an unambiguous name.

K

Karplus correlation (Section 9.9D): An empirical correlation between the magnitude of an NMR coupling constant and the dihedral angle between two coupled protons. The dihedral angles derived in this manner can provide information about molecular geometries.

Kekulé structure (Sections 2.1D and 14.4): A structure in which lines are used to represent bonds. The Kekulé structure for benzene is a hexagon of carbon atoms with alternating single and double bonds around the ring, and with one hydrogen atom attached to each carbon.

Ketal (See **Acetal** and Section 16.7B)

Keto and enol forms (Sections 18.1–18.3): Tautomeric forms of a compound related by a common resonance-stabilized intermediate. An *enol* structure consists of an alcohol functionality bonded to the sp^2 carbon of an alkene. Shifting the hydroxyl proton to the alkene and creation of a carbon-oxygen π-bond results in the *keto* form of the species.

Ketose (Section 22.2A): A monosaccharide containing a ketone group or a hemiacetal or acetal derived from it.

Kinetic control (Sections 7.6B, 13.10A): A principle stating that when the ratio of products of a reaction is determined by relative rates of reaction, the most abundant product will be the one that is formed fastest. Also called rate control.

Kinetic energy (Section 3.9): Energy that results from the motion of an object. Kinetic energy $(KE) = {}^1/_2 mv^2$, where m is the mass of the object and v is its velocity.

Kinetic enolate (Section 18.4A): In a situation in which more than one enolate anion can be formed, the *kinetic enolate anion* is that which is formed most rapidly. This is usually the enolate anion with the less substituted double bond; the decrease in steric hindrance permits more rapid deprotonation by the base. A kinetic enolate anion is formed predominantly under conditions that do not permit the establishment of an equilibrium.

Kinetic resolution (Section 5.10B): A process in which the rate of a reaction with one enantiomer is different than with the other, leading to a preponderance of one product stereoisomer. This process is said to be "stereoselective" in that it leads to the preferential formation of one stereoisomer over other stereoisomers that could possibly be formed.

Kinetics (Section 6.5): A term that refers to rates of reactions.

L

Lactam (Section 17.8I): A cyclic amide.

Lactone (Section 17.7C): A cyclic ester.

LCAO (linear combination of atomic orbitals, Section 1.11): A mathematical method for arriving at wave functions for molecular obitals that involves adding or subtracting wave functions for atomic orbitals.

Leaving group (Sections 6.2, 6.4, and 6.13E): The substituent that departs from the substrate in a nucleophilic substitution reaction.

Leveling effect of a solvent (Section 3.15): An effect that restricts the use of certain solvents with strong acids and bases. In principle, no acid stronger than the conjugate acid of a particular solvent can exist to an appreciable extent in that solvent, and no base stronger than the conjugate base of the solvent can exist to an appreciable extent in that solvent.

Levorotatory (Section 5.8B): A compound that rotates plane-polarized light in a counterclockwise direction.

Lewis structure (or **electron-dot structure**) (Sections 1.4B and 1.5): A representation of a molecule showing electron pairs as a pair of dots or as a dash.

Lewis acid–base theory (Section 3.3): An acid is an electron pair acceptor, and a base is an electron pair donor.

Lipid (Section 23.1): A substance of biological origin that is soluble in nonpolar solvents. Lipids include fatty acids, triacylglycerols (fats and oils), steroids, prostaglandins, terpenes and terpenoids, and waxes.

Lipid bilayers (Section 23.6A): A two-layer noncovalent molecular assembly comprised primarily of phospholipids. The hydrophobic phospholipid "tail" groups of each layer orient toward each other in the center of the two-layered structure due to attractive dispersion forces. The hydrophilic "head" groups of the lipids orient toward the aqueous exterior of the bilayer. Lipid bilayers are important in biological systems such as cell membranes.

Lipophilic group (or **hydrophobic group**) (Sections 2.13D and 23.2C): A nonpolar group that avoids an aqueous surrounding and seeks a nonpolar environment.

Lithium diisopropylamide (LDA) (Section 18.4): $(i\text{-}C_3H_7)_2N^-Li^+$ The lithium salt of diisopropylamine. A strong base used to form *lithium enolates* from carbonyl compounds.

Lock-and-key hypothesis (Section 24.9): An hypothesis that explains enzyme specificity on the basis of complementary geometry between the enzyme (the "lock") and the substrate (the "key"), such that their shapes "fit together" correctly for a reaction to occur.

LUMO (Sections 3.3A and 13.9C): The lowest unoccupied molecular orbital.

M

Macromolecule (Section 10.10): A very large molecule.

Magnetic resonance imaging (MRI) (Section 9.12): A technique based on NMR spectroscopy that is used in medicine.

Malonic ester synthesis (Section 18.7): A reaction in which the α-hydrogen of diethyl propanedioate (diethyl malonate, also called "malonic ester") is removed, creating a resonance-stabilized anion which can serve as a nucleophile in an S_N2 reaction. The α-carbon can be substituted twice; the ester functionalities can be converted into a carboxylic acid which, after decarboxylation, will yield a substituted ketone.

Mannich reaction (Section 19.8): The reaction of an enol with an iminium cation (formed from the reaction of a primary or secondary amine with formaldehyde) to yield a β-aminoalkyl carbonyl compound.

Markovnikov's rule (Sections 8.2 and 8.19): A rule for predicting the regiochemistry of electrophilic additions to alkenes and alkynes that can be stated in various ways. As originally stated (in 1870) by Vladimir Markovnikov, the rule provides that "if an unsymmetrical alkene combines with a hydrogen halide, the halide ion adds to the carbon with the fewer hydrogen atoms." More commonly the rule has been stated in reverse: that in the addition of HX to an alkene or alkyne the hydrogen atom adds to the carbon atom that already has the greater number of hydrogen atoms. A modern expression of Markovnikov's rule is: *In the ionic addition of an unsymmetrical reagent to a multiple bond, the positive portion of the reagent (the electrophile) attaches itself to a carbon atom of the reagent in the way that leads to the formation of the more stable intermediate carbocation.*

Mass spectrometry (MS) (Section 9.13): A technique, useful in structure elucidation, that involves the generation of ions from a molecule, the sorting and detecting of the ions, and the display of the result in terms of the mass/charge ratio and relative amount of each ion.

Matrix-assisted laser desorption-ionization (MALDI) (Section 9.18A): A method in mass spectrometry for ionizing analytes that do not ionize well by electrospray ionization. The analyte is mixed with low molecular weight organic molecules that can absorb energy from a laser and then transfer this energy to the analyte, producing $+1$ ions which are then analyzed by the mass spectrometer.

