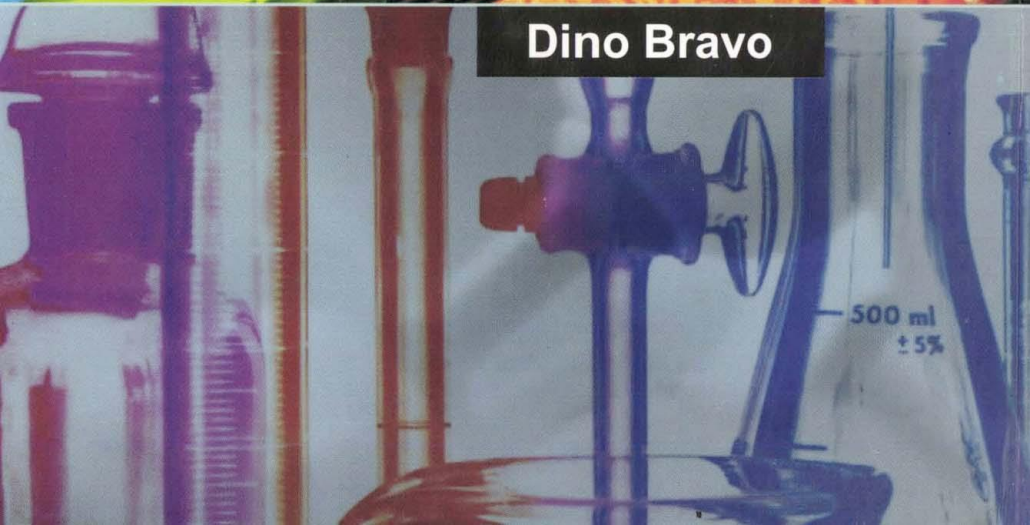


Kevin's Glossary

Chemistry



Dino Bravo



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Abstraction : A chemical reaction or *transformation*, the main feature of which is the bimolecular removal of an atom (neutral or charged) from a *molecular entity*. For example: $\text{CH}_3\text{COCH}_3 + (\text{i-C}_3\text{H}_7)_2\text{N}^- \longrightarrow (\text{CH}_3\text{COCH}_2)^- + (\text{i-C}_3\text{H}_7)_2\text{NH}$ (proton abstraction from acetone) $\text{CH}_4 + \text{Cl}^- \longrightarrow \text{H}_3\text{C}^- + \text{HCl}$ (hydrogen abstraction from methane)

Acid : A *molecular entity* or *chemical species* capable of donating a hydron (proton) or capable of forming a covalent bond with an electron pair.

Acidity : For *Brønsted acids* it means the tendency of a compound to act as a *hydron* donor. It can be quantitatively expressed by the acid dissociation constant of the compound in water or some other specified medium. For *Lewis acids* it relates to the association constants of *Lewis adducts* and π -*adducts*. (2) Of a medium: The use of the term is mainly restricted to a medium containing *Brønsted acids*, where it means the tendency of the medium to hydronate a specific reference base. It is quantitatively expressed by the appropriate *acidity function*.

Acidity function : Any function that measures the thermodynamic *hydron*-donating or -accepting ability of a solvent system, or a closely related thermodynamic property, such as the tendency of the *lyate ion* of the solvent system to form *Lewis adducts*. (The term "basicity function" is not in common use in connection with basic solutions.) Acidity functions are not unique properties of the solvent system alone, but depend on the solute (or family of closely related solutes) with respect to which the

thermodynamic tendency is measured. Commonly used acidity functions refer to concentrated acidic or basic solutions. Acidity functions are usually established over a range of composition of such a system by UV/VIS spectrophotometric or NMR measurements of the degree of hydronation (protonation or Lewis adduct formation) for the members of a series of structurally similar indicator bases (or acids) of different strength: the best known of these functions is the Hammett acidity function H_0 (for uncharged indicator bases that are primary aromatic amines).

Activated complex : An activated complex, often characterized by the superscript \ddagger , is defined as that assembly of atoms which corresponds to an arbitrary infinitesimally small region at or near the col (saddle point) of a potential energy surface.

Addition : Refers to *addition reaction* or *addition transformation*.

Loosely, the formation of an *adduct*. (For an example, see *Lewis acid*.)

Loosely, any *association* or *attachment*.

Addition reaction : A *chemical reaction* of two or more reacting *molecular entities*, resulting in a single reaction product containing all atoms of all components, with formation of two chemical bonds and a net reduction in bond multiplicity in at least one of the reactants. The reverse process is called an *elimination* reaction. The addition may occur at only one site (1/1/addition), at two adjacent sites (1/2/addition) or at two non-adjacent sites (1/3/- or 1/4/addition, etc.). For example (a) $H^+ + Br^- + (CH_3)_2C=CH_2 \longrightarrow (CH_3)_2CBr-CH_3$ (1/2/addition) (b) $Br_2 + CH_2=CH-CH=CH_2 \longrightarrow BrCH_2-CH=CH-CH_2Br$ (1/4/addition) and $BrCH_2-CH(Br)-CH=CH_2$ (1/2/addition). If the reagent or the source of the addends of an addition are not specified, then it is called an *addition transformation*.

Additivity principle : The hypothesis that each of several structural features of a *molecular entity* makes a separate and additive contribution to a property of the substance concerned. More specifically, it is the hypothesis that each of the several *substituent* groups in a parent molecule makes a separate and additive

contribution to the standard Gibbs energy change (or *Gibbs energy of activation*) corresponding to a particular equilibrium (or *rate of reaction*).

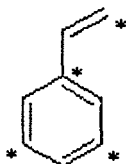
Adduct : A new *chemical species* AB, each *molecular entity* of which is formed by direct combination of two separate molecular entities A and B in such a way that there is change in *connectivity*, but no loss, of atoms within the *moieties* A and B. Stoichiometries other than 1:1 are also possible, e.g. a bis-adduct (2:1). An “*intramolecular adduct*” can be formed when A and B are *groups* contained within the same molecular entity. This is a general term which, whenever appropriate, should be used in preference to the less explicit term *complex*. It is also used specifically for products of an *addition reaction*.

Agostic : The term designates structures in which a hydrogen atom is bonded to both a carbon atom and a metal atom. The term is also used to characterize the interaction between a CH bond and an unsaturated metal centre, and to describe similar bonding of a transition metal with Si-H compounds. The expression “ μ -hydrido-bridged” is also used to describe the bridging hydrogen.

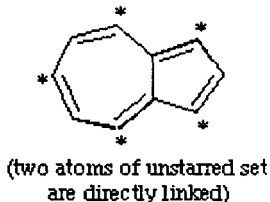
Allylic substitution reaction : A *substitution reaction* occurring at position 1/ of an allylic system, the double bond being between positions 2/ and 3/. The incoming group may be attached to the same atom 1/ as the *leaving group*, or the incoming group becomes attached at the relative position 3/, with movement of the double bond from 2/3 to 1/2. For example : $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br} \longrightarrow \text{CH}_3\text{CH}=\text{CHCH}_2\text{OAc}$ or $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Br} \longrightarrow \text{CH}_3\text{CH}(\text{OAc})\text{CH}=\text{CH}_2$ (written as a *transformation*).

Alternant : A *conjugated system* of pi electrons is termed alternant if its atoms can be divided into two sets so that no atom of one set is directly linked to any other atom of the same set.

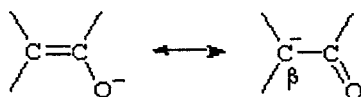
Example of alternate π system



Example of non-alternant π system



Ambident : A description applied to a *chemical species* whose *molecular entities* each possess two alternative and strongly interacting distinguishable reactive centres, to either of which a *bond* may be made in a reaction: the centres must be connected in such a way that reaction at either site stops or greatly retards subsequent attack at the second site. The term is most commonly applied to *conjugated nucleophiles*, for example the enolate ion (which may



react with *electrophiles* either at the β -carbon atom or at oxygen) or γ -pyridones, and also to the vicinally ambident cyanide ion, cyanate ion, thiocyanate ion, sulfinate ion, nitrite ion, and unsymmetrical hydrazines. Ambident electrophiles are exemplified by carboxylic esters $RC(O)OCR_3$ which react with nucleophiles either at the carbonyl carbon or the alkoxy carbon. Molecular entities, such as dianions of dicarboxylic acids, containing two non-interacting (or feebly interacting) reactive centres, are not generally considered to be ambident and are better described as "bifunctional". The Latin root of the word implies two reactive centres, but the term has in the past also incorrectly been applied to chemical species with more than two reactive centres. For such species the existing term "polydent" (or, better, "multident") is more appropriate.

Amphiphilic : A compound containing a large organic cation or anion which possesses a long unbranched hydrocarbon chain, e.g. $H_3C(CH_2)_nCO_2^-M^+H_3C(CH_2)_nSO_3^-M^+H_3C(CH_2)_nN(CH_3)_3^+X^-$ ($n > 7$). The existence of distinct polar (hydrophilic) and non polar (hydrophobic) regions in the molecule promotes the formation of *micelles* in dilute aqueous solution.

Amphiprotic (solvent) : Self-ionizing solvent possessing both characteristics of *Brønsted acids* and *bases*, for example H_2O and CH_3OH , in contrast to *aprotic solvent*.

Amphoteric : A *chemical species* that behaves both as an acid and as a base is called amphoteric. This property depends upon the medium in which the species is investigated: H_2SO_4 is an acid when studied in water, but becomes amphoteric in *superacids*.

Anionotropic rearrangement (or anionotropy) : A rearrangement in which the migrating group moves with its electron pair from one atom to another.

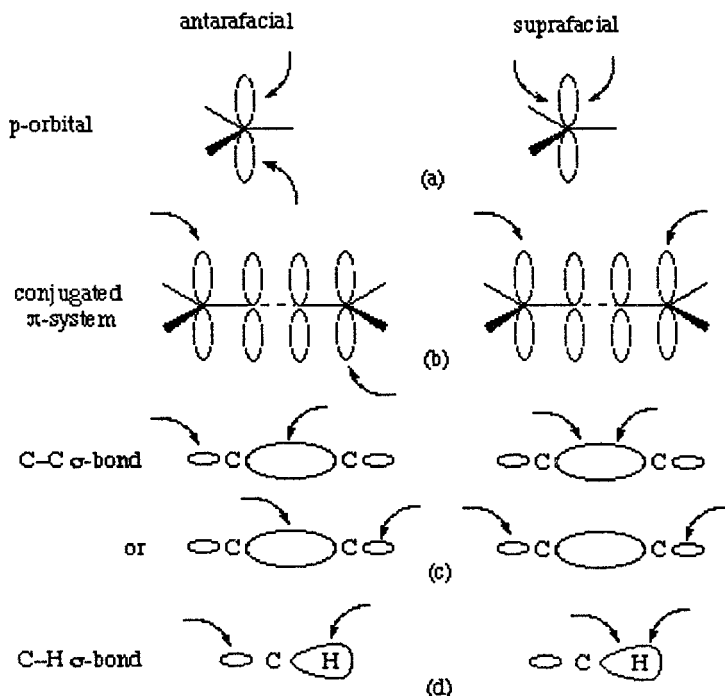
Annellation : Alternative, but less desirable term for *annulation*. The term is widely used in German and French language.

Annulation : A *transformation* involving fusion of a new ring to a molecule via two new bonds. Some authors use the term "annellation" for the fusion of an additional ring to an already existing one, and "annulation" for the formation of a ring from one or several acyclic precursors, but this distinction is not made generally.

Annulene : Mancude (i.e. having formally the maximum number of noncumulative double bonds) monocyclic hydrocarbon without side chains of the general formula C_nH_n (n is an even number) or C_nH_{n+1} (n is an odd number). Note that in systematic nomenclature an annulene with seven or more carbon atoms may be named [n]annulene, where n is the number of carbon atoms, e.g. [9]annulene for cyclonona-1,3,5,7-tetraene.

Antarafacial, suprafacial : When a part of a molecule ("molecular fragment") undergoes two changes in bonding (*bond-making* or *bond-breaking*), either to a common centre or to two related centres, external to itself, these bonding changes may be related in one of two spatially different ways. These are designated as "antarafacial" if opposite faces of the molecular fragment are involved, and "suprafacial" if both changes occur at the same face. The concept of "face" is clear from the diagrams in the cases of planar (or approximately planar) frameworks with isolated or interacting pi orbitals (Figs. a and b below). The terms antarafacial and suprafacial are, however, also employed in cases in which the essential part of the molecular fragment undergoing changes in bonding comprises two atoms linked only by a sigma bond. In these cases it is customary to refer to the phases of the local sigma-bonding orbital: occurrence of the two bonding changes at sites of like orbital phase is regarded as suprafacial, whereas that at two sites of opposite phase is antarafacial. The possibilities are shown for C-C and C-H sigma bonds in Figs. c and d. There may be two distinct and alternative stereochemical outcomes of a suprafacial process

involving a sigma bond between saturated carbon atoms, i.e. either retention or inversion at both centres. The antarafacial process results in inversion at one centre and retention at the second.



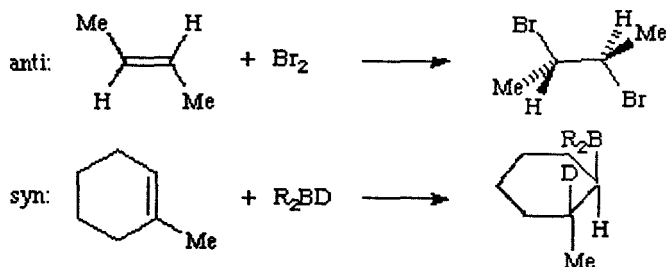
Anti : In the representation of stereochemical relationships “anti” means “on opposite sides” of a reference plane, in contrast to “syn” which means “on the same side”, as in the following examples.

Two substituents attached to atoms joined by a single *bond* are anti if the torsion angle (dihedral angle) between the bonds to the substituents is greater than 90° , or syn if it is less than 90° . (A further distinction is made between antiperiplanar, synperiplanar, anticlinal and synclinal.)

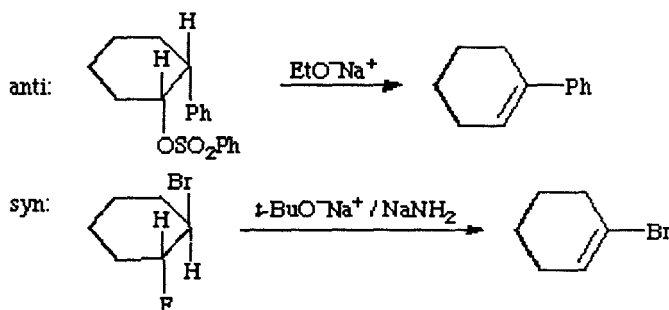
In the older literature the terms anti and syn were used to designate stereoisomers of oximes and related compounds. That usage was superseded by the terms “*trans*” and “*cis*” or *E* and *Z*, respectively.

When the terms are used in the context of *chemical reactions* or *transformations*, they designate the relative orientation of substituents in the substrate or product :

(1) Addition to a carbon-carbon double bond :



(2) Alkene-forming elimination:



AC ORGANIC RULES (1979). In the examples described under (1) and (2) anti processes are always *antarafacial*, and syn processes are *suprafacial*.

Aprotic (solvent) : Non-*protogenic* (in a given situation). (With extremely strong *Brønsted acids* or *bases*, solvents that are normally aprotic may accept or lose a proton. For example, acetonitrile is in most instances an aprotic solvent, but it is *protophilic* in the presence of concentrated sulfuric acid and *protogenic* in the presence of potassium *tert*-butoxide. Similar considerations apply to benzene, trichloromethane, etc.).

Aquation : The incorporation of one or more integral molecules of water into another species with or without displacement of one or more other atoms or groups. For example the incorporation of water

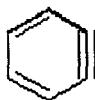
into the inner *ligand* sphere of an inorganic *complex* is an aquation reaction.

Aromatic, aromaticity : In the traditional sense, "having a chemistry typified by benzene".

A cyclically *conjugated molecular entity* with a stability (due to *delocalization*) significantly greater than that of a hypothetical localized structure (e.g. *Kekulé structure*) is said to possess aromatic character. If the structure is of higher energy (less stable) than such a hypothetical classical structure, the molecular entity is "antiaromatic". The most widely used method for determining aromaticity is the observation of diatropicity in the ^1H NMR spectrum. See also *Hückel* ($4n + 2$) rule, *Möbius aromaticity*.

The terms aromatic and antiaromatic have been extended to describe the stabilization or destabilization of *transition states* of *pericyclic reactions*. The hypothetical reference structure is here less clearly defined, and use of the term is based on application of the *Hückel* ($4n + 2$) rule and on consideration of the topology of orbital overlap in the transition state. Reactions of molecules in the *ground state* involving antiaromatic transition states proceed, if at all, much less easily than those involving aromatic transition states.

Aryne : A hydrocarbon derived from an arene by abstraction of two hydrogen atoms from adjacent carbon atoms; thus 1,2-didehydroarene. Arynes are commonly represented with a formal triple bond. The analogous heterocyclic compounds are called heteroarynes or hetarynes. E.g. benzyne Arynes are usually transient species.



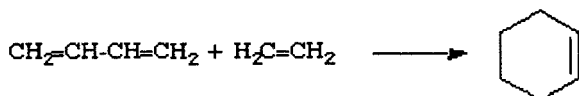
Association : The assembling of separate *molecular entities* into any aggregate, especially of oppositely charged free ions into *ion pairs* or larger and not necessarily well-defined clusters of ions held together by electrostatic attraction. The term signifies the

reverse of *dissociation*, but is not commonly used for the formation of definite *adducts* by *colligation* or *coordination*.

Asymmetric induction : The traditional term describing the preferential formation in a *chemical reaction* of one *enantiomer* or *diastereoisomer* over the other as a result of the influence of a chiral feature in the substrate, reagent, *catalyst* or environment. The term also refers to the formation of a new chiral feature preferentially in one *configuration* under such influence.

Atomic orbital : A one-electron wavefunction describing an electron in the effective field provided by a nucleus and the other electrons present.

Attachment : A *transformation* by which one *molecular entity* (the *substrate*) is converted into another by the formation of one (and only one) two-centre *bond* between the substrate and another molecular entity and which involves no other changes in *connectivity* in the substrate. For example, the formation of an acyl cation by attachment of carbon monoxide to a *carbenium ion* (R^+) : $R^+ + CO \longrightarrow (RCO)^+$. The product of an attachment may also be the *adduct* of the two reactants, but not all adducts can be represented as the products of an attachment. (For example, the Diels-Alder *cycloaddition* results in an adduct of buta-1,3-diene and ethene, but the reaction cannot be described as an attachment since bonds are formed between more than two centres.)



Autocatalytic reaction : A *chemical reaction* in which a product (or a reaction *intermediate*) also functions as *catalyst*. In such a reaction the observed *rate of reaction* is often found to increase with time from its initial value.

Automerization: Synonymous with *degenerate rearrangement*.

Autoprotolysis : A *proton* (hydron) *transfer* reaction between two identical molecules (usually a solvent), one acting as a *Brønsted acid* and the other as a *Brønsted base*. For example : $2 H_2O \longrightarrow H_3O^+ + OH^-$

Autoprotolysis constant : The product of the activities (or, more approximately, concentrations) of the species produced as the result of *autoprotolysis*. For solvents in which no other ionization processes are significant the term is synonymous with "ionic product". The autoprotolysis constant for water, K_w , is equal to the product of activities $a(\text{H}_3\text{O}^+)a(\text{OH}^-) = 1.0 \times 10^{-14}$ at 25 °C.