Mechanism (See **Reaction mechanism**)

Melting Point (Section 2.14A): The temperature at which an equilibrium exists between a well-ordered crystalline substance and the more random liquid state. It reflects the energy needed to overcome the attractive forces between the units (ions, molecules) that comprise the crystal lattice.

Meso compound (Section 5.12A): An optically inactive compound whose molecules are achiral even though they contain tetrahedral atoms with four different attached groups.

Mesylate (Section 11.10): A methanesulfonate ester. Methanesulfonate esters are compounds that contain the CH_3SO_3— group, i.e., CH_3SO_3R.

Meta directors (Section 15.10B): An electron-withdrawing group on an aromatic ring. The major product of electrophilic aromatic substitution on a ring bearing a meta-directing group will have the newly substituted electrophile located meta to the substituent.

Methanide (Section 7.8): A methyl anion, $^-{:}CH_3$, or methyl species that reacts as though it were a methyl anion.

Methylene (Section 8.15A): The carbene with the formula $:CH_2$.

Methylene group (Section 2.4B): The —CH_2— group.

Micelle (Section 23.2C): A spherical cluster of ions in aqueous solution (such as those from a soap) in which the nonpolar groups are in the interior and the ionic (or polar) groups are at the surface.

Michael addition (See **Conjugate addition** and Sections 18.9 and 19.7): A reaction between an active hydrogen compound and an α,β-unsaturated carbonyl compound. The attack by the anion of the active hydrogen compound takes place at the β-carbon of the α,β-unsaturated carbonyl compound. A Michael addition is a type of conjugate addition.

Molar absorptivity, ε (Section 13.9B): A proportionality constant that relates the observed absorbance (A) at a particular wavelength (λ) to the molar concentration of the sample (C) and the length (l) (in centimeters) of the path of the light beam through the sample cell:

$$\varepsilon = A/C \times l$$

Molecular formula (Section 1.3A): A formula that gives the total number of each kind of atom in a molecule. The molecular formula is a whole number multiple of the empirical formula. For example the molecular formula for benzene is C_6H_6; the empirical formula is CH.

Molecular ion (Sections 9.14, 9.15, and 9.17): The cation produced in a mass spectrometer when one electron is dislodged from the parent molecule, symbolized $M^{\dot{+}}$.

Molecular orbital (MO) (Sections 1.11 and 1.15): Orbitals that encompass more than one atom of a molecule. When atomic orbitals combine to form molecular orbitals, the number of molecular orbitals that results always equals the number of atomic orbitals that combine.

Molecularity (Section 6.5): The number of species involved in a single step of a reaction (usually the rate-determining step).

Molecule (Section 1.4B): An electrically neutral chemical entity that consists of two or more bonded atoms.

Monomer (Section 10.10): The simple starting compound from which a polymer is made. For example, the polymer polyethylene is made from the monomer ethylene.

Monosaccharide (Sections 22.1A and 22.2): The simplest type of carbohydrate, one that does not undergo hydrolytic cleavage to a simpler carbohydrate.

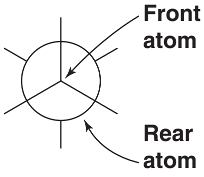
Mutarotation (Section 22.3): The spontaneous change that takes place in the optical rotation of α and β anomers of a sugar when they are dissolved in water. The optical rotations of the sugars change until they reach the same value.

N

Nanotube (Section 14.8C): A tubular structure with walls resembling fused benzene rings, capped by half of a “buckyball” (buckminsterfullerene) at each end. The entire structure exhibits aromatic character.

Neighboring-group participation (Problem 6.49): The effect on the course or rate of a reaction brought about by another group near the functional group undergoing reaction.

Newman projection formula (Section 4.8A): A means of representing the spatial relationships of groups attached to two atoms of a molecule. In writing a Newman projection formula we imagine ourselves viewing the molecule from one end directly along the bond axis joining the two atoms. Bonds that are attached to the front atom are shown as radiating from the center of a circle; those attached to the rear atom are shown as radiating from the edge of the circle:



Nitrogen rule (Section 9.17B): A rule that states that if the mass of the molecular ion in a mass spectrum is an even number, the parent compound contains an even number of nitrogen atoms, and conversely.

***N*-nitrosoamines** (Section 20.6C): Amines bearing an $N{=}O$ on the nitrogen, such as $R{-}NH{-}N{=}O$ or $Ar{-}NH{-}N{=}O$. Often referred to as “nitrosamines” in the popular press. N-nitrosoamines are very powerful carcinogens.

Node (Section 1.9): A place where a wave function (ψ) is equal to zero. The greater the number of nodes in an orbital, the greater is the energy of the orbital.

Nonbenzenoid aromatic compound (Section 14.8B): An aromatic compound, such as azulene, that does not contain benzene rings.

Nuclear magnetic resonance (NMR) spectroscopy (Sections 9.2 and 9.11A): A spectroscopic method for measuring the absorption of radio frequency radiation by certain nuclei when the nuclei are in a strong magnetic field. The most important NMR spectra for organic chemists are ^1H NMR spectra and ^{13}C NMR spectra. These two types of spectra provide structural information about the carbon framework of the molecule, and about the number and environment of hydrogen atoms attached to each carbon atom.

Nucleic acids (Sections 25.1, 25.4, and 25.5): Biological polymers of nucleotides. DNA and RNA are, respectively, nucleic acids that preserve and transcribe hereditary information within cells.

Nucleophile (Sections 3.4A, 6.2, 6.3, and 6.13B): A Lewis base, an electron pair donor that seeks a positive center in a molecule.

Nucleophilic addition-elimination (Section 17.4): Addition of a nucleophile to a carbonyl (or other trigonal) carbon, yielding a tetrahedral intermediate, followed by elimination of a leaving group to yield a trigonal planar product.

Nucleophilic addition to the carbonyl carbon (Section 16.6): A reaction in which a *nucleophile* (an electron-pair donor) forms a bond to the carbon of a *carbonyl* ($C{=}O$) group. To avoid violating the octet rule, the electrons of the carbon-oxygen π-bond shift to the oxygen, resulting in a four-coordinate (tetrahedral) carbon.

Nucleophilic aromatic substitution (Section 21.11A): A substitution reaction in which a nucleophile attacks an aromatic ring bearing strongly electron-withdrawing groups in ortho and/or para positions relative to the site of attack and the leaving group. This step is an addition reaction that yields and aryl carbanion (called a Meisenheimer Complex) which is stabilized by the electron-withdrawing groups on the ring. Loss of the leaving group in an elimination step regenerates the aromatic system, yielding a substituted aromatic compound by what was, overall, an addition-elimination process.

Nucleophilic substitution reaction (Section 6.2): A reaction initiated by a nucleophile (a species with an unshared electron pair) in which the nucleophile reacts with a substrate to replace a substituent (called the leaving group) that departs with an unshared electron pair.

Nucleophilicity (Section 6.13B): The relative reactivity of a nucleophile in an S_N2 reaction as measured by relative rates of reaction.

Nucleoside (Sections 22.15A, 25.2, and 25.3): A five-carbon monosaccharide bonded at the $1'$ position to a purine or pyrimidine.

Nucleotide (Sections 25.2 and 25.3): A five-carbon monosaccharide bonded at the 1′ position to a purine or pyrimidine and at the 3′ or 5′ position to a phosphate group.

O

Octet rule (Sections 1.4 and 1.6): An empirical rule stating that atoms not having the electronic configuration of a noble gas tend to react by either transferring electrons or sharing electrons so as to achieve the valence electron configuration (i. e., eight electrons) of a noble gas.

Off-resonance decoupling (Section 9.11D): An NMR method for investigating the number of protons attached to a carbon atom by which each carbon signal is split into (n + 1) signals, where n = the number of protons on the carbon under observation.

Oil (Section 23.2): A triacylglycerol (see below) that is liquid at room temperature.

Olefin (Section 7.1): An old name for an alkene.

Oligonucleotide synthesis (Section 25.7): Synthesis of specific sequence of nucleotides, often by automated solid-phase techniques, in which the nucleotide chain is built up by adding a protected nucleotide in the form of a phosphoramidite to a protected nucleotide linked to a solid phase, (usually a "controlled pore glass") in the presence of a coupling agent. The phosphite triester product is oxidized to a phosphate triester with iodine, producing a chain that has been lengthened by one nucleotide. The protecting group is then removed, and the steps (coupling, oxidation, deprotection) are repeated. After the desired oligonucleotide has been synthesized it is cleaved from the solid support and the remaining protecting groups removed.

Oligopeptide (Section 24.4): A peptide comprised of 3 – 10 amino acids.

Oligosaccharides (Section 22.1A): A carbohydrate that hydrolyzes to yield 2–10 monosaccharide molecules.

Optical purity (Section 5.9B): A percentage calculated for a mixture of enantiomers by dividing the observed specific rotation for the mixture by the specific rotation of the pure enantiomer and multiplying by 100. The optical purity equals the enantiomeric purity or enantiomeric excess.

Optically active compound (Sections 5.8 and 5.9): A compound that rotates the plane of polarization of plane-polarized light.

Orbital (Section 1.10): A volume of space in which there is a high probability of finding an electron. Orbitals are described mathematically by the squaring of wave functions, and each orbital has a characteristic energy. An orbital can hold two electrons when their spins are paired.

Organometallic compound (Section 12.5): A compound that contains a carbon–metal bond.

Orthogonal protecting groups (Section 24.7D): Protecting groups in which one set of protecting groups is stable under conditions for removal of the other, and vice versa.

Ortho-para directors (Section 15.10B): An electron-donating group on an aromatic ring. The major product of electrophilic aromatic substitution on a ring bearing such a group will have the newly substituted electrophile located ortho and/or para to the ortho-para-directing group.

Osazone (Section 22.8): A 1,2-bisarylhydrazone formed by reaction of an aldose or ketose with three molar equivalents of an arylhydrazone. Most common are phenylosazones, formed by reaction with phenylhydrazine, and 2,4-dinitrophenylhydrazones.

Oxidation (Sections 12.2 and 12.4): A reaction that increases the oxidation state of atoms in a molecule or ion. For an organic substrate, oxidation usually involves increasing its oxygen content or decreasing its hydrogen content. Oxidation also accompanies any reaction in which a less electronegative substituent is replaced by a more electronegative one.

Oxidative cleavage (Sections 8.17 and 8.20): A reaction in which the carbon-carbon double bond of an alkene or alkyne is both cleaved and oxidized, yielding compounds with carbon-oxygen double bonds.

Oxidizing agent (Section 12.2): A chemical species that causes another chemical species to become oxidized (lose electrons, or gain bonds to more electronegative elements, often losing bonds to hydrogen in the process). The oxidizing agent is reduced in this process.

Oxime (Section 16.8B): An imine in which a hydroxyl group is bonded to the nitrogen atom.

Oxonium ion (Sections 3.13 and 11.12): A chemical species with an oxygen atom that bears a formal positive charge.

Oxonium salt (Section 11.12): A salt in which the cation is a species containing a positively charged oxygen.

Oxymercuration (Sections 8.6 and 11.4): The addition of $—OH$ and $—HgO_2CR$ to a multiple bond.

Oxymercuration-demercuration (Section 8.6): A two-step process for adding the elements of water (H and OH) to a double bond in a Markovnikov orientation without rearrangements. An alkene reacts with mercuric acetate (or trifluoroacetate), forming a bridged mercurinium ion. Water preferentially attacks the more substituted side of the bridged ion, breaking the bridge and resulting, after loss of a proton, in an alcohol. Reduction with $NaBH_4$ replaces the mercury group with a hydrogen atom, yielding the final product.

Ozonolysis (Sections 8.17B and 8.20): The oxidative cleavage of a multiple bond using O_3 (ozone). The reaction leads to the formation of a cyclic compound called an *ozonide*, which is then reduced to carbonyl compounds by treatment with dimethyl sulfide (Me_2S) or zinc and acetic acid.

P

***p* orbitals** (Section 1.10): A set of three degenerate (equal energy) atomic orbitals shaped like two tangent spheres with a nodal plane at the nucleus. For *p* orbitals of second row elements, the principal quantum number, *n* (see **Atomic orbital**), is 2; the azimuthal quantum number, *l*, is 1; and the magnetic quantum numbers, *m*, are +1, 0, or −1.

Paraffin (Section 4.15): An old name for an alkane.

Partial hydrolysis (Section 24.5D): Random cleavage of a polypeptide with dilute acid, resulting in a family of peptides of varying lengths that can be more easily sequenced than the parent polypeptide. Once each fragment peptide is sequenced, the areas of overlap indicate the sequence of the initial peptide.

Pauli exclusion principle (Section 1.10A): A principle that states that no two electrons of an atom or molecule may have the same set of four quantum numbers. It means that only two electrons can occupy the same orbital, and then only when their spin quantum numbers are opposite. When this is true, we say that the spins of the electrons are paired.

Peptide (Section 24.4): A molecule comprised of amino acids bonded via amide linkages.

Peptide bond, peptide linkage (Section 24.4): The amide linkage between amino acids in a peptide.

Peracid (See **Peroxy acid,** Section 11.13A)

Periplanar (See **Coplanar**, Section 7.6D)

Peroxide (Section 10.1A): A compound with an oxygen–oxygen single bond.

Peroxy acid (Section 11.13A): An acid with the general formula RCO_3H, containing an oxygen–oxygen single bond.