A value : The conformational preference of an equatorial compared to an axial substituent in a monosubstituted cyclohexane. This steric substituent parameter equals $\Delta_r G^\circ$ in kcal/mol for the equatorial to axial equilibration on cyclohexane. The values are also known as "Winstein-Holness" *A* values.

α -addition (alpha-addition) : A *chemical reaction* resulting in a single reaction product from two or three reacting chemical species, with formation of two new chemical *bonds* to the same atom in one of the reactant *molecular entities*. The synonymous term 1/1/addition is also used. For example: $\text{Cl}_2\text{C:} + \text{CH}_3\text{OH} \longrightarrow \text{Cl}_2\text{CHOCH}_3$ (This particular example can also be viewed as an *insertion reaction*.) In inorganic chemistry such α -addition reactions, generally to a metallic central atom, are known as "oxidative additions". α -Addition is the reverse of α -*elimination* or 1/1/elimination.

α -effect : A positive deviation of an α -nucleophile (a nucleophile bearing an unshared pair of electrons on an atom adjacent to the nucleophilic site) from a Brønsted-type plot of $\lg k_{\text{nuc}}$ vs. $\text{p}K_a$ constructed for a series of related normal nucleophiles. More generally, it is the influence of the atom bearing a lone pair of electrons on the reactivity at the adjacent site. HOZ and BUNCCEL (1985). See also *Brønsted relation*. The use of the term has been extended to include the effect of any substituent on an adjacent reactive centre, for example in the case of the " α -silicon effect".

α -elimination : A *transformation* of the general type $\text{RR}'\text{ZXY} \longrightarrow \text{RR}'\text{Z} + \text{XY}$ (or $\text{X} + \text{Y}$, or $\text{X}^+ + \text{Y}^-$) where the central atom Z is commonly carbon. The reverse reaction is called α -*addition*.

Ab initio : A calculation or prediction that is based purely on theory rather than on experimental data. Accurate *ab initio* predictions are an important test of a theory. (*Lat.*, "*from first principles*")

Abrasive : A very hard, brittle, heat-resistant substance that is used to grind the edges or rough surfaces of an object. boron carbide, diamond, and corundum are abrasives.

Absolute error : Absolute uncertainty. Compare with relative error : The uncertainty in a measurement, expressed with appropriate units. For example, if three replicate weights for an object are 1.00 g, 1.05 g, and 0.95 g, the absolute error can be expressed as ± 0.05 g. Absolute error is also used to express inaccuracies; for example, if the "true value" is 1.11 g and the measured value is 1.00 g, the absolute error could be written as $1.00 \text{ g} - 1.11 \text{ g} = -0.11 \text{ g}$. Note that when absolute errors are associated with indeterminate errors, they are preceded with " \pm "; when they are associated with determinate errors, they are preceded by their sign.

Absolute temperature : Temperature measured on a scale that sets absolute zero as zero. In the SI system, the kelvin scale is used to measure absolute temperature.

Absolute zero : The temperature at which the volume of an ideal gas becomes zero; a theoretical coldest temperature that can be approached but never reached. Absolute zero is zero on the Kelvin scale, -273.15°C on the Celsius scale, and -459.67°F on the Fahrenheit scale.

Absorbance : (A, D, E) optical density; extinction; decadic absorbance. A measure of the amount of light absorbed by a sample. The absorbance (A) equals minus the base-10 log of the transmittance.

Absorption : absorb; absorbent. Compare with adsorption and sorption.

Penetration of molecules into the bulk of a solid or liquid, forming either a solution or compound. Absorption can be a chemical process (a strong solution of NaOH absorbs CO_2 from the air) or a physical process (palladium absorbs hydrogen gas).

Capture and transformation of energy by a substance; for example, copper looks reddish because it absorbs blue light. An absorbent captures another material and distributes it

throughout; an adsorbent captures another material and distributes it on its surface only.

Absorption spectroscopy : Compare with absorption spectrum.

A technique for determining the concentration and structure of a substance by measuring the amount of electromagnetic radiation the sample absorbs at various wavelengths.

Absorption spectrum. Absorption spectra. Compare with absorption spectroscopy. A plot that shows how much radiation a substance absorbs at different wavelengths. Absorption spectra are unique for each element and compound and they are often used as chemical "fingerprints" in analytical chemistry. The spectrum can be represented by a plot of either absorbance* or transmittance versus wavelength, frequency, or wavenumber.

Absorptivity. (a) extinction coefficient; absorption cross section; decadic absorptivity. Compare with molar absorptivity and absorbance.

The absorbance of a solution per unit of path length and per unit concentration; $a = A/(bc)$ where a , A , b , and c are the absorptivity, absorbance, path length, and concentration, respectively. Absorptivity varies with wavelength of the incident light.

Accelerator : A substance that makes vulcanization of rubber occur more quickly or at a lower temperature.

A substance that makes crosslinking in a polymer occur more quickly or at a lower temperature, *e. g.*, accelerators are added to Super Glue to make it set up quickly.

Accuracy : Compare with precision and trueness. Accuracy is the correctness of a single measurement. The accuracy of a measurement is assessed by comparing the measurement with the true or accepted value, based on evidence independent of the measurement. The closeness of an **average** to a true value is referred to as "trueness".

Acetate : (CH_3COO^- , $\text{C}_2\text{H}_3\text{O}_2^-$) acetate ion.

An ion formed by removing the acidic hydrogen of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$.

A compound derived by replacing the acidic hydrogen in acetic acid.

A fiber made of cellulose acetate.

Acetic acid : (CH_3COOH , $\text{HC}_2\text{H}_3\text{O}_2$) ethanoic acid; vinegar acid; methanecarboxylic acid. A simple organic acid that gives vinegar its characteristic odor and flavor. Glacial acetic acid is pure acetic acid.

Acid. ([Lat. *acidus*, sour]) Compare with base.

A compound which releases hydrogen ions (H^+) in solution (*Arrhenius*).

A compound containing detachable hydrogen ions (*Bronsted-Lowry*).

A compound that can accept a pair of electrons from a base (*Lewis*).

Acid anhydride. Compare with acid. Nonmetallic oxides or organic compounds that react with water to form acids. For example, SO_2 , CO_2 , P_2O_5 , and SO_3 are the acid anhydrides of sulfurous, carbonic, phosphoric, and sulfuric acids, respectively. Acetic anhydride ($\text{CH}_3\text{CO}_2\text{O}$) reacts with water to form acetic acid.

Acid-base indicator : A weak acid that has acid and base forms with sharply different colors. Changes in pH around the acid's pKa are "indicated" by color changes.

Acid dissociation constant : (K_a) acid ionization constant. Compare with base hydrolysis constant. The equilibrium constant for the dissociation of an acid into a hydrogen ion and an anion. For example, the acid dissociation constant for acetic acid is the equilibrium constant for $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$, which is $K_a = [\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$.

Acid error : Compare with alkaline error. A systematic error that occurs when glass pH electrodes are used in strongly acidic solutions. Glass electrodes give pH readings that are consistently too high in these solutions.

Acid halide. acid chloride; acyl halide; acyl chloride. Compounds containing a carbonyl group bound to a halogen atom.

Acidic solution : A solution in which the hydrogen ion activity is higher than that of the hydroxide ion, when the solvent is water.

Acidulant : A substance added to food or beverages to lower pH and to impart a tart, acid taste. Phosphoric acid is an acidulant added to cola drinks.

Actinide : Elements 89-102 are called actinides. Electrons added during the Aufbau construction of actinide atoms go into the $5f$ subshell. Actinides are unstable and undergo radioactive decay. The most common actinides on Earth are uranium and thorium.

Activated charcoal : activated carbon; active carbon. A porous form of carbon that acts as a powerful adsorbent, used to decolorize liquids, recover solvents, and remove toxins from water and air.

Activated complex : Transition state. An intermediate structure formed in the conversion of reactants to products. The activated complex is the structure at the maximum energy point along the reaction path; the activation energy is the difference between the energies of the activated complex and the reactants.

Activation energy : (E_a) The minimum energy required to convert reactants into products; the difference between the energies of the activated complex and the reactants.

Active site : A pocket or crevice on an enzyme molecule that fits reactant molecules like a hand in a glove. The active site lowers the activation energy for reaction.

Activity : (a) An effective concentration used in thermodynamic calculations in place of the actual concentration to allow equations developed for ideal solutions to be used to treat real solutions.

Activity coefficient. (γ) : The ratio of activity to concentration; $a = \gamma c$ where a , γ , and c are the activity, activity coefficient, and concentrations, respectively. Activity coefficients are usually obtained from measurements of the emf of electrochemical cells or the colligative properties of solutions.

Adiabat : Adiabatic line. Compare with adiabatic. A line on an indicator diagram that represents an adiabatic process.

Adiabatic : Adiabatic process; isentropic process. A process that neither absorbs nor releases energy into the surroundings. For example, a chemical reaction taking place in a closed thermos bottle can be considered adiabatic. Very fast processes can often be considered adiabatic with respect to heat exchange with the surroundings, because heat exchange is not instantaneous.

Adiabatic ionization energy. Compare with vertical ionization energy. The lowest energy required to remove an electron from an atom, ion, or molecule in the gas phase. The adiabatic ionization energy is the difference between the ground state energy of the ion formed and the energy of the original atom, molecule, or ion.

Addition compound : Complex compound. Compare with hydrate. An addition compound contains two or more simpler compounds that can be packed in a definite ratio into a crystal. A dot is used to separate the compounds in the formula. For example, $\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$ is an addition compound of zinc sulfate and water. This represents a compound, and not a mixture, because there is a definite 1:7 ratio of zinc sulfate to water in the compound. Hydrates are a common type of addition compound.

Adhesion : (cohesion) Attraction between different substances on either side of a phase boundary.

Adsorb. Adsorbed; adsorbing. To collect molecules of a substance on a surface.

Adsorbent : Compare with absorbent. A substance that collects molecules of another substance on its surface. For example, gases that make water taste bad are strongly adsorbed on activated charcoal granules in water filters.

Adsorption : Adsorb; adsorbed. Compare with absorption and sorption. Adsorption is collection of a substance on the surface of a solid or a liquid. For example, gases that make water taste bad are strongly adsorbed on charcoal granules in water filters.

Adsorption chromatography : A technique for separating or analyzing mixtures that contain at least one component that is preferentially adsorbed by the stationary phase as it moves over it.

Adsorption indicator : A substance that indicates an excess of a reactant in a precipitation reaction. For example, dichlorofluorescein is added to an NaCl solution being titrated with silver nitrate. Before the endpoint, excess chloride ions make the surface of the AgCl precipitate negative, and dichlorofluorescein anions remain in solution. After the endpoint, the excess silver ions make the surface of the AgCl precipitate positive, and the dichlorofluorescein anions are adsorbed onto their surface. Adsorption changes the color of the indicator from yellow-green to pink.

Aeration : Aerate. Preparation of a saturated solution of air gases by either spraying the solution in air or by bubbling air through it.

Aerosol : Compare with colloid. A colloid in which solid particles or liquid droplets are suspended in a gas. Smoke is an example of a solid aerosol; fog is an example of a liquid aerosol.

Agar : A gel made from seaweed used to make salt bridges.

Alanine : (A, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$) Ala; alpha-aminopropionic acid.

A naturally occurring aliphatic amino acid which is required for protein synthesis but is not essential in the diet. Beta-alanine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{COOH}$) also occurs naturally.

Alcohol : (ROH) Compare with phenol and hydroxide. An alcohol is an organic compound with a carbon bound to a hydroxyl group. Examples are methanol, CH_3OH ; ethanol, $\text{CH}_3\text{CH}_2\text{OH}$; propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$. Compounds with -OH attached to an aromatic ring are called phenols rather than alcohols.

Aldehyde : (RCHO) An aldehyde is an organic compound with a carbon bound to a $-(\text{C}=\text{O})-\text{H}$ group. Examples are formaldehyde (HCHO), acetaldehyde, CH_3CHO , and benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$.

Aliphatic : Compare with aromatic. An organic compound that does not contain ring structures.

Aliquot : A sample of precisely determined amount taken from a material.

Alkali metal : (alkaline earth metal) alkali metal element. The Group 1 elements, lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr) react with cold water for form strongly alkaline hydroxide solutions, and are referred to as "alkali metals". Hydrogen is *not* considered an alkali metal, despite its position on some periodic tables.

Alkaline : Having a pH greater than 7.

Alkaline earth : An oxide of an alkaline earth metal, which produces an alkaline solution in reaction with water.

Alkaline earth metal : (alkali metal) The Group 2 elements, beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) form alkaline oxides and hydroxides and are called "alkaline earth metals".

Alkaline error : Compare with acid error. A systematic error that occurs when glass electrodes are used to read the pH of an extremely alkaline solution; the electrode responds to sodium ions as though they were hydrogen ions, giving a pH reading that is consistently too low.

Alkalinity : A measure of a material's ability to neutralize acids. Alkalinities are usually determined using titration.

Alkaloid : A class of bitter-tasting, basic organic compounds with nitrogen-containing rings. Alkaloids often have powerful effects on living things. Examples are cocaine, nicotine, strychnine, caffeine, and morphine.

Alkane : Paraffin. Compare with hydrocarbon and alkene. A series of organic compounds with general formula C_nH_{2n+2} . Alkane names end with **-ane**. Examples are propane (with $n=3$) and octane (with $n=8$).

Alkene : A compound that consists of only carbon and hydrogen, that contains at least one carbon-carbon double bond. Alkene names end with **-ene**. Examples are ethylene ($CH_2=CH_2$); 1-propene ($CH_2=CH_2CH_3$), and 2-octene ($CH_3CH_2=CH_2(CH_2)_4CH_3$).

Alkoxide : ($RO^- M^+$) alkoxide ion. An ionic compound formed by removal of hydrogen ions from the hydroxyl group in an alcohol using reactive metals, e. g. sodium. For example, potassium metal

reacts with methanol (CH_3OH) to produce potassium methoxide (KOCH_3).

Alkyl : ($-\text{C}_n\text{H}_{2n+1}$) alkyl group. A molecular fragment derived from an alkane by dropping a hydrogen atom from the formula. Examples are methyl (CH_3) and ethyl (CH_2CH_3).

Alkyl halide : An alkyl group attached to a halogen atom.

Alkyne : A compound that consists of only carbon and hydrogen, that contains at least one carbon-carbon triple bond. Alkyne names end with **-yne**. Examples are acetylene ($\text{CH}\equiv\text{CH}$); 1-propyne ($\text{CH}_2\equiv\text{CH}_2\text{CH}_3$), and 2-octyne ($\text{CH}_3\text{CH}_2\equiv\text{CH}_2(\text{CH}_2)_4\text{CH}_3$).

Allo-. A prefix that designates the more stable of a pair of geometric isomers. *allo-* is sometimes used less precisely to designate isomers or close relatives of a compound.

Allobar : A form of an element that has isotopic abundances that are different from the naturally occurring form. For example, "depleted" uranium has had most of the uranium-235 removed, and is an allobar of natural uranium.

Allomer : Allomerism. Substances with different chemical composition but the same crystalline form.

Allosteric effect : allosteric interaction. A change in the behavior of one part of a molecule caused by a change in another part of the molecule.

Allotrope : Allotropy; allotropic; allotropism. Compare with isotope and polymorph. Some elements occur in several distinct forms called allotropes. Allotropes have different chemical and physical properties. For example, graphite and diamond are allotropes of carbon.

Alloy : Alloying; alloyed. Compare with amalgam. A mixture containing mostly metals. For example, brass is an alloy of copper and zinc. Steel contains iron and other metals, but also carbon.

Allyl : Allylic; allyl group; allyl radical. A molecular fragment derived by removing a methyl hydrogen from propene ($-\text{CH}_2-\text{CH}_2=\text{CH}_2$). For example, "allyl chloride" is 3-chloropropene, $\text{Cl}-\text{CH}_2-\text{CH}_2=\text{CH}_2$.

Alpha particle : (${}^4_2\text{He}$) A particle that is commonly ejected from radioactive nuclei, consisting of two protons and two neutrons. Alpha particles are helium nuclei. Alpha particles have a mass of $6.644\,655\,98 \times 10^{-27}$ kg or 4.001 506 1747 atomic mass units.

Alpha ray : (α -ray) alpha radiation. A stream of alpha particles. Alpha rays rapidly dissipate their energy as they pass through materials, and are far less penetrating than beta particles and gamma rays.

Amalgam. Compare with alloy. An alloy that contains mercury.

American Chemical Society ACS. A large and influential professional society for professionals and students in chemistry and related fields.

Amide : An amide is an organic compound that contains a carbonyl group bound to nitrogen: $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}' \end{array}$. The simplest amides are formamide (HCONH_2) and acetamide (CH_3CONH_2).

Amine : Compare with ammine. An amine is an organic compound that contains a nitrogen atom bound only to carbon and possibly hydrogen atoms. Examples are methylamine, CH_3NH_2 ; dimethylamine, CH_3NHCH_3 ; and trimethylamine, $(\text{CH}_3)_3\text{N}$.

Amino acid : Amino acids are molecules that contain at least one amine group ($-\text{NH}_2$) and atleast one carboxylic acid group ($-\text{COOH}$). When these groups are both attached to the same carbon, the acid is an α -amino acid. α -amino acids are the basic building blocks of proteins.

Ammine : Compare with amine. A metal ion complex containing ammonia as a ligand. The ammonia nitrogen is bound directly to a metal ion in ammines; amines differ in that the ammonia nitrogen is directly bound to a carbon atom.

Ammonia : (NH_3) Compare with ammonium.

Pure NH_3 is a colorless gas with a sharp, characteristic odor. It is easily liquified by pressure, and is very soluble in water. Ammonia acts as a weak base. Aqueous solutions of ammonia are (incorrectly) referred to as "ammonium hydroxide".

Ammonium ion : (NH_4^+) ammonium.

NH_4^+ is a cation formed by neutralization of ammonia, which acts as a weak base.

Amorphous : amorphous solid. Compare with crystal. A solid that does not have a repeating, regular three-dimensional arrangement of atoms, molecules, or ions.

Amperage : The amount of charge moved per second by an electric current, measured in amperes.

Ampere : (A) amp. The SI unit of electric current, equal to flow of 1 coulomb of charge per second. An ampere is the amount of current necessary to produce a force of 0.2 micronewtons per meter between two arbitrarily long, arbitrarily thin wires, placed parallel in a vacuum and exactly 1 m apart. Named for 19th century physicist André Marie Ampère.

Amperometry : amperometric. Determining the concentration of a material in a sample by measuring electric current.

Amphi- : A prefix used to name certain members of a series of geometric isomers or stereoisomers.

Amphiprotic solvent. Compare with aprotic solvent. Solvents that exhibit both acidic and basic properties; amphiprotic solvents undergo autoprotolysis. Examples are water, ammonia, and ethanol.

Amphoteric : ampholyte. A substance that can act as either an acid or a base in a reaction. For example, aluminum hydroxide can neutralize mineral acids ($\text{Al}(\text{OH})_3 + 3 \text{HCl} = \text{AlCl}_3 + 3 \text{H}_2\text{O}$) or strong bases ($\text{Al}(\text{OH})_3 + 3 \text{NaOH} = \text{Na}_3\text{AlO}_3 + 3 \text{H}_2\text{O}$).

Amplitude : The displacement of a wave from zero. The maximum amplitude for a wave is the height of a peak or the depth of a trough, relative to the zero displacement line.

Amylopectin. Compare with amylose. A form of starch made of glucose molecules linked in a branching pattern.

Amylose. Compare with amylopectin. A form of starch made of long, unbranched chains of α -D-glucose molecules.

Aprotic solvent. Compare with amphiprotic solvent. A solvent that does not act as an acid or as a base; aprotic solvents don't undergo autoprotolysis. Examples are pentane, pet ether, and toluene.

Analysis : chemical analysis. Determination of the composition of a sample.

Analyte : An analyte is the sample constituent whose concentration is sought in a chemical analysis.

Angstrom : (Å) Ångstrom; Ångstrom units. A non-SI unit of length used to express wavelengths of light, bond lengths, and molecular sizes. $1 \text{ Å} = 10^{-10} \text{ m} = 10^{-8} \text{ cm}$.

Angular momentum quantum number : (ℓ) azimuthal quantum number; orbital angular momentum quantum number. A quantum number that labels the subshells of an atom. Sometimes called the *orbital angular momentum quantum number*, this quantum number dictates orbital shape. ℓ can take on values from 0 to $n-1$ within a shell with principal quantum number n .

Anhydrous : Anhydrous compound; anhydride. Compare with hydrate. A compound with all water removed, especially water of hydration. For example, strongly heating copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) produces anhydrous copper(II) sulfate (CuSO_4).

Anion : Compare with cation. An anion is a negatively charged ion. Nonmetals typically form anions.

Anode : Compare with cathode. The electrode at which oxidation occurs in a cell. Anions migrate to the anode.

Anodize : To coat a metal with a protective film by electrolysis.

Anthocyanin. anthocyan. A family of pigments that give flowers, fruits, and leaves of some plants their red or blue coloring. Anthocyanins consist of sugar molecules bound to a benzopyrylium salt (called anthocyanidin).

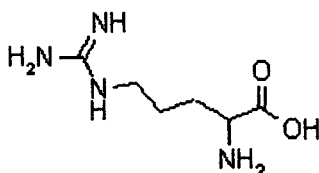
Antibonding orbital : antibonding; antibonding molecular orbital. A molecular orbital that can be described as the result of destructive interference of atomic orbitals on bonded atoms.

Antibonding orbitals have energies higher than the energies its constituent atomic orbitals would have if the atoms were separate.

Antichlor : A chemical compound that reacts with chlorine-based bleaches to stop the bleaching. Thiosulphate compounds are antichlors.

Antioxidant : Antioxidants are compounds that slow oxidation processes that degrade foods, fuels, rubber, plastic, and other materials. Antioxidants like butylated hydroxyanisole (BHA) are added to food to prevent fats from becoming rancid and to minimize decomposition of vitamins and essential fatty acids; they work by scavenging destructive free radicals from the food.

Antiozonant : Antiozonant. Substances that reverse or prevent severe oxidation by ozone. Antiozonants are added to rubber to prevent them from becoming brittle as atmospheric ozone reacts with them over time. Aromatic amines are often used as antiozonants.



Antipyretic : A substance that can lessen or prevent fever.

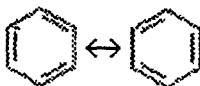
Aqua regia : A mixture of nitric and hydrochloric acids, usually 1:3 or 1:4 parts HNO₃ to HCl, used to dissolve gold.

Aqueous : (aq) aqueous solution. A substance dissolved in water.

Arene : A hydrocarbon that contains at least one aromatic ring.

Arginine : (R, C₆H₁₄N₄O₂) Arg. An essential amino acid and building block of proteins. Arginine acts as a base under physiological conditions; the double-bonded nitrogen on the end of the side chain readily captures a hydrogen ion, becoming positively charged. This charged side group makes arginine hydrophilic.

Aromatic ring : (Ar) An exceptionally stable planar ring of atoms with resonance structures that consist of alternating double and single bonds, e. g. benzene :



Aromatic compound : A compound containing an aromatic ring. Aromatic compounds have strong, characteristic odors.

Arrhenius equation : In 1889, Svante Arrhenius explained the variation of rate constants with temperature for several elementary reactions using the relationship $k = A \exp(-E_a/RT)$ where the rate constant k is the total frequency of collisions between reaction molecules A times the fraction of collisions $\exp(-E_a/RT)$ that have an energy that exceeds a threshold activation energy E_a at a temperature of T (in kelvins). R is the universal gas constant.

Aryl : (Ar) aryl group. A molecular fragment or group attached to a molecule by an atom that is on an aromatic ring.

Asparagine : Asn. A natural amino acid that is the amide of aspartic acid.

Aspartic acid : (D,HOOCC₂H(NH₂)COOH) Asp. A nonessential amino acid that is abundant in molasses. The carboxylic acid group on the side chain is ionized under physiological conditions, making aspartic acid residues in proteins hydrophilic.

Atmosphere. (atm) A unit of pressure, equal to a barometer reading of 760 mm Hg. 1 atmosphere is 101325 pascals and 1.01325 bar.

Atomic mass unit : (amu,u) amu; dalton. A unit of mass equal to 1/12 the mass of a carbon-12 nucleus, which is $1.660\,538\,73 \times 10^{-27}$ kg \pm $0.000\,000\,13 \times 10^{-27}$ kg. Abbreviated as *amu* or *u*. Sometimes called the *dalton*, after John Dalton, architect of the first modern atomic theory.

Atomic nucleus : Nucleus; nuclei; atomic nuclei. A tiny, incredibly dense positively charged mass at the heart of the atom. The nucleus is composed of protons and neutrons (and other

particles). It contains almost all of the mass of the atom but occupies only a tiny fraction of the atom's volume.

Atomic number : (Z) The number of protons in an atomic nucleus. The atomic number and the element symbol are two alternate ways to label an element. In nuclide symbols, the atomic number is a leading subscript; for example, in $^{12}_6\text{C}$, the "6" is the atomic number.

Atomic orbital : A wavefunction that describes the behavior of an electron in an atom.

Atomic radius : Metallic radius; covalent radius; atomic radii. Compare with ionic radius. One half the distance between nuclei of atoms of the same element, when the atoms are bound by a single covalent bond or are in a metallic crystal. The radius of atoms obtained from covalent bond lengths is called the covalent radius; the radius from interatomic distances in metallic crystals is called the metallic radius.

Atomic theory : An explanation of chemical properties and processes that assumes that tiny particles called atoms are the ultimate building blocks of matter.

Atomic unit : Compare with Bohr radius and hartree. A system of non-SI units used in quantum chemistry to simplify calculations and mathematical expressions. The definitions of atomic units include physical constants (like the speed of light, the rest mass of the electron, and other quantities that never change), so that all constants drop out of expressions when atomic units are used.

Atomic weight : atomic mass. The average mass of an atom of an element, usually expressed in atomic mass units. The terms mass and weight are used interchangeably in this case. The atomic weight given on the periodic table is a weighted average of isotopic masses found in a typical terrestrial sample of the element.

Atom : Compare with molecule and ion. An atom is the smallest particle of an element that retains the chemical properties of the element. Atoms are electrically neutral, with a positively charged nucleus that binds one or more electrons in motion around it.

Atto-:Prefix used in the SI system meaning "multiply by 10^{-18} "

Aufbau principle : aufbau construction; building-up principle. An approximate procedure for writing the ground state electronic configuration of atoms. The configuration of an atom is obtained by inserting one electron into the configuration of the atom immediately to its left on the periodic table. The electron is inserted into the subshell indicated by the element's period[†] and block.

Auto-ignition temperature. Minimum temperature at which the vapour / air mixture over a liquid spontaneously catches fire.

Autoxidation : Autooxidation; autoxidize; autoxidizing. Oxidation caused by exposure to air. Rust is an example of autoxidation. Autoxidation makes ether taken from half-filled bottles very dangerous, because air oxidizes ether to highly explosive organic peroxides.

Autoprotolysis : Autoionization; autoionization constant; autoprotolysis constant. Transfer of a hydrogen ion between molecules of the same substance, e. g. the autoprotolysis of methanol ($2 \text{ CH}_3\text{OH} = \text{CH}_3\text{OH}_2^+ + \text{CH}_3\text{O}^-$). Autoprotolysis of water into hydronium ions and hydroxide ions results in equilibrium concentrations that satisfy $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$, where the *autoprotolysis constant* K_w is equal to 1.01×10^{-14} at 25°C .

Auxochrome. A group or substructure in a molecule that influences the intensity of absorption of the molecule.

Average bond enthalpy : Average enthalpy change per mole when the same type of bond is broken in the gas phase for many similar substances

Avogadro : Amadeo Avogadro. Italian chemist and physicist Amadeo Avogadro (1776-1856) proposed a correct molecular explanation for Gay-Lussac's law of combining volumes. His work provided a simple way to determine atomic weights and molecular weights of gases.

Avogadro number : (N_A , L) Avogadro's number; Avogadro constant. The number of particles in one mole, equal to $6.02214199 \times 10^{23} \text{ mol}^{-1}$ ($\pm 0.00000047 \text{ mol}^{-1}$).

Avogadro's law : Equal volumes of an ideal gas contain equal numbers of molecules, if both volumes are at the same temperature

and pressure. For example, 1 L of ideal gas contains twice as many molecules as 0.5 L of ideal gas at the same temperature and pressure.

Axial : An atom, bond, or lone pair that is perpendicular to equatorial atoms, bonds, and lone pairs in a trigonal bipyramidal molecular geometry.

Azeotrope : Azeotropic mixture; azeotropy. A solution that does not change composition when distilled. For example, if a 95% (w/w) ethanol solution in water is boiled, the vapor produced also is 95% ethanol- and it is not possible to obtain higher percentages of ethanol by distillation.

Azo : Azo compound; azo group; azo dye. The azo group has the general structure Ar-N=N-Ar' , where Ar and Ar' indicate substituted aromatic rings. Compounds containing the azo compounds are often intensely colored and are economically important as dyes. Methyl orange is an example of an azo dye.

Absolute zero : The temperature (-273.15°C or 0 K) at which the volume and pressure of an ideal gas extrapolate to zero.

Absorption spectrum : The spectrum of dark lines against a light background that results from the absorption of selected frequencies of electromagnetic radiation by an atom or molecule.

Accuracy : The extent to which a measurement agrees with the true value of the quantity being measured.

Acid-base complex : The product of the reaction between a Lewis acid and a Lewis base. This complex contains a covalent bond formed by donating a pair of non-bonding electrons from the Lewis base to the Lewis acid.

Acid-base indicator : A weak acid or weak base, such as litmus or phenolphthalein, which changes color when it gains or loses an H^+ ion.

Acid-dissociation equilibrium constant (K_a) : A measure of the relative strength of an acid. For a generic acid with the formula HA, K_a can be calculated as : $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

Acidic buffer : A mixture of a weak acid and its conjugate base that has a pH less than 7 that can resist changes in pH when relatively small amounts of acid or base are added.

Activation energy : The energy that must be provided to the reactants in a chemical reaction to reach an intermediate or activated state from which the products of the reaction can form.

Active metal : A metal, such as sodium or potassium, that is unusually reactive.

Activity : A measure of the number of disintegrations of a radioactive nuclide per unit of time; reported in units of curies or becquerels.

Acyl Chloride : A compound in which a chlorine atom is bound to the carbon atom of a $C=O$ (carbonyl) group, e.g., CH_3COCl .

Addition polymer : A polymer formed without the loss of any atoms in the monomer. Polyethylene $(-CH_2CH_2-)_n$ is an addition polymer of ethylene ($H_2C=CH_2$).

Addition reaction : A reaction in which a molecule adds across a $C=C$ or $C=O$ double bond.

Adhesion : The force of attraction between different substances, such as glass and water.

Alcohol : Compounds with an $-OH$ group attached to a carbon atom, such as CH_3OH .

Aldehyde : Literally, an alcohol that has been *dehydrogenated*. Compounds with at least one hydrogen atom attached to a $C=O$ (carbonyl) group, such as formaldehyde (H_2CO) or acetaldehyde (CH_3CHO).

Algorithm : A set of rules for calculating something that can be taught to a reasonably intelligent system, such as a computer.

Alkali : Historically, a compound that neutralizes acids. Now known as a base.

Alkali metal : A metal in Group IA, such as Li, Na, K, and so on.

Alkaline earth metal : A metal in Group IIA, such as Be, Mg, Ca, and so on.

Alkaloid : A class of organic compounds that contain nitrogen, isolated from plants.

Alkane : A hydrocarbon with the generic formula C_nH_{2n+2} that contains only C-C and C-H bonds.

Alkene : An unsaturated hydrocarbon that contains one or more C=C double bonds.

Alkoxide : The conjugate base of an alcohol; for example, the CH_3O^- ion.

Alkyl halide : A derivative of an alkane in which a hydrogen atom has been replaced by a halogen, such as CH_3Cl .

Alkyne : A hydrocarbon that contains one or more carbon-to-carbon triple bonds.

Allotropes : Forms of an element with different structures and therefore different chemical and physical properties, such as O_2 and O_3 .

Alloy : A mixture of two or more elements that acts like a metal. Bronze, for example, is an alloy of copper and tin.

Alpha particle : A positively charged particle consisting of two protons and two neutrons emitted by one of the radioactive elements. An alpha particle is equivalent to an He^{2+} ion.

Amide : A compound that can be thought of as the product of the reaction between a carboxylic acid (RCO_2H) and an amine, such as CH_3CONH_2 . This term is also used to describe the NH_2^- ion.

Amine : Compound with an $-NH_2$, $-NHR$, or $-NR_2$ substituent attached to a carbon atom.

Amino acid : One of the essential building blocks from which proteins are made. Amino acids have the generic formula $H_3N^+CH(R)CO_2^-$.

Amontons' law : A statement of the relationship between the temperature and pressure of a constant amount of gas at constant volume: $P \propto T$.

Amorphous : Literally, without form or shape. Used to describe substances that are solids but not crystals.

Amphoteric : Used to describe a compound, such as H_2O or $\text{Al}(\text{OH})_3$, that can act as either an acid or a base.

Amplitude : The height of a wave. The difference between the center of gravity of the wave and the highest (or lowest) point on the wave.

Amu : Atomic mass unit. The unit in which the relative masses of atoms are expressed.

Angular momentum : For a particle in a spherical orbit, the product of the mass of the particle times its velocity times the radius of the orbit.

Angular quantum number (l) : The quantum number used to describe the shape of an atomic orbital.

Anhydrous : Literally, without water. Used, for example, to differentiate between liquid (anhydrous) ammonia at temperatures below its boiling point (-33°C) and solutions of ammonia dissolved in water.

Anion : A negatively charged ion, such as the Cl^- ion.

Anode : The positive end of an electric field. Used to describe the electrode in an electrochemical cell toward which anions flow and the electrode at which oxidation occurs.

Antibonding molecular orbital : A molecular orbital in which electrons are held in a region of space that does not lie between the atoms.

Approximation Methods : A technique for obtaining approximate answers to calculations that are difficult, if not impossible, to solve exactly.

Aqueous : Literally, watery. Used to describe solutions of substances dissolved in water.

Aromatic compound : A compound, such as benzene (C_6H_6), that seems to contain $\text{C}=\text{C}$ double bonds but does not react as an alkene does.

Arrhenius acid : A substance that dissociates when it dissolves in water to give the H^+ ion.

Arrhenius base : A substance that dissociates when it dissolves in water to give the OH^- ion.

Arrhenius equation : Describes the relationship between the rate constant for a chemical reaction and the temperature at which the reaction is run.

Atactic : Used to describe polymers in which the side chains are randomly distributed on either side of the polymer backbone.

Atom : The smallest particle of an element that retains any of the properties of the element.

Atomic number (Z) : The number of protons in the nucleus of an atom.

Atomic orbital : A region in space where electrons on an atom can be found.

Atomic weight : The weighted average of the atomic masses of the different isotopes of an element. A single ^{12}C atom, for example, has a mass of 12 amu, but naturally occurring carbon also contains a 1.1% ^{13}C . The atomic weight of carbon is therefore 12.011 amu.

Aufbau principle : The principle that atomic orbitals are filled one at a time, starting with the orbital that has the lowest energy.

Avogadro's number : The number of particles in a mole of these particles: 6.0220×10^{23} .

Avogadro's hypothesis : The hypothesis that equal volumes of different gases at the same temperature and pressure contain the same number of particles.

Axial : Describes the two positions in a trigonal bipyramid that lie above and below the trigonal plane.

B

Back titration. Indirect titration. Determining the concentration of an analyte by reacting it with a known number of moles of excess reagent. The excess reagent is then titrated with a second reagent. The concentration of the analyte in the original solution is then related to the amount of reagent consumed.

A symbolic representation of a chemical reaction in which both sides of the equation contain equivalent numbers of atoms of each element. Charge and mass are both conserved in a balanced equation.

Balanced equation : Balanced. A description of a chemical reaction that gives the chemical formulas of the reactants and the products of the reaction, with coefficients introduced so that the number of each type of atom and the total charge is unchanged by the reaction. For example, a balanced equation for the reaction of sodium metal (Na(s)) with chlorine gas (Cl₂(g)) to form table salt (NaCl(s)) would be $2 \text{ Na(s)} + \text{Cl}_2\text{(g)} = 2 \text{ NaCl(s)}$, NOT $\text{Na(s)} + \text{Cl}_2\text{(g)} = \text{NaCl(s)}$.

A set of empirical rules for certain formations of 3- to 7-membered rings. The predicted pathways are those in which the length and nature of the linking chain enables the terminal atoms to achieve the proper geometries for reaction. The disfavoured cases are subject to severe distortions of bond angles and bond distances.

Balmer series : Balmer lines. A series of lines in the emission spectrum of hydrogen that involve transitions to the $n=2$ state from states with $n>2$.

Band : A set of closely spaced energy levels in an atom, molecule, or metal.

A set of closely spaced lines in an absorption spectrum or emission spectrum.

A range of frequencies or wavelengths.

Band of stability : A narrow band of neutron-to-proton ratios that correspond to stable nuclides.

Bar : Unit of pressure. $1 \text{ bar} = 10^5 \text{ pascals} = 1.01325 \text{ atmospheres}$.

Barcom : The Barcelona Commission, which has the objective of protecting the Mediterranean Sea against pollution.

Barometer : An instrument that measures atmospheric pressure. A mercury barometer is a closed tube filled with mercury inverted in a mercury reservoir. The height of the mercury column indicates atmospheric pressure (with $1 \text{ atm} = 760 \text{ mm of mercury}$). An aneroid barometer consists of an evacuated container with a flexible wall. When atmospheric pressure changes, the wall flexes and moves a pointer which indicates the changing pressure on a scale.

Base : A *chemical species* or *molecular entity* having an available pair of electrons capable of forming a *covalent bond* with a *hydron* (proton) or with the vacant orbital of some other species

A substance that can accept a proton from another substance.