Phase sign (Section 1.9): Signs, either $+$ or $-$, that are characteristic of all equations that describe the amplitudes of waves.

Phase transfer catalysis (Section 11.16): A reaction using a reagent that transports an ion from an aqueous phase into a nonpolar phase where reaction takes place more rapidly. Tetraalkylammonium ions and crown ethers are phase-transfer catalysts.

Phospholipid (Section 23.6): Compound that is structurally derived from *phosphatidic acid*. Phosphatidic acids are derivatives of glycerol in which two hydroxyl groups are joined to fatty acids, and one terminal hydroxyl group is joined in an ester linkage to phosphoric acid. In a phospholipid the phosphate group of the phosphatidic acid is joined in ester linkage to a nitrogen-containing compound such as choline, 2-aminoethanol, or L-serine.

Physical property (Section 2.14): Properties of a substance, such as melting point and boiling point, that relate to physical (as opposed to chemical) changes in the substance.

Pi (π) bond (Section 1.13): A bond formed when electrons occupy a bonding π molecular orbital (i.e., the lower energy molecular orbital that results from overlap of parallel *p* orbitals on adjacent atoms).

Pi (π) molecular orbital (Section 1.13): A molecular orbital formed when parallel *p* orbitals on adjacent atoms overlap. Pi molecular orbitals may be *bonding* (*p* lobes of the same phase sign overlap) or *antibonding* (*p* orbitals of opposite phase sign overlap).

pK_a (Section 3.6B): The pK_a is the negative logarithm of the acidity constant, K_a. p$K_a = -\log K_a$.

Plane of symmetry (Sections 5.6 and 5.12A): An imaginary plane that bisects a molecule in a way such that the two halves of the molecule are mirror images of each other. Any molecule with a plane of symmetry will be achiral.

Plane-polarized light (Section 5.8A): Light in which the oscillations of the electrical field occur only in one plane.

Polar aprotic solvent (Section 6.13C): A polar solvent that does not have a hydrogen atom attached to an electronegative element. Polar aprotic solvents do *not* hydrogen bond with a Lewis base (e.g., a nucleophile).

Polar protic solvent (Section 6.13D): A polar solvent that has at least one hydrogen atom bonded to an electronegative element. These hydrogen atoms of the solvent can form hydrogen bonds with a Lewis base (e.g., a nucleophile).

Polar covalent bond (Section 2.2): A covalent bond in which the electrons are not equally shared because of differing electronegativities of the bonded atoms.

Polar molecule (Section 2.3): A molecule with a dipole moment.

Polarimeter (Section 5.8B): A device used for measuring optical activity.

Polarizability (Section 6.13C): The susceptibility of the electron cloud of an uncharged molecule to distortion by the influence of an electric charge.

Polymer (Section 10.10): A large molecule made up of many repeating subunits. For example, the polymer polyethylene is made up of the repeating subunit $-(CH_2CH_2)_n-$.

Polymerase chain reaction (PCR) (Section 25.8): A method for multiplying (amplifying) the number of copies of a DNA molecule. The reaction uses DNA polymerase enzymes to attach additional nucleotides to a short oligonucleotide “primer” that is bound to a complementary strand of DNA called a “template.” The nucleotide that the polymerases attach are those that are complementary to the base in the adjacent position on the template strand. Each cycle doubles the amount of target DNA that existed prior to the reaction step, yielding an exponential increase in the amount of DNA over time.

Polymerizations (Section 10.10): Reactions in which individual subunits (called *monomers*) are joined together to form long-chain macromolecules.

Polypeptide (Section 24.4): A peptide comprised of many (>10) amino acids.

Polysaccharide (Sections 22.1A and 22.13): A carbohydrate that, on a molecular basis, undergoes hydrolytic cleavage to yield many molecules of a monosaccharide. Also called a glycan.

Polyunsaturated fatty acid/ester (Section 23.2): A fatty acid or ester of a fatty acid whose carbon chain contain two or more double bonds.

Potential energy (Section 3.9): Potential energy is stored energy; it exists when attractive or repulsive forces exist between objects.

Potential energy diagram (Section 4.8); A graphical plot of the potential energy changes that occurs as molecules (or atoms) react (or interact). Potential energy is plotted on the vertical axis, and the progress of the reaction on the horizontal axis

Primary carbon (Section 2.5): A carbon atom that has only one other carbon atom attached to it.

Primary structure (Sections 24.1, 24.5, and 24.6): The covalent structure of a polypeptide or protein. This structure is determined, in large part, by determining the sequence of amino acids in the protein.

Prochiral center (Section 12.3C): A group is prochiral if replacement of one of two identical groups at a tetrahedral atom, or if addition of a group to a trigonal planar atom, leads to a new chirality center. At a tetrahedral atom where there are two identical groups, the identical groups can be designated pro-*R* and pro-*S* depending on what configuration would result when it is imagined that each is replaced by a group of next higher priority (but not higher than another existing group).

Prostaglandins (Section 23.5): Natural C_{20} carboxylic acids that contain a five-membered ring, at least one double bond, and several oxygen-containing functional groups. Prostaglandins mediate a variety of physiological processes.

Prosthetic group (Sections 24.9 and 24.12): An enzyme cofactor that is permanently bound to the enzyme.

Protecting group (Sections 11.11D, 11.11E, 12.9, 15.14A, 16.7C, and 24.7A): A group that is introduced into a molecule to protect a sensitive group from reaction while a reaction is carried out at some other location in the molecule. Later, the protecting group is removed. Also called blocking group. (See also **orthogonal protecting group**.)

Protein (Section 24.4): A large biological polymer of α-amino acids joined by amide linkages.

Proteome Proteome (Sections 25.1 and 25.9): The set of all proteins encoded within the genome of an organism and expressed at any given time.

Proteomics (Section 24.14): The study of all proteins that are expressed in a cell at a given time.

Protic solvent (Sections 3.12, 6.13C, and 6.13D): A solvent whose molecules have a hydrogen atom attached to a strongly electronegative element such as oxygen or nitrogen. Molecules of a protic solvent can therefore form hydrogen bonds to unshared electron pairs of oxygen or nitrogen atoms of solute molecules or ions, thereby stabilizing them. Water, methanol, ethanol, formic acid, and acetic acid are typical protic solvents.

Proton decoupling (Section 9.11B): An electronic technique used in ^{13}C NMR spectroscopy that allows decoupling of spin–spin interactions between ^{13}C nuclei and ^1H nuclei. In spectra obtained in this mode of operation all carbon resonances appear as singlets.

Proton off-resonance decoupling (Section 9.11D): A technique used in ^{13}C NMR spectroscopy that allows one-bond couplings between ^{13}C nuclei and ^1H nuclei. In spectra obtained in this mode of operation, CH_3 groups appear as quartets, CH_2 groups appear as triplets, CH groups appear as doublets, and carbon atoms with no attached hydrogen atoms appear as singlets.