Example: aqueous ammonia ($\text{NH}_3(\text{aq})$). A base can react with an acid in water to form a salt and water.

Alkali; alkaline; basic. Compare with acid.

A compound that reacts with an acid to form a salt.

A compound that produces hydroxide ions in aqueous solution (*Arrhenius*).

A molecule or ion that captures hydrogen ions. (*Bronsted-Lowry*).

A molecule or ion that donates an electron pair to form a chemical bond. (*Lewis*).

Base hydrolysis constant : (K_b) base ionization constant; basic hydrolysis constant. Compare with acid dissociation constant.

Base unit : Base units are units that are fundamental building blocks in a system of measurement. There are seven base units in the SI system.

Base-ionization equilibrium constant (K_b) : A measure of the relative strength of a base. For the generic base B, K_b can be calculated as : $K_b = \frac{[BH^+][OH^-]}{[B]}$

Basic buffer : A mixture of a weak acid and its conjugate base that has a pH less than 7 that can resist changes in pH when relatively small amounts of acid or base are added.

Basic salt : a salt that contains at least one hydroxide ion. The hydroxide ion can then behave as a base in chemical reactions. *Example:* the reaction of hydrochloric acid (HCl) with the base, aluminium hydroxide ($Al(OH)_3$) can form two basic salts, $Al(OH)_2Cl$ and $Al(OH)Cl_2$.

Basicity : For *Brønsted bases* it means the tendency of a compound to act as *hydron* (proton) acceptor. The basicity of a *chemical species* is normally expressed by the *acidity* of the conjugate acid (see *conjugate acid-base pair*). For *Lewis bases* it relates to the association constants of *Lewis adducts* and π -*adducts*.

Basis function : A mathematical function that can be used to build a description of wavefunctions for electrons in atoms or molecules.

Basis set : A set of mathematical functions that are combined to approximate the wavefunctions for electrons in atoms and molecules.

Bat : Best Available Techniques. BAT Standards are used to judge the performance of industrial processes and to provide a target for improvement plans. They are gathered in a BAT Reference Document (BREF).

Bathochromic shift (effect) : Shift of a spectral band to lower frequencies (longer wavelengths) owing to the influence of substitution or a change in environment. It is informally referred to as a red shift and is opposite to *hypsochromic shift* (blue shift).

Battery : A group of voltaic cells connected in series.

A group of voltaic cells connected in series.

A number of electrochemical cells placed in series.

Literally, a set of similar items, such as an artillery battery.
Used to describe a battery of electrochemical cells connected in series.

Battery acid : A solution of approximately 6M sulfuric acid used in the lead storage battery.

Baumé : Baumé scale; degrees Baumé; Baume; Baumé scale. A, Be scale related to specific gravities, devised by the French chemist Antoine Baumé for marking hydrometers. At 60°F, specific gravity can be calculated from degrees Baumé by the following formulas : liquids lighter than water: $\text{sp. gr.} = 140/({}^\circ\text{Bé} + 130)$
liquids heavier than water: $\text{sp. gr.} = 145/(145 - {}^\circ\text{Bé})$

Bauxite : a hydrated impure oxide of aluminium ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, with the amount of water x being variable). It is the main ore used to obtain aluminium metal. The reddish-brown colour of bauxite is mainly caused by the iron oxide impurities it contains.

BCF : Bio Concentration Factor

Beehive shelf : an inverted earthenware bowl with a hole in the upper surface and a slot in the rim. Traditionally, the earthenware was brown and looked similar to a beehive, hence its name. A delivery tube passes through the slot and a gas jar is placed over the hole. This provides a convenient way to collect gas over water in a pneumatic trough.

Beer's law : ($A = abc$ or $A = \epsilon bc$) Beer-Lambert law. In absorption spectroscopy, the absorbance of a dilute solution is equal to its absorptivity times the path length times the concentration of the absorbing solute.

Bell jar : a tall glass jar with an open bottom and a wide, stoppered neck that is used in conjunction with a beehive shelf and a pneumatic trough in some experiments involving gases. The name derives from historic versions of the apparatus, which resembled a bell in shape.

Bell-Evans-Polanyi principle : The linear relation between *energy of activation* (E_a) and enthalpy of reaction (ΔH_r) sometimes observed within a series of closely related reactions. $E_a = A + B\Delta H_r$.

Benzyne : 1,2-Didehydrobenzene (the *aryne* derived from benzene) and its derivatives formed by substitution. The terms *m*- and *p*-benzyne are occasionally used for 1,3- and 1,4-didehydrobenzene, respectively.

BEPs : Best Environmental Practices. BEP means the application of the most appropriate combination of environmental control measures or strategies in order to reduce the impact of specific substances or applications.

Beryllium : (Be) Be; glucinium. Element 4, atomic weight 9.0122, an extremely toxic metal used as a neutron source and in phosphors.

Beta decay : A nuclear reaction in which beta particles (electrons, β^- , or positrons, β^+) are absorbed by or emitted from the nucleus of an atom.

Beta particle : (β^-) An electron emitted by an unstable nucleus, when a neutron decays into a proton and an electron. In some cases, beta radiation consists of positrons ("antielectrons" which are identical to electrons but carry a +1 charge.") Note that beta particles are created in nuclear decay; they do not exist as independent particles within the nucleus.

Bidentate : A ligand that binds twice. See chelating ligand.

A ligand that has two "teeth" or atoms that coordinate directly to the central atom in a complex. For example, 1,10-phenanthroline is a bidentate ligand of iron.

Bifunctional catalysis : Catalysis (usually for *hydron* transfer) by a bifunctional *chemical species* involving a mechanism in which both *functional groups* are implicated in the *rate-controlling step*, so that the corresponding *catalytic coefficient* is larger than that expected for catalysis by chemical species containing only one of these functional groups. The term should not be used to describe the *concerted* action of two different catalysts ("concerted catalysis").

Bimolecular : A step in a chemical reaction in which two molecules are consumed.

Binary compound : Compare with compound. A compound that contains two different elements. NaCl is a binary compound; NaClO is not.

Binding energy : The energy released when the nucleus of an atom is formed by combining neutrons and protons.

Binding site : A specific region (or atom) in a *molecular entity* that is capable of entering into a stabilizing interaction with another molecular entity. An example of such an interaction is that of an active site in an enzyme with its *substrate*. Typical forms of interaction are by *hydrogen bonding*, *coordination*, and *ion pair* formation. Two binding sites in different molecular entities are said to be complementary if their interaction is stabilizing.

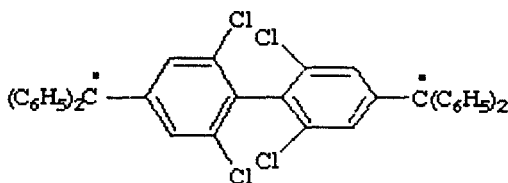
Bioaccumulation : Bioaccumulation denotes the accumulation of a substance in a living organism as a result of its intake both in the food and also from the environment. Determination of the B-factor (Bioaccumulation Factor) is extremely important in the risk analysis of a compound.

Biochemistry : The chemistry of living things, including the structure and function of biological molecules and the mechanism and products of their reactions.

Bioconcentration : Accumulation of a substance in an organism by absorption from the environment irrespective of any intake with food. The concept is of particular importance for aquatic life with regard to the absorption of those fat-soluble substances which are only broken down slowly.

Biomagnification : This term denotes the accumulation of substances in a living organism with the food intake. Simple organisms such as algae can absorb minute quantities of a substance which are transferred through the food chain to higher living species such as fish, bird, etc. Biomagnification along a food chain will result in the highest concentrations of a substance being found at the top of the food chain.

Biradical : An even-electron *molecular entity* with two (possibly delocalized) radical centres which act nearly independently of each other, e.g.



Species in which the two radical centres interact significantly are often referred to as “biradicaloids”. If the two radical centres are located on the same atom, the species are more properly referred to by their generic names: carbenes, nitrenes, etc. The lowest-energy triplet state of a biradical lies below or at most only a little above its lowest singlet state (usually judged relative to $k_B T$, the product of the Boltzmann constant k_B and the absolute temperature T). The states of those biradicals whose radical centres interact particularly weakly are most easily understood in terms of a pair of local doublets. Theoretical descriptions of low-energy states of biradicals display the presence of two unsaturated valences (biradicals contain one fewer bond than permitted by the rules of valence): the dominant valence bond structures have two dots, the low energy molecular orbital *configurations* have only two electrons in two approximately nonbonding molecular orbitals, two of the natural orbitals have occupancies close to one, etc. The term is synonymous with “diradical”.

Blast furnace : a tall furnace charged with a mixture of iron ore, coke and limestone and used for the refining of iron metal. The name comes from the strong blast of air introduced during smelting.

Bleach : A dilute solution of sodium hypochlorite or calcium hypochlorite which kills bacteria and destroys colored organic materials by oxidizing them.

A substance that removes colour in stains on materials, either by oxidising or reducing the staining compound.
Example: sulphur dioxide (SO_2).

Bleach is produced by reacting chlorine into a dilute sodium hydroxide solution. This solution is also known as “Eau de

Labarraque", and "Eau de Javel". Bleach is used for whitening paper, soap, straw and cotton, and for disinfection, water purification and in sanitary cleaners.

Block : A region of the periodic table that corresponds to the type of subshell (s, p, d, or f) being filled during the Aufbau construction of electron configurations.

One of the main divisions of the Periodic Table. Blocks are named for the outermost, occupied electron shell of an element. *Example:* The Transition Metals all belong to the d-block.

Body-centered cubic : A structure in which the simplest repeating unit consists of nine equivalent lattice points, eight of which are at the corners of a cube and the ninth of which is in the center of the body of the cube.

Bohr atom : Bohr's theory; Bohr's atomic theory; Bohr model. A model of the atom that explains emission and absorption of radiation as transitions between stationary electronic states in which the electron orbits the nucleus at a definite distance. The Bohr model violates the Heisenberg uncertainty principle, since it postulates definite paths and momenta for electrons as they move around the nucleus. Modern theories usually use atomic orbitals to describe the behavior of electrons in atoms.

Bohr model : A model of the distribution of electrons in an atom based on the assumption that the electron in a hydrogen atom is in one of a limited number of circular orbits.

Bohr radius : (a_0) bohr. Compare with atomic unit. The atomic unit of length, equal to $0.529\,177\,2083 \times 10^{-10}$ m, with an uncertainty of $0.000\,000\,0019 \times 10^{-10}$ m.

Boiling point : (bp) standard boiling point; normal boiling point. The temperature at which the vapor pressure of a liquid is equal to the external pressure on the liquid. The standard boiling point is the temperature at which the vapor pressure of a liquid equals standard pressure.

The temperature at which a liquid boils, changing from a liquid to a gas. Boiling points change with atmospheric

pressure. *Example:* The boiling point of pure water at standard atmospheric pressure is 100 °C.

The temperature at which the vapor pressure of a liquid is equal to the pressure on the liquid.

The boiling point of a solution is higher than the boiling point of the pure solvent. Boiling point elevation is a colligative property.

Boiling point elevation : The increase in the boiling point of a solvent that occurs when a solute is added to form a solution.

A thin glass tube closed at one end and used for chemical tests, etc. The composition and thickness of the glass is such that it cannot sustain very high temperatures and is intended for heating liquids to boiling point.

Boltzmann constant : (k) Boltzmann's constant. A fundamental constant equal to the ideal gas law constant divided by Avogadro's number, equal to $1.3805 \times 10^{-23} \text{ J K}^{-1}$.

Boltzmann equation : A statistical definition of entropy, given by $S = k \ln W$, where S and k are the entropy and Boltzmann's constant, respectively, and W is the probability of finding the system in a particular state.

Bond : Chemical bonding is either a transfer or sharing of electrons by two or more atoms. There are a number of types of chemical bond, some very strong (such as covalent and ionic bonds), others weak (such as hydrogen bonds). Chemical bonds form because the linked molecule is more stable than the unlinked atoms from which it formed. *Example:* the hydrogen molecule (H_2) is more stable than single atoms of hydrogen, which is why hydrogen gas is always found as molecules of two hydrogen atoms.

There is a chemical bond between two atoms or groups of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent "molecular species". In the context of this Glossary, the term refers usually to the *covalent bond*.

Bond energy (mean bond energy) : The average value of the gas-phase *bond-dissociation energies* (usually at a temperature of 298 K) for all *bonds* of the same type within the same *chemical species*. The mean bond energy for methane, for example, is one-fourth the enthalpy of reaction for $\text{CH}_4(\text{g}) \longrightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$. Tabulated bond energies are generally values of bond energies averaged over a number of selected typical chemical species containing that type of bond.

Bond energy : Compare with bond enthalpy. Energy change per mole when a bond is broken in the gas phase for a particular substance.

The energy required to break a given chemical bond.

Bond enthalpy : Compare with average bond enthalpy. Enthalpy change per mole when a bond is broken in the gas phase for a particular substance.

Bond length : The average distance between the nuclei of two bonded atoms in a stable molecule.

Bond number : The number of electron-pair *bonds* between two nuclei in any given *Lewis formula*. For example in ethene the bond number between the carbon atoms is two, and between the carbon and hydrogen atoms is one.

Bond order : In Lewis structures, the number of electron pairs shared by two atoms.

In molecular orbital theory, the net number of electron pairs in bonding orbitals (calculated as half the difference between the number of electrons in bonding orbitals and the number of electrons in antibonding orbitals).

A theoretical index of the degree of bonding between two atoms relative to that of a normal single bond, i.e. the bond provided by one localized electron pair. In the valence-bond theory it is a weighted average of the bond numbers between the respective atoms in the *contributing structures*. In molecular-orbital theory it is calculated from the weights of the atomic orbitals in each of the occupied molecular orbitals. For example, in valence-bond theory (neglecting

other than Kekulé structures) the bond order between adjacent carbon atoms in benzene is 1.5; in Hückel molecular orbital theory it is 1.67. Other variants of molecular orbital theory provide other values for bond orders.

The number of bonds between a pair of atoms.

Bond strength : Some measure of how difficult it is to break a chemical bond, for example, a bond energy or a bond enthalpy.

Bond-dissociation energy, D (SI unit: kJ mol^{-1} , or J (per molecule) The enthalpy (per mole) required to break a given *bond* of some specific *molecular entity* by *homolysis*, e.g. for $\text{CH}_4 \longrightarrow \text{H}_3\text{C}^\cdot + \text{H}^\cdot$ Symbolized as $D(\text{CH}_3\text{-H})$ (cf. *heterolytic bond-dissociation energy*).

Bond-dissociation enthalpy : The energy needed to break an X-Y bond to give X and Y atoms in the gas phase.

Bonding electrons : A pair of electrons used to form a covalent bond between adjacent atoms.

Bonding molecular orbital : A molecular orbital in which the electrons reside in the region in space between the atoms.

Borderline mechanism : A mechanism intermediate between two extremes, for example a nucleophilic substitution intermediate between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$, or intermediate between electron transfer and $\text{S}_{\text{N}}2$.

Boron : (B) B. Element 5, atomic weight 10.811. Hard yellow crystals or brown amorphous powder, used as a neutron absorber in nuclear chemistry and as a hardener in alloys.

Boundary : In thermodynamics, the boundary separates the system from its surroundings.

Boyle's law : A statement of the relationship between the pressure and volume of a constant amount of gas at constant temperature: $P \propto 1/V$.

At constant temperature, and for a given mass of gas, the volume of the gas (V) is inversely proportional to pressure that builds up (P): $P \propto 1/V$.

The pressure of a ideal gas is inversely proportional to its volume, if the temperature and amount of gas is held constant. Doubling gas pressure halves gas volume, if temperature and amount of gas don't change. If the initial pressure and volume are P_1 and V_1 and the final pressure and volume are P_2V_2 , then $P_1V_1 = P_2V_2$ at fixed temperature and gas amount.

Bragg equation : A statement of the relationship between the wavelength of the incident x-ray (λ), the distance between adjacent planes of atoms in a crystal (d), and the angle (θ) between the plane of the incident radiation and the uppermost plane of atoms in a crystal being subjected to x-ray diffraction analysis.

Brass : A shiny yellow to yellow-orange alloy that contains about two parts copper for every one part zinc.

Bredt's rule : A double bond cannot be placed with one terminus at the bridgehead of a bridged ring system unless the rings are large enough to accommodate the double bond without excessive strain. For example, while bicyclo[2.2.1]hept-1-ene is only capable of existence as a *transient*, its higher homologues having a double bond at the bridgehead position have been isolated: e.g.



Bicyclo[3.3.1]non-1-ene



Bicyclo[4.2.1]non-1(8)-ene

Breeder reactor : A nuclear reactor that produces more fuel than it consumes.

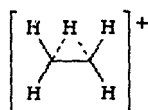
Bref : BAT Reference Document.

Bridged carbocation : A *carbocation* (real or hypothetical) in which there are two (or more) carbon atoms that could in alternative *Lewis formulae* be designated as *carbenium centres* but which is instead represented by a structure in which a *group* (a hydrogen atom or a hydrocarbon residue, possibly with substituents in non-involved positions) bridges these potential carbenium centres. One may distinguish "electron-sufficient bridged carbocations" and "electron-deficient bridged carbocations". Examples of the former are phenyl-bridged ions (for which the trivial name "phenonium ion" has been

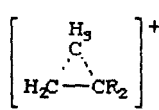
used), such as (A). These ions are straightforwardly classified as *carbenium ions*. The latter type of ion necessarily involves three-centre bonding. Structures (C) and (D) contain five-coordinate carbon atoms. The "hydrogen-bridged carbocation" (B) contains a two-co-ordinate hydrogen atom. Hypercoordination, which includes two-coordination for hydrogen and five- but also higher coordination for carbon is generally observed in bridged carbocations.



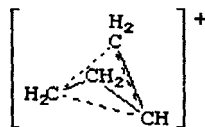
(A)



(B)



(C)



(D)

Bridging ligand : A *ligand* attached to two or more, usually metallic, central atoms.

Brine : A solution of salt (sodium chloride, NaCl) in water.

Bromide : Any compound that contains either the Br⁻ ion or bromine with an oxidation state of -1, such as NaBr or HBr.

Brønsted acid (Brönsted acid) : A *molecular entity* capable of donating a *hydron* (proton) to a base, (i.e. a "hydron donor") or the corresponding *chemical species*. For example: H₂O, H₃O⁺, CH₃CO₂H, H₂SO₄, HSO₄⁻, HCl, CH₃OH, NH₃. See also *conjugate acid-base pair*.

Any substance that can donate an H⁺ ion to a base. Brønsted acids are H⁺-ion or proton donors.

Brønsted base (Brönsted base) : 1. A *molecular entity* capable of accepting a *hydron* (proton) from an acid (i.e. a "hydron acceptor") or the corresponding *chemical species*. For example: OH⁻, H₂O, CH₃CO₂⁻, HSO₄⁻, SO₄²⁻, Cl⁻. See also *conjugate acid-base pair*.

Any substance that can accept an H⁺ ion from an acid. Brønsted bases are H⁺-ion or proton acceptors.

Brønsted relation (Brönsted relation) : The term applies to either of the equations $k_{HA/p} = G(K_{HA}q/p)^{\alpha}$ $k_A/q = G(K_{HA}q/p)^{\beta}$ (or their logarithmic forms) where α , β and G are constants for a given reaction series (α and β are called "Brønsted exponents"), k_{HA} and k_A are catalytic coefficients (or rate coefficients) of reactions whose

rates depend on the concentrations of HA and/or of A^- . K_{HA} is the acid dissociation constant of the acid HA, p is the number of equivalent acidic protons in the acid HA, and q is the number of equivalent basic sites in its conjugate base A^- . The chosen values of p and q should always be specified. (The charge designations of HA and A^- are only illustrative.) The Brønsted relation is often termed the "Brønsted *catalysis law*" (or the "Catalysis Law"). Although justifiable on historical grounds, this name is not recommended, since Brønsted relations are known to apply to many uncatalysed and pseudo-catalysed reactions (such as simple proton (*hydron*) transfer reactions). The term "pseudo-Brønsted relation" is sometimes used for reactions which involve *nucleophilic catalysis* instead of acid-base catalysis. Various types of Brønsted parameters have been proposed such as β_{lg} , β_{nuc} , β_{eq} for leaving group, nucleophile and equilibrium constants, respectively.

Bronze : A yellow to yellow-brown alloy that contains mostly copper and tin, with small amounts of other metals.

Brvsted acid : A material that gives up hydrogen ions in a chemical reaction.

Brvsted base : A material that accepts hydrogen ions in a chemical reaction.

Brownian motion : Brownian movement. Small particles suspended in liquid move spontaneously in a random fashion. The motion is caused by unbalanced impacts of molecules on the particle. Brownian motion provided strong circumstantial evidence for the existence of molecules.

Btu (British thermal unit) : The heat needed to raise the temperature of 1 pound of water by 1°F.

Büchner flask : A thick-walled side-arm flask designed to withstand the changes in pressure that occur when the flask is connected to a suction pump.

Büchner funnel : A special design of plastic or ceramic funnel which has a flat stage on which a filter paper can be placed. It is intended for use under suction with a Büchner flask.

Buckminsterfullerene : (C_{60}) C_{60} ; fullerene; buckyball. A form of carbon consisting of 60 carbon atoms bound together to make a roughly spherical "buckyball" (which looks rather like a soccer ball).

Buffer (solution) : A mixture of substances in solution that resists a change in the acidity or alkalinity of the solution when small amounts of an acid or alkali are added.

A mixture of a weak acid (HA) and its conjugate base (A^-) or a weak base (B) and its conjugate acid (BH^+). Buffers resist a change in the pH of a solution when small amounts of acid or base are added.

pH buffer; buffer solution. A solution that can maintain its pH value with little change when acids or bases are added to it. Buffer solutions are usually prepared as mixtures of a weak acid with its own salt or mixtures of salts of weak acids. For example, a 50:50 mixture of 1 M acetic acid and 1 M sodium acetate buffers pH around 4.7.

Buffer capacity : The amount of acid or base a buffer solution can absorb without significant changes in pH.

Bunnett-Olsen equations : The equations for the relation between $\lg([SH^+]/[S]) + H_o$ and $H_o + \lg[H^+]$ for base S in aqueous mineral acid solution, where H_o is Hammett's *acidity function* and $H_o + \lg[H^+]$ represents the activity function $\lg(\gamma_s \gamma_{H^+})/\gamma_{SH^+}$ for the nitroaniline reference bases to build H_o . $\lg([SH^+]/[S]) - \lg[H^+] = (\Phi - 1)(H_o + \lg[H^+]) + pK_{SH^+}$ $\lg([SH^+]/[S]) + H_o = \Phi(H_o + \lg[H^+]) + pK_{SH^+}$

Bunsen burner : A gas burner with adjustable air intake, commonly used in laboratories.

Buret : Burette. A cylindrical glass tube closed by a stopcock on one end and open on the other, with volume gradations marked on the barrel of the tube, used to precisely dispense a measured amount of a liquid.

Burette : A long, graduated glass tube with a tap at one end. A burette is used vertically, with the tap lowermost. Its main use is as a reservoir for a chemical during titration.

Burn : A combustion reaction in which a flame is produced. A flame occurs where *gases* combust and release heat and light. At least two gases are therefore required if there is to be a flame. *Example:* methane gas (CH_4) burns in oxygen gas (O_2) to produce carbon dioxide (CO_2) and water (H_2O) and give out heat and light.

Butanol : An alcohol containing four carbon atoms. Example: 1-butanol.



Cage : An aggregate of molecules, generally in the condensed phase, that surrounds the fragments formed, for example, by thermal or photochemical dissociation. Because the cage hinders the separation of the fragments by diffusion, they may preferentially react with one another ("cage effect") but not necessarily to re-form the precursor species. For example, $R-N=N-R$, heat $\longrightarrow [R\cdot + N_2 + R\cdot]_{\text{cage}} \longrightarrow R-R + N_2$.

The equilibrium constant for the hydrolysis reaction associated with a base. For example, K_b for ammonia is the equilibrium constant for $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$, or $K_b = [NH_4^+][OH^-]/[NH_3]$.

^{14}C dating : A technique for estimating the age of a sample that assumes that the ^{14}C isotope in the sample decays with a half-life of 5730 years.

An atom in a molecule that causes chirality, usually an atom that is bound to four different groups. A molecule can have chirality without having a chiral center, and a molecule may also have more than one chiral centers.

Caffeine : $(C_8H_{10}N_4O_2)$ methyltheobromine; guaranine; 1,3,7-trimethylxanthine; 1,3,7-trimethyl-2,6-dioxopurine. A substance found in tea, coffee, and cola that acts as a stimulant. It is extremely soluble in supercritical fluid carbon dioxide and somewhat soluble in water; aqueous solutions of caffeine quickly break down.

Cage compound : A polycyclic compound having the shape of a cage. The term is also used for *inclusion compounds*.

Calcining : A process in which an ore loses a gas while being heated.

Calibration : Calibration is correcting a measuring instrument by measuring values whose true values are known. Calibration minimizes systematic error.

Caloric theory : An obsolete theory, which assumed that heat (or caloric) is a fluid that is conserved.

Calorie : The amount of heat required to raise the temperature of 1 g of water at 14.5°C to 15.5°C. One calorie is equivalent to exactly 4.184 J.

Calorimeter : An apparatus used to measure the heat given off or absorbed in a chemical reaction.

An insulated container designed to prevent heat gain or loss with the environment and thus allow changes of temperature within reacting chemicals to be measured accurately. It is named after the old unit of heat, the calorie.

An insulated vessel for measuring the amount of heat absorbed or released by a chemical or physical change.

Calorimetry : Experimental determination of heat absorbed or released by a chemical or physical change.

The science of measuring heat flow.

Calutron : A device that separates isotopes (e. g. ^{235}U from ^{238}U) by ionizing the sample, accelerating the ions in a strong electric field, and then passing them through a strong magnetic field. The magnetic field bends the trajectories of the ions with high charge-to-mass ratio more, allowing ions to be separated by mass and collected.

Calx : The powder formed when metals react with air.

Canal rays : The positively charged particles formed when electrons are removed from the gas particles in a cathode-ray tube. Because they carry a positive charge, canal rays move in the opposite direction from cathode-rays.

Capacitor : A device for storing *electric charge*, consisting of two metal plates separated by an insulating material.

Capillary : A very small diameter (glass) tube. Capillary tubing has a small enough diameter to allow surface tension effects to retain water within the tube.

Capillary action : The tendency for a liquid to be sucked into small spaces, such as between objects and through narrow-pore tubes. The force to do this comes from surface tension.

Captodative effect : Effect on the stability of a carbon centred *radical* determined by the combined action of a captor (electron withdrawing) and a dative (electron releasing) substituent, both attached to the radical centre. The term is also used for certain unsaturated compounds.

Carbanion : A compound that contains a negatively charged carbon atom, such as the CH_3^- ion.

Generic name for anions containing an even number of electrons and having an unshared pair of electrons on a tervalent carbon atom (e.g. Cl_3C^- or $\text{HC}\equiv\text{C}^-$) or - if the ion is mesomeric (see *mesomerism*) - having at least one significant *contributing structure* with an unshared pair of electrons on a tervalent carbon atom, for example, $\text{CH}_3\text{C}(\text{O}^-)=\text{CH}-\text{C}(=\text{O})\text{CH}_3 \longleftrightarrow \text{CH}_3\text{C}(=\text{O})-\text{CH}^-\text{C}(=\text{O})\text{CH}_3$

Carbene : Generic name for the species $\text{H}_2\text{C}:$ and substitution derivatives thereof, containing an electrically neutral bivalent carbon atom with two nonbonding electrons. The nonbonding electrons may have antiparallel spins (singlet state) or parallel spins (triplet state). Use of the alternative name "methylene" as a generic term is not recommended.

Carbenium centre : The three-coordinate carbon atom in a *carbenium ion* to which the excess positive charge of the ion (other than that located on heteroatoms) may be formally considered to be largely attributed, i.e., which has one vacant p-orbital. (N.B. It is not always possible to uniquely identify such an atom.) This formal attribution of charge often does not express the real charge distribution.

Carbenium ion : A generic name for *carbocations*, real or hypothetical, that have at least one important *contributing structure* containing a tervalent carbon atom with a vacant p-orbital. (The

name implies a protonated carbene or a substitution derivative thereof.) The term was proposed (and rejected) as a replacement for the traditional usage of the name *carbonium ion*. To avoid ambiguity, the name should not be used as the root for the systematic nomenclature of carbocations. The corresponding difficulty confused carbonium ion nomenclature for many years. For example, the term "ethylcarbonium ion" has at times been used to refer either to CH_3CH_2^+ (ethyl cation) or (correctly) to $\text{CH}_3\text{CH}_2\text{CH}_2^+$ (propyl cation). For the nomenclature of carbenium ions see

Carbenoid : A *carbene* like *chemical species* but with properties and *reactivity* differing from the free carbene itself, e.g. $\text{R}^1\text{R}^2\text{C}(\text{Cl})\text{M}$ (M = metal)

Carbide : A compound that contains a negatively charged carbon atom or carbon in a negative oxidation state, such as calcium carbide (CaC_2)

Carbocation : A cation containing an even number of electrons with a significant portion of the excess positive charge located on one or more carbon atoms. This is a general term embracing *carbenium ions*, all types of *carbonium ions*, vinyl cations, etc. Carbocations may be named by adding the word "cation" to the name of the corresponding *radical*. Such names do not imply structure (e.g. whether three-coordinated or five-coordinated carbon atoms are present). See also *bridged carbocation*, *radical ion*.

An electron deficient carbon with only three single bonds. It is positively charged. A primary carbocation is bonded to only one other carbon, a secondary carbocation is bonded to two other carbon atoms and a tertiary carbocation is bonded to three other carbon atoms. The tertiary carbocation is most stable due to the stabilizing effect of the alkyl groups which donate electrons to stabilize the ion.

Carbohydrate : A compound containing only carbon, hydrogen and oxygen. Carbohydrates have the formula $\text{C}_n(\text{H}_2\text{O})_n$, where n is variable. *Example*: glucose ($\text{C}_6\text{H}_{12}\text{O}_6$).

A polyhydroxyl aldehyde or a polyhydroxyl ketone. Many of these compounds are commonly called sugars.

A class of organic compounds including sugars and starches. The name comes from the fact that many (but not all) carbohydrates have empirical formula CH_2O .

Literally, a hydrate of carbon. Originally defined as any compound with an empirical formula of CH_2O ; now defined as polyhydroxy aldehydes or ketones. Includes starches and sugars.

Carbon : C. An element with atomic number 6. Carbon is a nonmetal found in all organic compounds. Carbon occurs naturally as diamond, graphite, and buckminsterfullerene.

Carbon dioxide : (CO_2) A colorless, odorless gas produced by respiration and combustion of carbon-containing fuels.

Carbon monoxide : (CO) A colorless, odorless, poisonous gas produced by incomplete combustion.

Carbonate : (CO_3^{2-}) An inorganic ion with a charge of -2, containing carbon bound directly to three oxygens in a flat triangular arrangement.

A compound containing CO_3^{2-} ions.

A salt of carbonic acid. Carbonate ions have the chemical formula CO_3^{2-} . *Examples*: calcium carbonate CaCO_3 and sodium carbonate Na_2CO_3 .

Carbonate hardness : Carbonate water hardness. Compare with water hardness. Water hardness due to the presence of calcium and magnesium carbonates and bicarbonates. The "noncarbonate hardness" is due mostly to calcium and magnesium sulfates, chlorides, and nitrates.

Carbonium ion : A compound that contains a positively charged carbon atom, such as the CH_3^+ ion.

Carbonium ion : The term should be used with great care since several incompatible meanings are currently in use. It is not acceptable as the root for systematic nomenclature for *carbocations*.

In most of the existing literature the term is used in its traditional sense for what is here defined as *carbenium ion*.

A carbocation, real or hypothetical, that contains at least one five-coordinate carbon atom.

A carbocation, real or hypothetical, whose structure cannot adequately be described by two-electron two-centre *bonds* only. (The structure may involve carbon atoms with a *coordination number* greater than five.)

Carbonyl : A divalent group consisting of a carbon atom with a double-bond to oxygen. For example, acetone ($\text{CH}_3\text{-(C=O)-CH}_3$) is a carbonyl group linking two methyl groups. Also refers to a compound of a metal with carbon monoxide, such as iron carbonyl, Fe(CO)_5 .

In organic chemistry, the C=O functional group. In inorganic chemistry, a complex formed when carbon monoxide (CO) binds to a metal.

Carbonyl compounds : Have a double bonded oxygen attached to a carbon. --C=O | ALDEHYDES-- have the carbonyl group at the end of the chain. R-C=O | or RCHO end in -al. H ie. methanal (formaldehyde) H-C=O | H KETONES-- have the carbonyl group not at the end of the chain. R--O=O number where it is and it ends in -one. | $\text{CH}_3 \text{ R'}$ | ie. $\text{O=C-CH}_2\text{-CH}_2\text{-CH}_3$ 2-pentanone

Carboxylate ion : The conjugate base of a carboxylic acid, such as the CH_3CO_2^- ion formed when acetic acid loses an H^+ ion.

Carboxylic acid : A compound that contains the $\text{-CO}^2\text{H}$ functional group.

Carboxyl; carboxyl group. A carboxylic acid is an organic molecule with a -(C=O)-OH group. The group is also written as -COOH and is called a carboxyl group. The hydrogen on the -COOH group ionizes in water; carboxylic acids are weak acids. The simplest carboxylic acids are formic acid (H-COOH) and acetic acid^{*} ($\text{CH}_3\text{-COOH}$).

Carboxylic acid ester : A compound that can be thought of as the product of the reaction between a carboxylic acid (RCO^2H) and an alcohol (R'OH). Any compound that contains the $\text{RCO}^2\text{R'}$ functional group.

Carboy : A very large bottle. Glass carboys are usually encased in a wire mesh or wooden box for protection.

Carbyne : Generic name for the species $\text{HC}\cdot$ and substitution derivatives thereof, such as $\text{EtO}_2\text{C}-\text{C}\cdot$ containing an electrically neutral univalent carbon atom with three non-bonding electrons. Use of the alternative name "methylidyne" as a generic term is not recommended.

Carotene : Carotene is an unsaturated hydrocarbon pigment found in many plants. Carotene is the basic building block of vitamin A.

Catalysis : The action of a *catalyst*.

Catalyst : A substance that increases the rate of a chemical reaction without being consumed in the reaction. A substance that lowers the activation energy for a chemical reaction by providing an alternate pathway for the reaction.

A substance that participates in a particular *chemical reaction* and thereby increases its rate but without a net change in the amount of that substance in the system. At the molecular level, the catalyst is used and regenerated during each set of *microscopic chemical events* leading from a *molecular entity* of reactant to a molecular entity of product. See also *autocatalytic reaction*, *bifunctional catalysis*, *catalytic coefficient*, *electron-transfer catalysis*, *general acid catalysis*, *general base catalysis*, *intramolecular catalysis*, *micellar catalysis*, *Michaelis-Menten kinetics*, *phase-transfer catalysis*, *pseudo-catalysis*, *rate of reaction*, *specific catalysis*.

A substance that speeds up a chemical reaction, but itself remains unaltered at the end of the reaction. *Example*: copper in the reaction of hydrochloric acid with zinc.

Catalyze, catalysis. A substance that increases the rate of a chemical reaction, without being consumed or produced by the reaction. Catalysts speed both the forward and reverse reactions, without changing the position of equilibrium. Enzymes are catalysts for many biochemical reactions.

Species that lowers the activation energies of both, the forward and the reverse reaction. A catalyst provides a different pathway for a reaction. It may appear in a rate law. A catalyst does not change thermodynamic data, such as the equilibrium constant or the free energy of a reaction.

Catalytic coefficient : If the *rate of reaction* (ν) is expressible in the form $\nu = (k_0 + \sum k_i [C_i]^{n_i}) [A]^\alpha [B]^\beta \dots$ where A, B, ... are reactants and C_i represents one of a set of catalysts, then the proportionality factor k_i is the catalytic coefficient of the particular *catalyst* C_i . Normally the partial order of reaction (n_i) with respect to a catalyst will be unity, so that k_i is an $(\alpha + \beta + \dots + 1)$ th order rate coefficient. The proportionality factor k_0 is the $(\alpha + \beta + \dots)$ th order rate coefficient of the uncatalysed component of the total reaction.

Catalytic converter : a device incorporated into some exhaust systems. The catalytic converter contains a framework and/or granules with a very large surface area and coated with catalysts that convert the pollutant gases passing over them into harmless products.

Catenation : The tendency of an element to form bonds to itself.

Cathode : The electrode at which reduction occurs.

The electrode at which reduction occurs; the positive terminal of a battery or the negative electrode of an electrolysis cell.

The electrode in an electrochemical cell at which reduction occurs.

The negative end of an electric field. The electrode in an electrochemical cell toward which cations flow and the electrode at which reduction occurs.

Cathode ray : A negatively charged beam that emanates from the cathode of a discharge tube. Cathode rays are streams of electrons.

The negatively charged particles (now recognized as electrons) that travel from the cathode toward the anode in a cathode-ray tube.

Cathodic Protection : The process in which a structural metal, such as iron, is protected from corrosion by connecting it to a metal that has a more negative reduction half-cell potential

The technique of protecting a metal object by connecting it to a more readily oxidisable metal. The metal object being protected is made into the cathode of a cell. *Example*: iron can be protected by coupling it with magnesium. Iron forms the cathode and magnesium the anode.

Cation : A positively charged ion. *Examples*: calcium ion (Ca^{2+}), ammonium ion (NH_4^+).

Compare with anion. A cation is a positively charged ion. Metals typically form cations.

Caustic : A substance that can cause burns if it touches the skin. *Example*: Sodium hydroxide, caustic soda (NaOH).

Cell : A vessel containing two electrodes and an electrolyte that can act as an electrical conductor.

Cell potential : A measure of the driving force behind an electrochemical reaction, which is reported in units of volts.

The driving force in a voltaic cell that pulls electrons from the reducing agent in one compartment to the oxidizing agent in the other; also called electromotive force; represented by the symbol E . To calculate E , one must add the half-cell potentials of the oxidation and reduction half-reactions.

Cellulose : A long polymer of glucose that contains beta-1,4-glycoside bonds.

A polysaccharide made of linked glucose molecules that strengthens the cell walls of most plants. See also: What is cellulose?