Psi (ψ) function (See **Wave function** and Section 1.9)

Pyranose (Section 22.2C): A sugar in which the cyclic acetal or hemiacetal ring is six membered.

Q

Quartet (Section 9.2C): An NMR signal comprised of four peaks in a 1:3:3:1 area ratio, caused by signal splitting from three neighboring NMR-active spin 1/2 nuclei.

Quaternary ammonium salt (Sections 20.2B and 20.3D): Ionic compounds in which a nitrogen bears four organic groups and a positive charge, paired with a counterion.

Quaternary structure (Sections 24.1 and 24.8C): The overall structure of a protein having multiple subunits (non-covalent aggregates of more than one polypeptide chain). Each subunit has a primary, secondary, and tertiary structure of its own.

R

R (Sections 2.4A and 4.3A): A symbol used to designate an alkyl group. Oftentimes it is taken to symbolize any organic group.

***R,S*-System** (Section 5.7): A method for designating the configuration of tetrahedral chirality centers.

Racemic form (racemate or **racemic mixture)** (Sections 5.9A, 5.9B, and 5.10A): An equimolar mixture of enantiomers. A racemic form is optically inactive.

Racemization (Section 6.12A): A reaction that transforms an optically active compound into a racemic form is said to proceed with racemization. Racemization takes place whenever a reaction causes chiral molecules to be converted to an achiral intermediate.

Radical (or **free radical**) (Sections 3.1A, 10.1, 10.6, and 10.7): An uncharged chemical species that contains an unpaired electron.

Radical addition to alkenes (Sections 10.9 and 10.10): A process by which an atom with an unshared electron, such as a bromine atom, adds to an alkene with homolytic cleavage of the π-bond and formation of a σ-bond from the radical to the carbon; the resulting carbon radical then continues the chain reaction to product the final product plus another species with an unshared electron.

Radical cation (Section 9.14): A chemical species containing an unshared electron and a positive charge.

Radical halogenation (Section 10.3): Substitution of a hydrogen by a halogen through a radical reaction mechanism.

Radical reaction (Section 10.1B): A reaction involving radicals. Homolysis of covalent bonds occurs in radical reactions.

Rate control (See **Kinetic control**)

Rate-determining step (Section 6.9A): If a reaction takes place in a series of steps, and if the first step is intrinsically slower than all of the others, then the rate of the overall reaction will be the same as (will be determined by) the rate of this slow step.

Reaction coordinate (Section 6.7): The abscissa in a potential energy diagram that represents the progress of the reaction. It represents the changes in bond orders and bond distances that must take place as reactants are converted to products.

Reaction mechanism (Sections 3.1 and 3.14): A step-by-step description of the events that are postulated to take place at the molecular level as reactants are converted to products. A mechanism will include a description of all intermediates and transition states. Any mechanism proposed for a reaction must be consistent with all experimental data obtained for the reaction.

Rearrangement (Sections 3.1, 7.8A, and 7.8B): A reaction that results in a product with the same atoms present but a different carbon skeleton from the reactant. The type of rearrangement called a 1,2 shift involves the migration of an organic group (with its electrons) from one atom to the atom next to it.

Reducing agent (Sections 12.2 and 12.3): A chemical species that causes another chemical species to become reduced (to gain electrons, or to lose bonds to electronegative elements, often gaining bonds to hydrogen in the process). The reducing agent is oxidized in this process.

Reducing sugar (Section 22.6A): Sugars that reduce Tollens' or Benedict's reagents. All sugars that contain hemiacetal or hemiketal groups (and therefore are in equilibrium with aldehydes or α-hydroxyketones) are reducing sugars. Sugars in which only acetal or ketal groups are present are nonreducing sugars.

Reduction (Sections 12.2 and 12.3): A reaction that lowers the oxidation state of atoms in a molecule or ion. Reduction of an organic compound usually involves increasing its hydrogen content or decreasing its oxygen content. Reduction also accompanies any reaction that results in replacement of a more electronegative substituent by a less electronegative one.

Reductive amination (Section 20.4C): A method for synthesizing primary, secondary, or tertiary amines in which an aldehyde or ketone is treated with a primary or secondary amine to produce an imine (when primary amines are used) or an iminium ion (when secondary amines are used), followed by reduction to produce an amine product.

Regioselective reaction (Sections 8.2C and 8.19): A reaction that yields only one (or a predominance of one) constitutional isomer as the product when two or more constitutional isomers are possible products.

Relative configuration (Section 5.15A): The relationship between the configurations of two chiral molecules. Molecules are said to have the same relative configuration when similar or identical groups in each occupy the same position in space. The configurations of molecules can be related to each other through reactions of known stereochemistry, for example, through reactions that cause no bonds to a stereogenic center to be broken.

Replication (Section 25.4C): A process in which DNA unwinds, allowing each chain to act as a template for the formation of its complement, producing two identical DNA molecules from one original molecule.

Resolution (Sections 5.16B and 20.3F): The process by which the enantiomers of a racemic form are separated.

Resonance (Sections 3.11A, 13.5, and 15.11B): An effect by which a substituent exerts either an electron-releasing or electron-withdrawing effect through the π system of the molecule.

Resonance energy (Section 14.5): An energy of stabilization that represents the difference in energy between the actual compound and that calculated for a single resonance structure. The resonance energy arises from delocalization of electrons in a conjugated system.

Resonance structures (or **resonance contributors**) (Sections 1.8, 1.8A, 13.3B, and 13.5A): Lewis structures that differ from one another only in the position of their electrons. A single resonance structure will not adequately represent a molecule. The molecule is better represented as a *hybrid* of all of the resonance structures.

Restriction endonucleases (Section 25.6): Enzymes that cleave double-stranded DNA at specific base sequences.

Retro-aldol reaction (Section 19.4B): Aldol reactions are reversible; under certain conditions an aldol product will revert to its aldol reaction precursors. This process is called a *retro-aldol reaction*.

Retrosynthetic analysis (Section 7.16B): A method for planning syntheses that involves reasoning backward from the target molecule through various levels of precursors and thus finally to the starting materials.

Ribonucleic acid (RNA) (Sections 25.1 and 25.5): One of the two classes of molecules (the other is DNA) that carry genetic information in cells. RNA molecules transcribe and translate the information from DNA for the mechanics of protein synthesis.

Ribozyme (Section 25.5B): A ribonucleic acid that acts as a reaction catalyst.

Ring flip (Sections 4.11 and 4.12): The change in a cyclohexane ring (resulting from partial bond rotations) that converts one ring conformation to another. A chair–chair ring flip converts any equatorial substitutent to an axial substituent and vice versa.