Celsius : ($^{\circ}\text{C}$) Celsius temperature scale; Celsius scale. A common but non-SI unit of temperature, defined by assigning temperatures of 0°C and 100°C to the freezing and boiling points of water, respectively.

Celsius scale (°C) : A temperature scale on which the freezing point of water is at 0 degrees and the normal boiling point at standard atmospheric pressure is 100 degrees.

Centi- : (c) Prefix used in the SI system meaning "one hundredth of". For example 1 cm means "one hundredth of a meter"; 2.3 cg could also be written " 2.3×10^{-2} g" or "0.023 g".

Centrifuge : An instrument for spinning small samples very rapidly. The fast spin causes the components of a mixture that have a different density to separate. This has the same effect as filtration.

Ceramic : A material based on clay minerals which has been heated so that it has chemically hardened.

Cgs : An older metric system of units that uses centimeters, grams, and seconds as base units.

Chain reaction : A reaction in which one of the starting materials is regenerated in the last step of the reaction.

A reaction in which one or more reactive reaction *intermediates* (frequently radicals) are continuously regenerated, usually through a repetitive cycle of elementary steps (the "propagation step"). For example, in the chlorination of methane by a radical *mechanism*, Cl^\cdot is continuously regenerated in the chain propagation steps : $\text{Cl}^\cdot + \text{CH}_4 \longrightarrow \text{HCl} + \text{H}_3\text{C}^\cdot$ $\text{H}_3\text{C}^\cdot + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}^\cdot$ In chain polymerization reactions, reactive intermediates of the same types, generated in successive steps or cycles of steps, differ in relative molecular mass, as in $\text{RCH}_2\text{C}^\cdot\text{HPh} + \text{H}_2\text{C}=\text{CHPh} \longrightarrow \text{RCH}_2\text{CHPhCH}_2\text{C}^\cdot\text{HPh}$.

Chain transfer : The abstraction, by the *radical* end of a growing chain-polymer, of an atom from another molecule. The growth of the polymer chain is thereby terminated but a new radical, capable of chain propagation and polymerization, is simultaneously created. For the example of alkene polymerization cited for a *chain reaction*, the reaction $\text{RCH}_2\text{C}^\cdot\text{HPh} + \text{CCl}_4 \longrightarrow \text{RCH}_2\text{CHClPh} + \text{Cl}_3\text{C}^\cdot$ represents a chain transfer, the radical $\text{Cl}_3\text{C}^\cdot$ inducing further polymerization: $\text{H}_2\text{C}=\text{CHPh} + \text{Cl}_3\text{C}^\cdot \longrightarrow \text{Cl}_3\text{CCH}_2\text{C}^\cdot\text{HPh}$
 $\text{Cl}_3\text{CCH}_2\text{C}^\cdot\text{HPh} + \text{H}_2\text{C}=\text{CHPh} \longrightarrow \text{Cl}_3\text{CCH}_2\text{CHPhCH}_2\text{C}^\cdot\text{HPh}$ The

phenomenon occurs also in other chain reactions such as cationic polymerization.

Chain-reaction mechanism : A mechanism for a chain reaction that consists of chain-initiating, chain-propagating, and chain-terminating steps.

Chalcogens : The members of Group 6 of the Periodic Table: oxygen, sulphur, selenium and tellurium. The word comes from the Greek meaning 'brass giver', because all these elements are found in copper ores, and copper is the most important metal in making brass.

Change of state : a change between two of the three states of matter, solid, liquid and gas. *Example*: when water evaporates it changes from a liquid to a gaseous state.

Charge population : The net electric charge on a specified atom in a *molecular entity*, as determined by some prescribed definition, e.g. that of MULLIKEN (1955).

Charge-transfer complex : A ground state *adduct* which exhibits an observable charge transfer absorption band.

Charles' law : A statement of the relationship between the temperature and volume of a constant amount of gas at constant pressure: $P \propto T$.

Charles' law : The volume of a gas is directly proportional to its temperature in kelvins, if pressure and amount of gas remain constant. Doubling the kelvin temperature of a gas at constant pressure will double its volume. If V_1 and T_1 are the initial volume and temperature, the final volume and temperature ratio $V_2/T_2 = V_1/T_1$ if pressure and moles of gas are unchanged.

Charles's Law : The volume (V) of a given mass of gas at constant pressure is directly proportional to its absolute temperature (T): $V \propto T$.

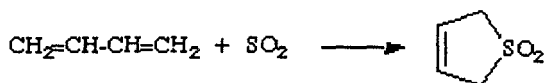
Chelate : A stable complex of a metal with one or more polydentate ligands. For example, calcium complexes with EDTA to form a chelate.

Chelating agent : Chelator. A ligand that binds to a metal using more than one atom; a polydentate ligand.

Chelating ligand : A ligand that can coordinate to a metal atom more than once.

Chelation : The formation or presence of *bonds* (or other attractive interactions) between two or more separate *binding sites* within the same ligand and a single central atom. A *molecular entity* in which there is chelation (and the corresponding *chemical species*) is called a "chelate". The terms bidentate (or didentate), tridentate, tetradentate... multidentate are used to indicate the number of potential binding sites of the ligand, at least two of which must be used by the ligand in forming a "chelate". For example, the bidentate ethylenediamine forms a chelate with CuI in which both nitrogen atoms of ethylenediamine are bonded to copper. (The use of the term is often restricted to metallic central atoms.) The phrase "separate binding sites" is intended to exclude cases such as $[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]^-$, ferrocene, and (benzene) tricarbonylchromium in which ethene, the cyclopentadienyl group, and benzene, respectively, are considered to present single binding sites to the respective metal atom, and which are not normally thought of as chelates (see *hapto*).

Cheletropic reaction : A form of *cycloaddition* across the terminal atoms of a fully *conjugated system* with formation of two new sigma bonds to a single atom of the ("monocentric") reagent. There is formal loss of one pi bond in the substrate and an increase in *coordination number* of the relevant atom of the reagent. An example is the *addition* of sulfur dioxide to butadiene :



The reverse of this type of reaction is designated "cheletropic elimination". WOODWARD and HOFFMANN (1969).

Chelotropic reaction : Alternative (and etymologically more correct) name for *cheletropic reaction*. DEWAR (1971).

Chemical : Of or pertaining to chemistry.

A substance.

Chemical bond : Bond; bonding; chemical bonding. A chemical bond is a strong attraction between two or more atoms. Bonds hold atoms in molecules and crystals together. There are

many types of chemical bonds, but all involve electrons which are either shared or transferred between the bonded atoms.

Chemical change : Reaction; chemical reaction. Compare with physical change. A chemical change is a dissociation, recombination, or rearrangement of atoms.

Chemical equation : A compact notation for describing a chemical change. The formulas of the reactants are added together on the left hand side of the equation; the formulas of the products are added together on the right side. Coefficients are inserted before the formulas to ensure that the equation is balanced. The phase in which each substance is found is usually indicated in parentheses after each formula. For example, $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) = 2 \text{H}_2\text{O}(\text{g})$ indicates that 2 moles of hydrogen gas combine with one mole of oxygen gas to produce two moles of steam.

A symbolic representation of the relationship between the reactants and products of a chemical reaction.

Chemical flux : A concept related to *rate of reaction*, particularly applicable to the progress in one direction only of component reaction steps in a complex system or to the progress in one direction of reactions in a system at dynamic equilibrium (in which there are no observable concentration changes with time). Chemical flux (ϕ) is a derivative with respect to time, and has the dimensions of amount of substance per unit volume transformed per unit time. The sum of all the chemical fluxes leading to destruction of B is designated the "total chemical flux out of B" (symbol $\Sigma \phi_{-B}$); the corresponding formation of B by concurrent elementary reactions is the "total chemical flux into B or A" (symbol $\Sigma \phi_{+B}$). For the

mechanism $\text{A} + \text{B} \xrightleftharpoons[-1]{1} \text{C} + \text{D} \xrightarrow{2} \text{E}$ the total chemical flux into C is caused by the single reaction (1): $\Sigma \phi_{+C} = \phi_1$ whereas the chemical flux out of C is a sum over all reactions that remove C: $\Sigma \phi_{-C} = \phi_{-1} + \phi_2$ where ϕ_{-1} is the "chemical flux out of C into B (and/or A)" and ϕ_2 is the "chemical flux out of C into E". The rate of appearance of C is then given by $d[\text{C}]/dt = \Sigma \phi_{+C} - \Sigma \phi_{-C}$. In this system ϕ_1 (or $\Sigma \phi_{+A}$) can be regarded as the hypothetical rate of decrease in the concentration of A due to the single (unidirectional)

reaction (1) proceeding in the assumed absence of all other reactions.

For a non-reversible reaction $A \xrightarrow{1} P$ $-d[A]/dt = \phi_1$ If two substances A and P are in *chemical equilibrium*, $A \rightleftharpoons P$ then $\Sigma \phi_A = \Sigma \phi_{-A} = \Sigma \phi_P = \Sigma \phi_{-P}$ and $-d[A]/dt = d[P]/dt = 0$ GOLD (1979).

Chemical kinetics : The study of the rates of chemical reactions.

Chemical potential : (μ) The chemical potential is a partial molar Gibbs free energy^{*}, defined as $\mu_i = (\partial G / \partial n_i)_{T,P,n_j}$. The definition means that the chemical potential is the change in Gibbs free energy when one mole of a substance is added to a very large amount of a sample. Chemical potential is a measure of chemical stability that can be used to predict and interpret phase changes and chemical reactions. Substances with higher chemical potential will react or move from one phase to another to lower the overall Gibbs free energy of the system. For example, consider a mixture of ice and water. If the ice melts, the chemical potential of the water was lower than that of the ice. If the water freezes, the chemical potential of the ice was lower.

Chemical property : Chemical properties. Compare with physical property. Measurement of a chemical property involves a chemical change. For example, determining the flammability of gasoline involves burning it, producing carbon dioxide and water.

Chemical reaction : A process that results in the interconversion of *chemical species*. Chemical reactions may be *elementary reactions* or *stepwise reactions*. (It should be noted that this definition includes experimentally observable interconversions of conformers.) Detectable chemical reactions normally involve sets of *molecular entities*, as indicated by this definition, but it is often conceptually convenient to use the term also for changes involving single molecular entities (i.e. "microscopic chemical events").

Chemical relaxation : If the equilibrium mixture of a *chemical reaction* is disturbed by a sudden change, especially of some external parameter (such as temperature, pressure, or electrical field strength), the system will readjust itself to a new position of the chemical equilibrium or return to the original position, if the perturbation is temporary. The readjustment is known as chemical relaxation. In

many cases, and in particular when the displacement from equilibrium is slight, the progress of the system towards equilibrium can be expressed as a first-order law $[C_t - (C_{eq})_2] = [(C_{eq})_1 - (C_{eq})_2] \exp(-t/\tau)$ where $(C_{eq})_1$ and $(C_{eq})_2$ are the equilibrium concentrations of one of the chemical species involved in the reaction before and after the change in the external parameter, and C_t is its concentration at time t . The time parameter τ , named relaxation time, is related to the *rate constants* of the chemical reaction involved. Measurements of the relaxation times by relaxation methods [involving a temperature jump (T-jump), pressure jump, electric field jump or a periodic disturbance of an external parameter, as in ultrasonic techniques] are commonly used to follow the kinetics of very fast reactions.

Chemical shift (NMR), δ (SI unit: 1) : The variation of the resonance frequency of a nucleus in nuclear magnetic resonance (NMR) spectroscopy in consequence of its magnetic environment. The chemical shift of a nucleus, δ , is expressed in ppm by its frequency, ν_{opd} , relative to a standard, ν_{ref} , and defined as $\delta = 10^6(\nu_{\text{opd}} - \nu_{\text{ref}})/\nu_0$ where ν_0 is the operating frequency of the spectrometer. For ^1H and ^{13}C NMR the reference signal is usually that of tetramethylsilane (SiMe_4). Other references are used in the older literature and in other solvents, such as D_2O . If a resonance signal occurs at lower frequency or higher applied field than an arbitrarily selected reference signal, it is said to be upfield, and if resonance occurs at higher frequency or lower applied field, the signal is downfield. Resonance lines upfield from SiMe_4 have positive, and resonance lines downfield from SiMe_4 have negative δ -values.

Chemical species : An ensemble of chemically identical *molecular entities* that can explore the same set of molecular energy levels on the time scale of the experiment. The term is applied equally to a set of chemically identical atomic or molecular structural units in a solid array. For example, two conformational *isomers* may be interconverted sufficiently slowly to be detectable by separate NMR spectra and hence to be considered to be separate chemical species on a time scale governed by the radiofrequency of the spectrometer used. On the other hand, in a slow chemical reaction the same mixture of conformers may behave as a single chemical species, i.e. there is virtually complete equilibrium population of the

total set of molecular energy levels belonging to the two conformers. Except where the context requires otherwise, the term is taken to refer to a set of molecular entities containing isotopes in their natural abundance. The wording of the definition given in the first paragraph is intended to embrace both cases such as graphite, sodium chloride, or a surface oxide, where the basic structural units may not be capable of isolated existence, as well as those cases where they are. In common chemical usage, and in this Glossary, generic and specific chemical names (such as *radical* or hydroxide ion) or chemical formulae refer either to a chemical species or to a *molecular entity*.

Chemiluminescence : A chemical reaction that releases energy as electromagnetic radiation.

A chemical reaction that gives off energy in the form of light instead of heat.

Chemistry : The study of matter and its transformations.

Chemoselective, chemoselectivity : Chemoselectivity is the preferential reaction of a chemical reagent with one of two or more different functional groups. A reagent has a high chemoselectivity if reaction occurs with only a limited number of different functional groups. For example, sodium tetrahydroborate is a more chemoselective reducing agent than is lithium tetrahydroaluminate. The concept has not been defined in more quantitative terms. The term is also applied to reacting molecules or intermediates which exhibit selectivity towards chemically different reagents. Some authors use the term chemospecificity for 100% chemoselectivity. However, this usage is discouraged.

Chiral : An object whose mirror image is not the same as itself. Compounds with four different substituents on a carbon atom are chiral.

Chirality. Having nonsuperimposable mirror images. For example, a shoe or a glove is chiral.

Chiral center : A tetrahedral carbon atom that bears four different substituents, (asymmetric center).

Chirality : handedness, the quality of having non-superimposable mirror images.

Chloride : A compound that contains either the Cl^- ion or chlorine with an oxidation state of -1, such as HCl .

Chromatography : Chromatography is a method for separating mixtures based on differences in the speed at which they migrate over or through a stationary phase.

A separation technique using the ability of surfaces to adsorb substances with different strengths. The substances with the least adherence to the surface move faster and leave behind those that adhere more strongly.

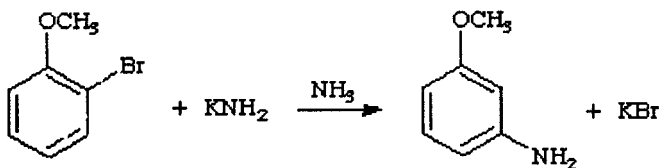
A technique for separating the components of a mixture on the basis of differences in their affinity for a stationary and a mobile phase.

Chromophore : Compare with auxochrome. A group or substructure on a molecule that is responsible for the absorption of light.

The part (atom or group of atoms) of a *molecular entity* in which the electronic transition responsible for a given spectral band is approximately localized. The term arose in the dyestuff industry, referring originally to the groupings in the molecule that are responsible for the dye's colour.

CIDNP (Chemically Induced Dynamic Nuclear Polarization) : Non-Boltzmann nuclear spin state distribution produced in thermal or photochemical reactions, usually from *colligation* and diffusion, or *disproportionation* of *radical pairs*, and detected by NMR spectroscopy by enhanced absorption or emission signals.

Cine-substitution : A *substitution reaction* (generally *aromatic*) in which the entering group takes up a position adjacent to that occupied by the *leaving group*. For example,



Cis : Literally, on the same side. Describes isomers in which similar substituents are on the same side of a C=C double bond or in adjacent coordination sites on a transition metal.

Class (a) metal ion : A metal ion that combines preferentially with *ligands* containing ligating atoms that are the lightest of their Periodic Group. See also *class (b) metal ion, hard acid*.

Class (b) metal ion : A metal ion that combines preferentially with *ligands* containing ligating atoms other than the lightest of their Periodic Group. See also *class (a) metal ion, hard acid*.

Clausius-Clapeyron equation : The Clausius-Clapeyron equation predicts the temperature dependence of vapor pressures of pure liquids or solids : $\ln (P/P^\circ) = \frac{\Delta H}{RT}$ where P is the vapor pressure, P° is a vapor pressure at a known temperature T° , ΔH is an enthalpy of vaporization if the substance is a liquid or an enthalpy of sublimation if it's a solid, R is the ideal gas law constant, and T is the temperature (in kelvins).

Closed system : A system which can exchange only energy with its surroundings.

Closest packed : The structure in which equivalent particles pack as tightly as possible. Each particle that forms the closest-packed structure is surrounded by six nearest neighbors in the same plane arranged toward the corners of a hexagon, three neighbors in the plane above, and three neighbors in the plane below.

Coagulation : A term describing the tendency of small particles to stick together in clumps.

Coal gas : A gas, which is usually rich in methane (CH_4), produced when coal is heated in the absence of air.

Codon : A sequence of three nucleotides on a strand of m-RNA that codes for an amino acid.

Coherent : meaning that a substance holds together or sticks together well, and without holes or other defects. *Example*: Aluminium appears unreactive because, as soon as new metal is exposed to air, it forms a very complete oxide coating, which then stops further reaction occurring.

Cohesion : Compare with adhesion. Attraction between like molecules.

The force of attraction between molecules of the same substance. See adhesion.

Coinage metals : the elements copper, silver and gold, used to make coins.

Coke : a solid substance left after the gases have been extracted from coal.

Colligation : The formation of a covalent bond by the combination or recombination of two *radicals* (the reverse of *unimolecular homolysis*). For example : $\text{HO}\cdot + \text{H}_3\text{C}\cdot \longrightarrow \text{CH}_3\text{OH}$

Colligative property : Any property that depends on the number of solute particles in a solution but not their identity.

Colligative; colligative properties. Properties of a solution that depend on the number of solute molecules present, but not on the nature of the solute. Osmotic pressure, vapor pressure, freezing point depression, and boiling point elevation are examples of colligative properties.

Collision frequency : Collision frequencies; frequency of collision.

Collision theory : Collision model. A theory that explains reaction rates in terms of collisions between reactant molecules.

Collision theory model : A model used to explain the rates of chemical reactions, which assumes that molecules must collide in order to react.

Colloid : 1. A colloid is a heterogeneous mixture composed of tiny particles suspended in another material. The particles are larger than molecules but less than 1 μm in diameter. Particles this small do not settle out and pass right through filter paper. Milk is an example of a colloid. The particles can be solid, tiny droplets of liquid, or tiny bubbles of gas; the suspending medium can be a solid, liquid, or gas (although gas-gas colloids aren't possible).

A mixture of ultramicroscopic particles dispersed uniformly through a second substance to form a suspension which may

be almost like a solution or may set to a jelly (gel). The word comes from the Greek for glue.

Colorimeter : An instrument for measuring the light-absorbing power of a substance. The absorption gives an accurate indication of the concentration of some coloured solutions.

Colorimetry : A method for chemical analysis that relates color intensity to the concentration of analyte.

Column chromatography : Chromatography that uses a solid support in a vertical column or tube.

Column chromatography is a method for separating mixtures. A solution containing the mixture is passed through a narrow tube packed with a stationary phase. Different substances in the mixture have different affinities for the stationary phase, and so move through the tube at different rates. This allows the substances in the mixture to be detected or collected separately as they reach the end of the tube.

Combination reaction : A reaction in which two or more substances are chemically bonded together to produce a product. For example, $2 \text{Na(s)} + \text{Cl}_2\text{(g)} \rightarrow 2 \text{NaCl(s)}$ is a combination reaction.

Combined equilibria : Two or more equilibria that occur simultaneously and involve the same ion or molecule.

Combustion : 1. A reaction in which an element or compound is oxidised to release energy. Some combustion reactions are slow, such as the combustion of the sugar we eat to provide our energy. If the combustion results in a flame, it is called burning. A flame occurs where *gases* combust and release heat and light. At least two gases are therefore required if there is to be a flame. *Example:* the combustion or burning of methane gas (CH_4) in oxygen gas (O_2) produces carbon dioxide (CO_2) and water (H_2O) and gives out heat and light. Some combustion reactions produce light and heat but do not produce flames. *Example:* the combustion of carbon in oxygen produces an intense red-white light but no flame.

Combustion reaction. A chemical reaction between a fuel and an oxidizing agent that produces heat (and usually,

light). For example, the combustion of methane is represented as $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell)$.

Combustion reaction : the vigorous and exothermic reaction that takes place between certain substances, particularly organic compounds, and oxygen.

Combustion spoon : also known as a deflagrating spoon, it consists of a long metal handle with a small cup at the end. Its purpose is to allow the safe introduction of a (usually heated) substance into a gas jar filled with gas, when the reaction is likely to be vigorous. *Example*: the introduction of a heated sodium pellet into a gas jar containing chlorine.

Common-ion effect (on rates) : A reduction in the *rate* of certain reactions of a *substrate* RX in solution [by a path that involves a *pre-equilibrium* with formation of R^+ (or R^-) ions as reaction intermediates] caused by the addition to the reaction mixture of an electrolyte solute containing the "common ion" X^- (or X^+). For example, the rate of solvolysis of diphenylmethyl chloride in acetone-water is reduced by the addition of salts of the common ion Cl^- which causes a decrease in the quasi-equilibrium concentration of

the diphenylmethyl cation in the scheme: $\text{Ph}_2\text{CHCl} \xrightleftharpoons[-1]{1} \text{Ph}_2\text{CH}^+ + \text{Cl}^-$ (free ions, not ion pairs) $\text{Ph}_2\text{CH}^+ + \text{OH}_2 \xrightarrow{2} \text{Ph}_2\text{CHOH} + \text{H}^+(\text{solvated})$ This phenomenon is a direct consequence of the *mass-law effect* on ionization equilibria in electrolytic solution. **More** generally, the common-ion effect is the influence of the "common ion" on the reactivity due to the shift of the dissociation equilibrium. It may also lead to an enhancement of the *rate of reaction*.

Common-ion effect : The decrease in the solubility of a salt that occurs when the salt is dissolved in a solution that contains another source of one of its ions.

Compensation effect : In a considerable number of cases plots of $T \Delta^\ddagger S$ vs. $\Delta^\ddagger H$, for a series of reactions, e.g. for a reaction in a range of different solvents, are straight lines of approximately unit slope. Therefore, the terms $\Delta^\ddagger H$ and $T \Delta^\ddagger S$ in the expression partially compensate, and $\Delta^\ddagger G = \Delta^\ddagger H - T \Delta^\ddagger S$ often is a much

simpler function of solvent (or other) variation than $\Delta^\ddagger H$ or $T \Delta^\ddagger S$ separately.

Complete combustion : Compare with incomplete combustion. A combustion reaction that converts all of the fuel's carbon, hydrogen, sulfur, and nitrogen into carbon dioxide, water, sulfur dioxide, and N_2 respectively.

Complete ionic equation : total ionic equation. Compare with net ionic equation. A balanced equation that describes a reaction occurring in solution, in which all strong electrolytes are written as dissociated ions.

Complex : A *molecular entity* formed by loose *association* involving two or more component molecular entities (ionic or uncharged), or the corresponding *chemical species*. The bonding between the components is normally weaker than in a covalent *bond*. The term has also been used with a variety of shades of meaning in different contexts: it is therefore best avoided when a more explicit alternative is applicable. In inorganic chemistry the term "coordination entity" is recommended instead of "complex".

Complex ion : An ion formed by combination of simpler ions or molecules; for example, Co^{2+} combines with six molecules of water to form the complex ion $Co(H_2O)_6^{2+}$.

An ion in which a ligand is covalently bound to a metal. An ion formed when a Lewis acid such as the Cu^{2+} ion reacts with a Lewis base such as NH_3 to form an acid-base complex such as the $Cu(NH_3)_4^{2+}$ ion.

Complex-dissociation equilibrium constant (K_d) : The equilibrium constant for the reaction in which a complex dissociates, such as : $Cu(NH_3)_4^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4 NH_3(aq)$

Complex-formation equilibrium constant (K_f) : The equilibrium constant for the reaction in which a complex is formed, such as: $Cu^{2+}(aq) + 4 NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$

Complexing agent : complexant. A ligand that binds to a metal ion to form a complex.

Complexometric titration : chelometric titration. A titration based on a reaction between a ligand and a metal ion to form a

complex. For example, free Ca^{2+} in milk powder can be determined by titrating a milk powder sample with EDTA solution, which chelates calcium ion. Endpoints in complexometric titrations are often determined using organochromic indicators.

Component : A substance whose concentration must be specified to describe the state of a mixture in which reactions are occurring.

A substance present in a mixture in which no reactions occur.

Composite reaction : A *chemical reaction* for which the expression for the rate of disappearance of a reactant (or rate of appearance of a product) involves rate constants of more than a single *elementary reaction*. Examples are "opposing reactions" (where rate constants of two opposed chemical reactions are involved), "parallel reactions" (for which the rate of disappearance of any reactant is governed by the rate constants relating to several simultaneous reactions to form different respective products from a single set of reactants), and *stepwise reactions*.

Compound : A chemical consisting of two or more elements chemically bonded together. *Example*: Calcium can combine with carbon and oxygen to make calcium carbonate (CaCO_3), a compound of all three elements.

A substance with a constant composition that contains two or more elements.

Compare with element and mixture. A compound is a material formed from elements chemically combined in definite proportions by mass. For example, water is formed from chemically bound hydrogen and oxygen. Any pure water sample contains 2 g of hydrogen for every 16 g of oxygen.

Compressibility : The ability to be compressed. A characteristic of substances, such as gases, that can be compressed to fit into smaller containers.

Comproportionation : The reverse of *disproportionation*. The term "sympportionation" is also used.

Computational chemistry : A branch of chemistry concerned with the prediction or simulation of chemical properties, structures, or processes using numerical techniques.

Computer-assisted drug design : Using computational chemistry to discover, enhance, or study drugs and related biologically active molecules.

Concentrate : Compare with dilute. To increase the amount of substance present in a unit amount of mixture. For example, allowing solvent to evaporate from a solution concentrates the solution.

Concentrated : Compare with diluted. Having a relatively large amount of substance present in a unit amount of mixture. For example, a 12 M HCl solution is more concentrated than an 0.001 M HCl solution.

Concentration : A measure of the ratio of the amount of solute in a solution to the amount of either solvent or solution. Frequently expressed in units of moles of solute per liter of solution. See molarity.

Compare with dilution. (i) A measure of the amount of substance present in a unit amount of mixture. The amounts can be expressed as moles, masses, or volumes. (ii) The process of increasing the amount of substance in a given amount of mixture.

Concentration cell : A voltaic cell in which both compartments contain the same components, but at different concentrations.

Concerted process : Two or more *primitive changes* are said to be concerted (or to constitute a concerted process) if they occur within the same *elementary reaction*. Such changes will normally (though perhaps not inevitably) be "energetically coupled". (In the present context the term "energetically coupled" means that the simultaneous progress of the primitive changes involves a *transition state* of lower energy than that for their successive occurrence.) In a concerted process the primitive changes may be *synchronous* or *asynchronous*.

Condensation : Condensed. (i) The conversion of a gas into a liquid is called condensation. Condensation usually occurs when a gas is cooled below its boiling point. (ii) A reaction that involves

linking of two molecules with the elimination of water (or another small molecule).

The formation of a liquid from a gas. This is a change of state, also called a phase change.

The process by which vapor molecules reform a liquid; phase change from gas to liquid state.

Condensation nuclei : Microscopic particles of dust, salt and other materials suspended in the air, that attract water molecules. The usual result is the formation of water droplets.

Condensation polymer : A polymer formed by a chain of reactions in which a water molecule is eliminated as every link of the polymer is formed. *Examples*: polyesters, proteins, nylon.

Condensation polymer : A polymer, such as nylon, which is formed when a small molecule is condensed out or lost during polymerization.

Condensation reaction : A (usually stepwise) reaction in which two or more reactants (or remote reactive sites within the same *molecular entity*) yield a single main product with accompanying formation of water or of some other small molecule, e.g. ammonia, ethanol, acetic acid, hydrogen sulfide. The *mechanism* of many condensation reactions has been shown to comprise consecutive *addition* and *elimination* reactions, as in the base-catalysed formation of (*E*)-but-2-enal (crotonaldehyde) from acetaldehyde, via 3-hydroxybutanal (aldol). The overall reaction in this example is known as the aldol condensation. The term is sometimes also applied to cases where the formation of water or another simple molecule does not occur, as in "benzoin condensation".

Conduction : (i) The exchange of heat (heat conduction) by contact with another object, or (ii) allowing the flow of electrons (electrical conduction).

Conduction band : An energy band in a solid in which electrons are free to move, producing a net transfer of charge.

Conductivity : The ability of a substance to conduct. The conductivity of a solution depends on there being suitable free ions

in the solution. A conducting solution is called an electrolyte.
Example: dilute sulphuric acid.

Conductivity apparatus : An instrument used to determine whether a substance or solution can conduct an electric current.

Configuration (electronic) : A distribution of the electrons of an atom or a *molecular entity* over a set of one-electron wavefunctions called *orbitals*, according to the Pauli principle. From one configuration several states with different multiplicities may result. For example, the ground electronic configuration of the oxygen molecule (O_2) is $1\sigma_g^2, 1\sigma_u^2, 2\sigma_g^2, 2\sigma_u^2, 1\pi_u^4, 3\sigma_g^2, 1\pi_g^2$ resulting in the $^3\Sigma_g^-, ^1\Delta_g$, and $^3\Sigma_g^+$ multiplets

Configuration (molecular) : In the context of stereochemistry, the term is restricted to the arrangements of atoms of a *molecular entity* in space that distinguishes stereoisomers, the isomerism of which is not due to conformational differences.

Conformation : The spatial arrangements of atoms affording distinction between stereoisomers which can be interconverted by rotation about formally single bonds. Some authorities extend the term to include inversion at trigonal bipyramidal centres and other "polytopal rearrangements".

Conformers : Conformation. Molecular arrangements that differ only by rotations around single bonds. For example, the "boat" and "chair" forms of cyclohexane are conformers.

Congener : Elements belonging to the same group on the periodic table. For example, sodium and potassium are congeners.

Compounds produced by identical synthesis reactions and procedures.

Conjugate acid-base pair : The *Brønsted acid* BH^+ formed on protonation of a base B is called the conjugate acid of B, and B is the conjugate base of BH^+ . (The conjugate acid always carries one unit of positive charge more than the base, but the absolute charges of the species are immaterial to the definition.) For example: the *Brønsted acid* HCl and its conjugate base Cl^- constitute a conjugate acid-base pair.

Two substances related by the gain or loss of a proton. Every Brnsted acid has a conjugate Brnsted base. An acid (such as HCl) and its conjugate base (the Cl^- ion), or a base (the OH^- ion) and its conjugate acid (H_2O) represent a conjugate acid-base pair.

Conjugate oxidizing/reducing agents : Two substances related by the gain or loss of electrons. Every oxidizing agent (such as the Zn^{2+} ion) has a conjugate reducing agent (such as zinc metal).

Conjugated system, conjugation : In the original meaning a conjugated system is a molecular entity whose structure may be represented as a system of alternating single and multiple bonds: e.g. $\text{CH}_2=\text{CH}=\text{CH}=\text{CH}_2$ $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ In such systems, conjugation is the interaction of one p-orbital with another across an intervening sigma bond in such structures. (In appropriate molecular entities d-orbitals may be involved.) The term is also extended to the analogous interaction involving a p-orbital containing an unshared electron pair, e.g. : $\text{Cl}-\text{CH}=\text{CH}_2$ See also *delocalization*, *homoconjugation*, *resonance*.

Connectivity : In a chemical context, the information content of a line formula, but omitting any indication of *bond* multiplicity.

Constitution : The description of the identity and connectivity (and corresponding bond multiplicities) of the atoms in a *molecular entity* (omitting any distinction from their spatial arrangement).

Constitutional isomers : Two compounds that have the same formula, but different constituents. Dimethyl ether (CH_3OCH_3) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), for example, are constitutional isomers. See stereoisomers.

Constructive interference : Compare with destructive interference. When the peaks and troughs of two interfering waves match, the amplitudes add to give the resultant wave a higher amplitude.

Continuous spectrum : Compare with line spectrum and band spectrum. A plot of the relative absorbance or intensity of emitted light vs. wavelength or frequency that shows a smooth variation, rather than a series of sharp peaks or bands.

Contributing structure : The definition is based on the valence-bond formulation of the quantum mechanical idea of the wavefunction of a molecule as composed of a linear combination of wavefunctions, each representative of a formula containing bonds that are only single, double or triple with a particular pairing of electron spins. Each such formula represents a contributing structure, also called "resonance structure" to the total wavefunction, and the degree to which each contributes is indicated by the square of its coefficient in the linear combination. The contributing structures, also called "canonical forms", themselves thus have a purely formal significance: they are the components from which wavefunctions can be built. Structures may be covalent (or non-polar) or ionic (or polar). The representation is frequently kept qualitative so that we speak of important or major contributing structures and minor contributing structures. For example, two major non-equivalent contributing structures for the conjugate base of acetone are $\text{CH}_2=\text{C}(\text{CH}_3)-\text{O}^- \longleftrightarrow \text{H}_2\text{C}^--\text{C}(\text{CH}_3)=\text{O}$.

Convection : the exchange of heat energy with the surroundings produced by the flow of a fluid due to being heated or cooled.

Conversion factor : A conversion factor is a fraction that relates one unit to another. Multiplying a measurement by a conversion factor changes the units of the measurement. For example, since $1 \text{ in} = 2.54 \text{ cm}$, to convert 10 inches to centimeters, $(10 \text{ in}) 2.54 \text{ cm} / 1 \text{ in} = 25.4 \text{ cm}$.

Coordination : The formation of a covalent *bond*, the two shared electrons of which have come from only one of the two parts of the *molecular entity* linked by it, as in the reaction of a *Lewis acid* and a *Lewis base* to form a *Lewis adduct*; alternatively, the bonding formed in this way. In the former sense, it is the reverse of *unimolecular heterolysis*. "Coordinate covalence" and "coordinate link" are synonymous (obsolescent) terms. The synonym "dative bond" is obsolete. (The origin of the bonding electrons has by itself no bearing on the character of the bond formed. Thus, the formation of methyl chloride from a methyl cation and a chloride ion involves coordination; the resultant bond obviously differs in no way from the C-Cl bond in methyl chloride formed by any other path, e.g. by colligation of a methyl radical and a chlorine atom.) The term is also

used to describe the number of ligands around a central atom without necessarily implying two-electron bonds.

Coordination compound : A compound in which one or more ligands are coordinated to a metal atom.

Coordination number : The coordination number of a specified atom in a *chemical species* is the number of other atoms directly linked to that specified atom. For example, the coordination number of carbon in methane is four, and it is five in protonated methane, CH_5^+ . (The term is used in a different sense in the crystallographic description of ionic crystals.)

The number of atoms, ions, or molecules to which bonds can be formed.

The number of bonds formed by the central atom in a metal-ligand complex.

Coordinatively saturated : A transition metal complex that has formally 18 outer shell electrons at the central metal atom.

Coordinatively unsaturated : A transition metal complex that possesses fewer ligands than exist in the coordinatively saturated complex. These complexes usually have fewer than 18 outer shell electrons at the central metal atom.

Copolymer : A polymer composed of two or more different monomers. The different monomers can be linked randomly, or in repeating sequences, or in blocks, or as side chains off the main chain.

A polymer formed from two or more different monomers.

Core electron : Compare with valence electron. Electrons occupying completely filled shells under the valence shell.

Correlation analysis : The use of empirical correlations relating one body of experimental data to another, with the objective of finding quantitative estimates of the factors underlying the phenomena involved. Correlation analysis in organic chemistry often uses *linear free-energy relations* for rates or equilibria of reactions, but the term also embraces similar analysis of physical (most commonly spectroscopic) properties and of biological activity.

Corrosion : A process in which a metal is destroyed by a chemical reaction. When the metal is iron, the process is called rusting.

Corrode. Corrosion is a reaction that involves action of an oxidizing agent on a metal. The oxidizing agent is often oxygen dissolved in water. See How Iron Rusts for examples.

Corrosion : The oxidation of a metal. Corrosion is often regarded as unwanted and is more generally used to refer to the *slow* decay of a metal resulting from contact with gases and liquids in the environment. *Example*: Rust is the corrosion of iron.

Corrosive : causing corrosion.

Coulomb : (C) The SI unit of electric charge, equal to the amount of charge delivered by a current of 1 ampere running for 1 second. One mole of electrons has a charge of about 96487 C.

Coulombic interactions : electrostatic interactions. Attractions between opposite charges or repulsions between like charges that grow stronger as the charges become closer to each other.

Coupling constant (spin-spin coupling constant), J (SI unit: Hz (NMR) : A quantitative measure for nuclear spin-spin, nuclear-electron (hyperfine coupling) and electron-electron (fine coupling in EPR) coupling in magnetic resonance spectroscopy. The "indirect" or scalar NMR coupling constants are in a first approximation independent of the external magnetic field and are expressed in Hz.

Covalent bond : A bond between two atoms formed by the sharing of a pair of electrons.

A region of relatively high electron density between nuclei which arises at least partly from sharing of electrons and gives rise to an attractive force and characteristic internuclear distance. See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.

Covalent; covalently bound. Compare with covalent compound and ionic bond. A covalent bond is a very strong attraction between two or more atoms that are sharing their electrons. In structural formulas, covalent bonds are

represented by a line drawn between the symbols of the bonded atoms.

This is the most common form of strong chemical bonding and occurs when two atoms *share* electrons. *Example:* oxygen (O_2)

Covalent compound : A compound, such as water (H_2O), composed of neutral molecules in which the atoms are held together by covalent bonds.

Molecular compound. Compare with ionic bond and ionic compound. A compound made of molecules- not ions. The atoms in the compound are bound together by shared electrons. Also called a molecular compound.

Covalent radius : The radius of an atom in a covalent bond.