Ring strain (Section 4.10): The increased potential energy of the cyclic form of a molecule (usually measured by heats of combustion) when compared to its acyclic form.

S

***s* orbital** (Section 1.10): A spherical atomic orbital. For *s* orbitals the azimuthal quantum number $l = 0$ (see **Atomic orbital**).

Salt (Section 1.4A): The product of a reaction between an acid and a base. Salts are ionic compounds composed of oppositely charged ions.

Sanger *N*-terminal analysis (Section 24.5B): A method for determining the *N*-terminal amino acid residue of a peptide by its S_NAr (nucleophilic aromatic substitution) reaction with dinitrofluorobenzene, followed by peptide hydrolysis and comparison of the product with known standards.

Saponification (Sections 17.7B and 23.2C): Base-promoted hydrolysis of an ester.

Saturated compound (Sections 2.1, 7.13, and 23.2): A compound that does not contain any multiple bonds.

Sawhorse formula (Section 4.8): A chemical formula that depicts the spatial relationships of groups in a molecule in a way similar to dash-wedge formulas.

Secondary amine (Section 20.1): A derivative of ammonia in which there are two carbons bonded to a nitrogen atom. Secondary amines have a formula R_2NH, where the R groups can be the same or different.

Secondary carbon (Section 2.5): A carbon atom that has two other carbon atoms attached to it.

Secondary structure (Sections 24.1 and 24.8A): The local conformation of a polypeptide backbone. These local conformations are specified in terms of regular folding patterns such as pleated sheets, α helixes, and turns.

Shielding and deshielding (Section 9.6): Effects observed in NMR spectra caused by the circulation of sigma and pi electrons within the molecule. Shielding causes signals to appear at lower frequencies (upfield), deshielding causes signals to appear at higher frequencies (downfield).

Sigma (σ) bond (Section 1.12A): A single bond. A bond formed when electrons occupy the bonding σ orbital formed by the end-on overlap of atomic orbitals (or hybrid orbitals) on adjacent atoms. In a sigma bond the electron density has circular symmetry when viewed along the bond axis.

Sigma (σ) orbital (Section 1.12A): A molecular orbital formed by end-on overlap of orbitals (or lobes of orbitals) on adjacent atoms. Sigma orbitals may be *bonding* (orbitals or lobes of the same phase sign overlap) or *antibonding* (orbitals or lobes of opposite phase sign overlap).

Signal splitting (Sections 9.2C and 9.9): Splitting of an NMR signal into multiple peaks, in patterns such as doublets, triplets, quartets, etc., caused by interactions of the energy levels of the magnetic nucleus under observation with the energy levels of nearby magnetic nuclei.

Silylation (Sections 11.11E and 17.7C): Conversion of an alcohol, $R{-}OH$, to a silyl ether (usually of the form $R{-}O{-}SiR'_3$, where the groups on silicon may be the same or different). Silyl ethers are used as protecting groups for the alcohol functionality.

Singlet (Section 9.2C): An NMR signal with only a single, unsplit peak.

Site-specific cleavage (Section 24.5D): A method of cleaving peptides at specific, known sites using enzymes and specialized reagents. For example, the enzyme trypsin preferentially catalyzes hydrolysis of peptide bonds on the C-terminal side of arginine and lysine. Other bonds in the peptide are not cleaved by this reagent.

S_N1 reaction (Sections 6.9, 6.10, 6.12, 6.13, and 6.18B): Literally, substitution nucleophilic unimolecular. A multistep nucleophilic substitution in which the leaving group departs in a unimolecular step before the attack of the nucleophile. The rate equation is first order in substrate but zero order in the attacking nucleophile.

S_N2 reaction (Sections 6.5B, 6.6–6.8, 6.13, and 6.18A): Literally, substitution nucleophilic bimolecular. A bimolecular nucleophilic substitution reaction that takes place in a single step. A nucleophile attacks a carbon bearing a leaving group from the back side, causing an inversion of configuration at this carbon and displacement of the leaving group.

Solid-phase peptide synthesis (SPPS) (Section 24.7D): A method of peptide synthesis in which the peptide is synthesized on a solid support, one amino acid residue at a time. The first amino acid of the peptide is bonded as an ester between its carboxylic acid group and a hydroxyl of the solid support (a polymer bead). This is then treated with a solution of the second amino acid and appropriate coupling reagents, creating a dipeptide. Excess reagents, byproducts, etc. are washed away. Further linkages are synthesized in the same manner. The last step of the synthesis is cleavage of the peptide from the solid support and purification.

Solubility (Section 2.13D): The extent to which a given solute dissolves in a given solvent, usually expressed as a weight per unit volume (e.g., grams per 100 mL).

Solvent effect (Sections 6.13C and 6.13D): An effect on relative rates of reaction caused by the solvent. For example, the use of a polar solvent will increase the rate of reaction of an alkyl halide in an S_N1 reaction.

Solvolysis (Section 6.12B): Literally, cleavage by the solvent. A nucleophilic substitution reaction in which the nucleophile is a molecule of the solvent.

***sp* orbital** (Section 1.14): A hybrid orbital that is derived by mathematically combining one *s* atomic orbital and one *p* atomic orbital. Two *sp* hybrid orbitals are obtained by this process, and they are oriented in opposite directions with an angle of 180° between them.

sp^2 orbital (Section 1.13): A hybrid orbital that is derived by mathematically combining one *s* atomic orbital and two *p* atomic orbitals. Three sp^2 hybrid orbitals are obtained by this process, and they are directed toward the corners of an equilateral triangle with angles of 120° between them.

sp^3 orbital (Section 1.12A): A hybrid orbital that is derived by mathematically combining one *s* atomic orbital and three *p* atomic orbitals. Four sp^3 hybrid orbitals are obtained by this process, and they are directed toward the corners of a regular tetrahedron with angles of 109.5° between them.

Specific rotation (Section 5.8C): A physical constant calculated from the observed rotation of a compound using the following equation:

$$[\alpha]_D = \frac{\alpha}{c \times l}$$

where α is the observed rotation using the D line of a sodium lamp, *c* is the concentration of the solution or the density of a neat liquid in grams per milliliter, and *l* is the length of the tube in decimeters.

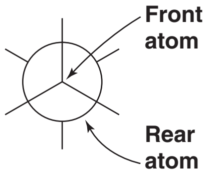
Spectroscopy (Section 9.1): The study of the interaction of energy with matter. Energy can be absorbed, transmitted, emitted or cause a chemical change (break bonds) when applied to matter. Among other uses, spectroscopy can be used to probe molecular structure.

Spin decoupling (Section 9.10): An effect that causes spin–spin splitting not to be observed in NMR spectra.

Spin–spin splitting (Section 9.9): An effect observed in NMR spectra. Spin–spin splittings result in a signal appearing as a multiplet (i.e., doublet, triplet, quartet, etc.) and are caused by magnetic couplings of the nucleus being observed with nuclei of nearby atoms.

Splitting tree diagrams (Section 9.9B): A method of illustrating the NMR signal splittings in a molecule by drawing “branches” from the original signal. The distance between the branches is proportional to the magnitude of the coupling constant. This type of analysis is especially useful when multiple splittings (splitting of already split signals) occur due to coupling with non-equivalent protons.

Staggered conformation (Section 4.8A): A temporary orientation of groups around two atoms joined by a single bond such that the bonds of the back atom exactly bisect the angles formed by the bonds of the front atom when shown in a Newman projection formula:



A staggered conformation

Step-growth polymer (See also **Condendsation polymer**, Section 17.12 and Special Topic C): A polymer produced when bifunctional monomers (or potentially bifunctional monomers) react with each other through the intermolecular elimination of water or an alcohol. Polyesters, polyamides, and polyurethanes are all step-growth (condensation) polymers

Stereochemistry (Sections 5.2, 6.8, and 6.14): Chemical studies that take into account the spatial aspects of molecules.

Stereogenic carbon (Section 5.3): A single tetrahedral carbon with four different groups attached to it. Also called an *asymmetric carbon, a stereocenter, or a chirality center*. The last usage is preferred.

Stereogenic center (Sections 5.3, 5.18):When the exchange of two groups bonded to the same atom produces stereoisomers, the atom is said to be a stereogenic atom, or stereogenic center.

Stereoisomers (Sections 1.13B, 4.9A, 4.13, 5.2B, and 5.14): Compounds with the same molecular formula that differ *only* in the arrangement of their atoms in space. Stereoisomers have the same connectivity and, therefore, are not constitutional isomers. Stereoisomers are classified further as being either enantiomers or diastereomers.

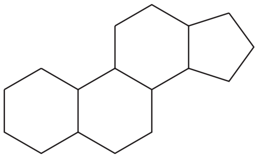
Stereoselective reaction (Sections 5.10B, 8.21C, and 12.3C): In reactions where chirality centers are altered or created, a stereoselective reaction produces a preponderance of one stereoisomer. Furthermore, a stereoselective reaction can be either enantioselective, in which case the reaction produces a preponderance of one enantiomer, or diastereoselective, in which case the reaction produces a preponderance of one diastereomer.

Stereospecific reaction (Section 8.13): A reaction in which a particular stereoisomeric form of the reactant reacts in such a way that it leads to a specific stereoisomeric form of the product.

Steric effect (Section 6.13A): An effect on relative reaction rates caused by the space-filling properties of those parts of a molecule attached at or near the reacting site.

Steric hindrance (Sections 4.8B and 6.13A): An effect on relative reaction rates caused when the spatial arrangement of atoms or groups at or near the reacting site hinders or retards a reaction.

Steroid (Section 23.4): Steroids are lipids that are derived from the following perhydrocyclopentanophenanthrene ring system:



Structural formula (Sections 1.3A and 1.17): A formula that shows how the atoms of a molecule are attached to each other.

Substituent effect (Sections 3.11D and 15.10): An effect on the rate of reaction (or on the equilibrium constant) caused by the replacement of a hydrogen atom by another atom or group. Substituent effects include those effects caused by the size of the atom or group, called steric effects, and those effects caused by the ability of the group to release or withdraw electrons, called electronic effects. Electronic effects are further classified as being inductive effects or resonance effects.

Substitution reaction (Sections 3.1, 6.2, 10.3, 15.1, and 17.4): A reaction in which one group replaces another in a molecule.

Substitutive nomenclature (Section 4.3F): A system for naming compounds in which each atom or group, called a substituent, is cited as a prefix or suffix to a parent compound. In the IUPAC system only one group may be cited as a suffix. Locants (usually numbers) are used to tell where the group occurs.

Substrate (Sections 6.2 and 24.9): The molecule or ion that undergoes reaction.

Sugar (Section 22.1A): A carbohydrate.

Sulfa drugs (Sections 20.9 and 20.10): Sulfonamide antibacterial agents, most of which have the general structure $p\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{NHR}$. Sulfa drugs act as *antimetabolites* (they inhibit the growth of microbes) by inhibiting the enzymatic steps that are involved in the synthesis of folic acid; when deprived of folic acid, the microorganism dies.

Sulfonamides (Section 20.9): An amide derivative of a sulfonic acid, usually made by. the reaction of ammonia, or a primary or secondary amine, with a sulfonyl chloride, resulting in compounds having the general formulas $\text{R}'\text{SO}_2\text{NH}_2$, $\text{R}'\text{SO}_2\text{NHR}$, or $\text{R}'\text{SO}_2\text{NR}_2$, respectively.

Sulfonate ester (Section 11.10): A compound with the formula $\text{ROSO}_2\text{R}'$ and considered to be derivatives of sulfonic acids, $\text{HOSO}_2\text{R}'$. Sulfonate esters are used in organic synthesis because of the excellent leaving group ability of the fragment $^-\text{OSO}_2\text{R}'$.

Superposable (Sections 1.13B and 5.1): Two objects are superposable if, when one object is placed on top of the other, all parts of each coincide. To be superposable is different than to be superimposable. Any two objects can be superimposed simply by putting one object on top of the other, whether or not all parts coincide. The condition of superposability must be met for two things to be identical.

Syn addition (Sections 7.14A and 7.15A): An addition that places both parts of the adding reagent on the same face of the reactant.

Syn dihydroxylation (Section 8.16A): An oxidation reaction in which an alkene reacts to become a 1,2-diol (also called a *glycol*) with the newly bonded hydroxyl groups added to the same face of the alkene.

Syndiotactic polymer (Special Topic B.1): A polymer in which the configuration at the stereogenic centers along the chain alternate regularly: (*R*), (*S*), (*R*), (*S*), etc.

Synthetic equivalent (Sections 8.21, 18.6, and 18.7): A compound that functions as the equivalent of a molecular fragment needed in a synthesis.

Synthon (Sections 8.21B, 18.6, and 18.7): The fragments that result (on paper) from the disconnection of a bond. The actual reagent that will, in a synthetic step, provide the synthon is called the *synthetic equivalent*.

T

Tautomerization (Section 18.2): An isomerization by which tautomers are rapidly interconverted, as in keto-enol tautomerization.

Tautomers (Section 18.2): Constitutional isomers that are easily interconverted. Keto and enol tautomers, for example, are rapidly interconverted in the presence of acids and bases.

Terminal residue analysis (Section 24.5): Methods used to determine the sequence of amino acids in a peptide by reactions involving the *N*- and *C*-terminal residues.

Terpene (Section 23.3): Terpenes are lipids that have a structure that can be derived on paper by linking isoprene units.

Terpenoids (Section 23.3): Oxygen-containing derivatives of terpenes.

Tertiary amine (Section 20.1): A derivative of ammonia in which there are three carbons bonded to a nitrogen atom. Tertiary amines have a formula R_3N where the R groups can be the same or different.

Tertiary carbon (Section 2.5): A carbon atom that has three other carbon atoms attached to it.

Tertiary structure (Sections 24.1 and 24.8B): The three dimensional shape of a protein that arises from folding of its polypeptide chains superimposed on its α helixes and pleated sheets.

Tetrahedral intermediate (Section 17.4): A species created by the attack of a nucleophile on a trigonal carbon atom. In the case of a carbonyl group, as the electrons of the nucleophile form a bond to the carbonyl carbon the electrons of the carbon-oxygen π-bond shift to the oxygen. The carbon of the carbonyl group becomes four-coordinate (tetrahedral), while the oxygen gains an electron-pair and becomes negatively charged.

Thermodynamic control (Sections 13.10A and 18.4A): A principle stating that the ratio of products of a reaction that reaches equilibrium is determined by the relative stabilities of the products (as measured by their standard free energies, $\Delta G°$). The most abundant product will be the one that is the most stable. Also called equilibrium control.

Thermodynamic enolate (Section 18.4A): In a situation in which more than one enolate anion can be formed, the *thermodynamic enolate* is the more stable of the possible enolate anions—usually the enolate with the more substituted double bond. A thermodynamic enolate is formed predominantly under conditions that permit the establishment of an equilibrium.

Torsional barrier (Section 4.8B): The barrier to rotation of groups joined by a single bond caused by repulsions between the aligned electron pairs in the eclipsed form.

Torsional strain (Sections 4.8B, 4.9, and 4.10): The strain associated with an eclipsed conformation of a molecule; it is caused by repulsions between the aligned electron pairs of the eclipsed bonds.

Tosylate (Section 11.10): A *p*-toluenesulfonate ester, which is a compound that contains the $p\text{-}CH_3C_6H_4SO_3—$ group, i.e., $p\text{-}CH_3C_6H_4SO_3R$

Transcription (Section 25.5): Synthesis of a messenger RNA (mRNA) molecule that is complimentary to a section of DNA that carries genetic information.

Transesterification (Section 17.7A): A reaction involving the exchange of the alkoxyl portion of an ester for a different alkoxyl group, resulting in a new ester.

Transition state (Sections 6.6, 6.7, and 6.10): A state on a potential energy diagram corresponding to an energy maximum (i.e., characterized by having higher potential energy than immediately adjacent states). The term transition state is also used to refer to the species that occurs at this state of maximum potential energy; another term used for this species is *the activated complex*.

Translation (Section 25.5E): The ribosomal synthesis of a polypeptide using an mRNA template.

Triacylglycerols (Section 23.2): An ester of glycerol (glycerin) in which all three of the hydroxyl groups are esterified.

Triflate (Section 11.10): A methanesulfonate ester, which is a compound that contains the $CH_3SO_3—$ group, i.e., $p\text{-}CH_3SO_3R$

Tripeptide (Section 24.4): A peptide comprised of three amino acids

Triple bonds (Sections 1.2 and 1.14): Bonds comprised of one sigma (σ) bond and two pi (π) bonds.

Triplet (Section 9.2C): An NMR signal comprised of three peaks in a 1:2:1 area ratio, caused by signal splitting from two neighboring NMR-active spin 1/2 nuclei.

Trisaccharides (Section 22.1A): A carbohydrate that, when hydrolyzed, yields three monosaccharide molecules.

Two-dimensional (2D) NMR (Section 9.12): NMR techniques such as COSY and HETCOR that correlate one property (e.g., coupling), or type of nucleus, with another. (See **COSY** and **HETCOR**.)

U

Ultraviolet–visible (UV–Vis) spectroscopy (Section 13.9): A type of optical spectroscopy that measures the absorption of light in the visible and ultraviolet regions of the spectrum. Visible–UV spectra primarily provide structural information about the kind and extent of conjugation of multiple bonds in the compound being analyzed.

Unimolecular reaction (Section 6.9): A reaction whose rate-determining step involves only one species.

Unsaturated compound (Sections 2.1, 7.13, and 23.2): A compound that contains multiple bonds.

Upfield (Section 9.2A): Any area or signal in an NMR spectrum that is to the right relative to another. (See **Downfield** for comparison.) A signal that is upfield of another occurs at lower frequency (and lower δ and ppm values) than the other signal.

V

Vicinal coupling (Section 9.9): The splitting of an NMR signal caused by hydrogen atoms on adjacent carbons. (See also **Coupling** and **Signal Splitting**.)

Vicinal (*vic*-) substituents (Section 7.10): Substituents that are on adjacent atoms.

Vinyl group (Sections 4.5 and 6.1): The $CH_2{=\!=}CH—$ group.

Vinylic halide (Section 6.1): An organic halide in which the halogen atom is attached to a carbon atom of a double bond.

Vinylic substituent (Section 6.1): Refers to a substituent on a carbon atom that participates in a carbon–carbon double bond.

VSEPR model (valence shell electron pair replusion) (Section 1.16): A method of predicting the geometry at a covalently bonded atom by considering the optimum geometric separation between groups of bonding and non-bonding electrons around the atom

W

Wave function (or ψ **function**) (Section 1.9): A mathematical expression derived from *quantum mechanics* corresponding to an energy state for an electron, i.e., for an orbital. The square of the ψ function, ψ^2, gives the probability of finding the electron in a particular place in space.

Wavelength, λ (Sections 2.15 and 13.9A): The distance between consecutive crests (or troughs) of a wave.

Wavenumber, $\bar{\nu}$ (Section 2.15): A way to express the frequency of a wave. The wavenumber is the number of waves per centimeter, expressed as cm^{-1}.

Waxes (Section 23.7): Esters of long-chain fatty acids and long-chain alcohols.

Williamson synthesis (Section 11.11B): The synthesis of an ether by the S_N2 reaction of an alkoxide ion with a substrate bearing a suitable leaving group (often a halide, sulfonate, or sulfate).

Y

Ylide (Section 16.10): An electrically neutral molecule that has a negative carbon with an unshared electron pair adjacent to a positive heteroatom.

Z

Zaitsev's rule (Sections 7.6B and 7.8A): A rule stating that an elimination will give as the major product the most stable alkene (i.e., the alkene with the most highly substituted double bond).

Zwitterion (See **Dipolar ion** and Section 24.2C): Another name for a dipolar ion.