Covalent solid : A solid, such as diamond, in which every atom is covalently bound to its nearest neighbors to form an extended array of atoms rather than individual molecules.

Cox-Yates equation : A modification of the *Bunnett-Olsen equation* of the form $\lg([SH^+]/[S]) - \lg[H^+] = m^*X + pK_{SH^+}$ where X is the activity function $\lg(\gamma S \gamma H^+ / \gamma SH^+)$ for an arbitrary reference base. The function X is called the excess acidity because it gives a measure of the difference between the acidity of a solution and that of an ideal solution of the same concentration. In practice $X = -(H_o + \lg[H^+])$ and $m^* = 1 - \Phi$.

Cracking : Breaking down complex molecules into simpler compounds, as in oil refining.

Critical mass : Spontaneous fission in uranium produces neutrons that induce fission of ^{235}U , which releases neutrons that can produce a chain reaction. The critical mass is the amount of fissionable material necessary for this chain reaction to sustain itself.

Critical micelle concentration (cmc) : There is a relatively small range of concentrations separating the limit below which virtually no *micelles* are detected and the limit above which virtually all additional surfactant molecules form micelles. Many properties of surfactant solutions, if plotted against the concentration, appear to change at a different rate above and below this range. By

extrapolating the loci of such a property above and below this range until they intersect, a value may be obtained known as the critical micellization concentration (critical micelle concentration), symbol cM , abbreviation cmc (or $c.m.c.$). As values obtained using different properties are not quite identical, the method by which the cmc is determined should be clearly stated.

Critical molar volume : (V_c) The molar volume at the critical point.

Critical point : Critical state. State at which two phases of a substance first become indistinguishable. For example, at pressures higher than 217.6 atm *and* temperatures above 374°C, the meniscus between steam and liquid water will vanish; the two phases become indistinguishable and are referred to as a supercritical fluid.

The temperature and pressure at which two phases of a substance in equilibrium become identical, forming a single phase.

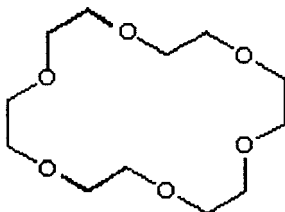
Critical pressure : (P_c) The pressure at the critical point.

Critical temperature : (T_c) The temperature at the critical point. A gas above the critical temperature will never condense into a liquid, no matter how much pressure is applied. Most substances have a critical temperature that is about 1.5 to 1.7 times the standard boiling point, in kelvin.

Cross-conjugation : In a system XC_6H_4GY this is conjugation involving the substituent X, the benzene ring, and the side-chain connective-plus-reaction site GY, i.e. either X is a +R group and GY is a -R group, or X is a -R group and GY is a +R group. In Hammett correlations this situation can lead to the need to apply exalted substituent constants σ^+ or σ^- , respectively, as in electrophilic or nucleophilic aromatic substitution, respectively. The term "through resonance" is synonymous. Cross conjugation has also been used to describe the interactions occurring in 2-phenylallyl and similar systems.

Crown : A *molecular entity* comprising a monocyclic *ligand* assembly that contains three or more *binding sites* held together by covalent bonds and capable of binding a *guest* in a central (or nearly central) position. The *adducts* formed are sometimes known as

"coronates". The best known members of this group are macrocyclic polyethers, such as "18-crown-6", containing several repeating units $-\text{CR}_2-\text{CR}_2\text{O}-$ (where R is most commonly H), and known as crown ethers.



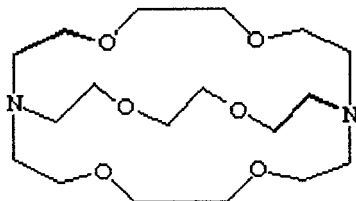
"18-crown-6"

Crucible : A small bowl with a lip, made of heat-resistant white glazed ceramic. It is used for heating substances using a Bunsen flame.

Crude oil : A chemical mixture of petroleum liquids. Crude oil forms the raw material for an oil refinery.

Cryogen : Cryogenic gas. A gas that has been liquified by lowering temperature, usually to a temperature under about -100°C .

Cryptand : A *molecular entity* comprising a cyclic or polycyclic assembly of *binding sites* that contains three or more binding sites held together by *covalent bonds*, and which defines a molecular cavity in such a way as to bind (and thus "hide" in the cavity) another molecular entity, the *guest* (a cation, an anion or a neutral species), more strongly than do the separate parts of the assembly (at the same total concentration of binding sites). The *adduct* thus formed is called a "cryptate". The term is usually restricted to bicyclic or oligocyclic molecular entities. Example



Corresponding monocyclic ligand assemblies (*crowns*) are sometimes included in this group, if they can be considered to define

a cavity in which a guest can hide. The terms "podand" and "spherand" are used for certain specific ligand assemblies. Coplanar cyclic polydentate ligands, such as porphyrins, are not normally regarded as cryptands.

Crystal : A sample of a crystalline solid that has a regular shape bound by plane surfaces (*facets*) that intersect at characteristic angles. The shape results from the arrangement of the substances atoms, ions, or molecules. Most crystals contain defects that can strongly affect their optical and electrical properties.

A substance that has grown freely so that it can develop external faces. Compare crystalline, where the atoms are not free to form individual crystals and amorphous, where the atoms are arranged irregularly.

A three-dimensional solid formed by regular repetition of the packing of atoms, ions, or molecules.

Crystal field splitting energy. (Δ) Ligands complexed to a metal ion will raise the energy of some of its d orbitals and lower the energy of others. The difference in energy is called the crystal field splitting energy.

Crystal field theory : Crystal field. The color, spectra, and magnetic properties of metal-ligand complexes can be explained by modeling the effect of ligands on metal's d orbital energies.

An extension of the valence-bond theory used to explain transition- metal compounds.

Crystal systems : Seven patterns or systems into which all crystals can be grouped: cubic, hexagonal, rhombohedral, tetragonal, orthorhombic, monoclinic and triclinic.

Crystalline : A solid in which the atoms, ions or molecules are organised into an orderly pattern without distinct crystal faces. *Examples:* copper (II) sulphate, sodium chloride. Compare amorphous.

Used to describe materials that behave as if they are made of regular crystals.

Crystalline solid : Crystalline. Compare with amorphous. A solid that has a repeating, regular three-dimensional arrangement of atoms, molecules, or ions.

Crystallisation : The process in which a solute comes out of solution slowly and forms crystals.

Crystallite : Compare with crystal. A perfect crystalline part of a larger imperfect crystal. Real crystals are usually built of a large number of crystallites.

Crystallization : Fractional crystallization; crystallisation. The process of forming pure crystals³³ by freezing a liquid, evaporating a solution, or precipitating a solid from solution. Impurities remain in the liquid, so crystallization is often to purify solid substances.

Recrystallization. Production of a purer sample of a substance by slow precipitation of crystals from a solution of the substance.

Cubic closest-packed : A structure formed by the stacking of closest-packed planes of atoms in an ABCABC... repeating pattern.

Cubic crystal system : Groupings of crystals that look like cubes.

Cubic hole : A hole in a simple cubic structure, which is surrounded by eight atoms or ions arranged toward the corners of a cube.

Cupric : (Cu^{2+}) cupric ion. *Deprecated.* The copper(II) ion, Cu^{2+} .

A compound that contains copper in the +2 oxidation state.

Cuprous : (Cu^{+}) cuprous ion. *Deprecated.* The copper(I) ion, Cu^{+} .

A compound that contains copper in the +1 oxidation state.

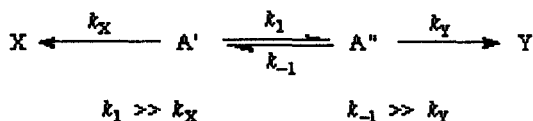
Curie : A unit for measuring the activity of a radioactive nuclide. By definition, $1 \text{ Ci} = 3.700 \times 10^{10}$ disintegrations per second.

Curie point : Temperature above which a ferromagnetic material loses its ferromagnetism.

Current : An electric current is produced by a flow of electrons through a conducting solid or ions through a conducting liquid. The rate of supply of this charge is measured in amperes (A).

The amount of charge carried per unit time.

Curtin-Hammett principle : In a *chemical reaction* that yields one product (X) from one conformational isomer (A') and a different product (Y) from another conformational isomer (A'') (and provided these two isomers are rapidly interconvertible relative to the rate of product formation, whereas the products do not undergo interconversion) the product composition is not in direct proportion to the relative concentrations of the conformational isomers in the *substrate*; it is controlled only by the difference in standard free energies ($d\Delta^\ddagger G$) of the respective *transition states*. It is also true that the product composition is formally related to the relative concentrations of the conformational isomers A' and A'' (i.e. the conformational equilibrium constant) and the respective rate constants of their reactions; these parameters are generally - though not invariably - unknown. The diagram below represents the energetic situation for transformation of interconverting isomers A and A' into products X and Y.



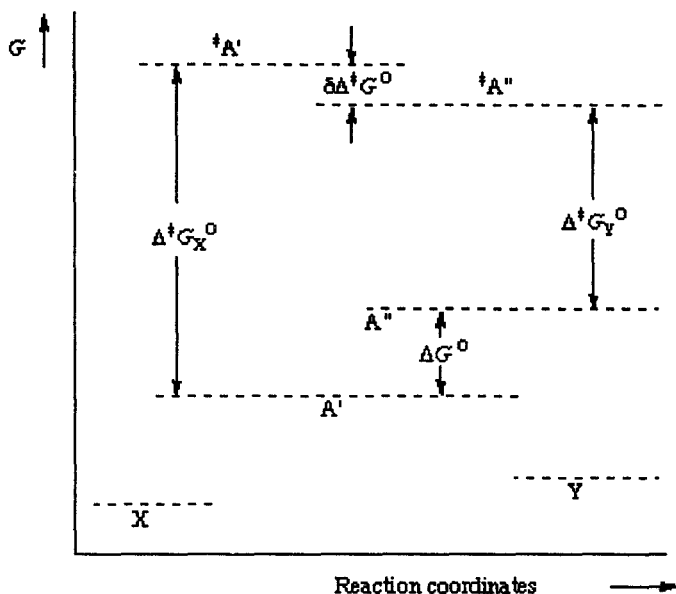


Figure : Curtin-Hammett principle.

Transformation of interconverting isomers A' and A'' into products X and Y .

Cyanide : (CN^-) An ion with a -1 charge containing one atom of carbon bound to one atom of nitrogen.

A compound that contains CN^- ions.

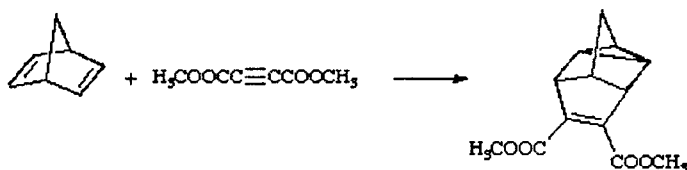
Cyanide process : A method for separating a metal from an ore. Crushed ore is treated with cyanide ion to produce a soluble metal cyanide complex. The complex is washed out of the ore and reduced to metallic form using an active metal (usually zinc).

Cybotactic region : That part of a solution in the vicinity of a solute molecule in which the ordering of the solvent molecules is modified by the presence of the solute molecule. The term solvent "cosphere" of the solute has also been used.

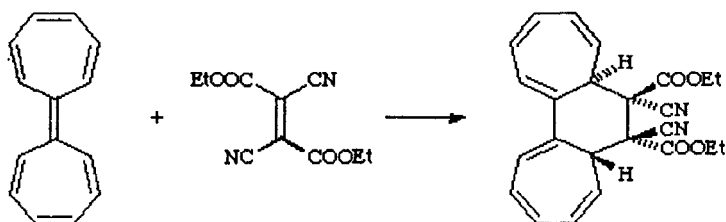
Cyclization : Formation of a ring compound from a chain by formation of a new bond.

Cycloaddition : A reaction in which two or more unsaturated molecules (or parts of the same molecule) combine with the

formation of a cyclic *adduct* in which there is a net reduction of the bond multiplicity. The following two systems of notations have been used for the more detailed specification of cycloadditions, of which the second, more recent system (described under (2)) is preferred : (1) An ($i+j+\dots$) cycloaddition is a reaction in which two or more molecules (or parts of the same molecule), respectively, provide units of i, j, \dots linearly connected atoms: these units become joined at their respective termini by new sigma bonds so as to form a cycle containing ($i+j+\dots$) atoms. In this notation, (a) a Diels-Alder reaction is a (4+2) cycloaddition, (b) the initial reaction of ozone with an alkene is a (3+2) cycloaddition, and (c) the reaction shown below is a (2+2+2) cycloaddition. (N.B.: parentheses (.....) are used in the description based on numbers of atoms.) (2) The symbolism [$i+j+\dots$] for a cycloaddition identifies the numbers i, j, \dots of electrons in the



units that participate in the transformation of reactants to products. In this notation the reaction (a) and (b) of the preceding paragraph would both be described as [2+4] cycloadditions, and (c) as a [2+2+2] cycloaddition. The symbol *a* or *s* (*a* = *antarafacial*, *s* = *suprafacial*) is often added (usually as a subscript after the number to designate the stereochemistry of addition to each fragment. A subscript specifying the orbitals, viz., σ , π (sigma, pi) with their usual significance) or *n* (for an orbital associated with a single atom only), may be added as a subscript before the number. Thus the normal Diels-Alder reaction is a [4s+2s] or [$\pi 4s + \pi 2s$] cycloaddition, whilst the reaction would be a [14a+2s] or [$\pi 14a + \pi 2s$] cycloaddition. (N.B. Square brackets [...] are used in the descriptions based on numbers of electrons.) Cycloadditions may be *pericyclic reactions* or (non-concerted) *stepwise reactions*. The term "dipolar cycloaddition" is used for cycloadditions of 1,3-dipolar compounds. HUISGEN (1968);



Cycloalkane : An alkane that contains a ring of carbon atoms.

Cycloelimination : The reverse of *cycloaddition*. The term is preferred to the synonyms "cycloreversion", "retro-addition", and "retrocycloaddition".

Cysteine : Compare with cystine. A naturally occurring amino acid with an SH group on its side chain.

Cystine : dicysteine. Compare with cysteine. A naturally occurring amino acid with a disulfide bridge group on its side chain, formed by condensation of two cysteine⁺ residues.



Δ HR : The average number of collisions that a molecule undergoes each second.

D-, **D-isomer**. Compare with **L-** : Prefix used to designate a dextrorotatory enantiomer.

Dalton's law : Dalton's law of partial pressure. The total pressure exerted by a mixture of gases is the sum of the pressures that each gas would exert if it were alone. For example, if dry oxygen gas at 713 torr is saturated with water vapor at 25 torr, the pressure of the wet gas is 738 torr.

Dalton's law of partial pressures : A statement of the relationship between the total pressure of a mixture of gases and the partial pressures of the individual components: $P_{\text{total}} = P_1 + P_2 + P_3 + \dots$

DeBroglie equation : Describes the relationship between the wavelength and momentum of an object. See wave-particle duality.

Debye : (**D**) Debye unit. Compare with dipole moment. A common non-SI unit of dipole moment, named for Dutch physical chemist Peter Debye. A charge separation equal to one electron charge placed one Ångstrom unit apart has a dipole moment of 4.8 D. In SI units, $1 \text{ D} = 3.338 \times 10^{-30}$ coulomb meters.

Decay (radioactive decay) : the way that a radioactive element changes into another element due to loss of mass through radiation. *Example*: uranium 238 decays with the loss of an alpha particle to form thorium 234.

Decomposition : Decompose; decomposable; decomposition reaction. Compare with synthesis. A reaction in which a compound is broken down into simpler compounds or elements. Compounds sometimes decompose if heated strongly or if subjected to a strong electric current (electrolysis).

The break down of a substance (for example, by heat or with the aid of a catalyst) into simpler components. In such a chemical reaction only one substance is involved. *Example*: hydrogen peroxide ($\text{H}_2\text{O}_2(\text{aq})$) into oxygen ($\text{O}_2(\text{g})$) and water ($\text{H}_2\text{O}(\text{l})$).

The breakdown of a single entity (normal molecule, reaction *intermediate*, etc.) into two or more fragments.

Decrepitation : when, as part of the decomposition of a substance, cracking sounds are also produced. *Example*: heating of lead nitrate ($\text{Pb}(\text{NO}_3)_2$).

Degenerate : degenerate orbital. A set of orbitals are said to be degenerate if they all have the same energy. This degeneracy can sometimes be "lifted" by external electric or magnetic fields.

Degenerate orbitals : Orbitals that have the same energy, such as the three 2p atomic orbitals on an isolated atom.

Degenerate rearrangement : A *molecular rearrangement* in which the principal product is indistinguishable (in the absence of isotopic labelling) from the principal reactant. The term includes both "degenerate *intramolecular* rearrangements" and reactions that involve *intermolecular* transfer of atoms or groups ("degenerate intermolecular rearrangements"): both are degenerate *isomerizations*. The occurrence of degenerate rearrangements may be detectable by isotopic labelling or by dynamic NMR techniques. For example : the [3,3] *sigmatropic rearrangement* of hexa-1, 5-diene (Cope rearrangement), Synonymous but less preferable terms are



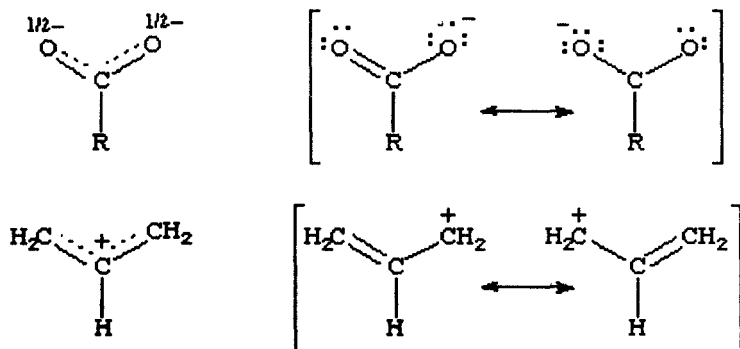
"automerization", "permutational isomerism", "isodynamic transformation", "topomerization".

Dehydrating agent : A reagent, such as P_4O_{10} , used to remove water.

Dehydration : The removal of water from a substance by heating it, placing it in a dry atmosphere or using a drying (dehydrating) reagent such as concentrated sulphuric acid.

Deliquescent : Deliquesce; deliquescence. Deliquescent compounds absorb so much moisture from the air that they dissolve. Examples are calcium chloride and sodium hydroxide.

Delocalization : A quantum mechanical concept most usually applied in organic chemistry to describe the π bonding in a *conjugated system*. This bonding is not localized between two atoms; instead, each link has a "fractional double bond character" or *bond order*. There is a corresponding "delocalization energy", identifiable with the stabilization of the system compared with a hypothetical alternative in which formal (localized) single and double *bonds* are present. Some degree of delocalization is always present and can be estimated by quantum mechanical calculations. The effects are particularly evident in *aromatic* systems and in symmetrical *molecular entities* in which a lone pair of electrons or a vacant p-orbital is conjugated with a double bond (e.g. carboxylate ions, nitro compounds, enamines, the allyl cation). Delocalization in such species may be represented by partial bonds or as *resonance* (here symbolized by a two-headed arrow) between *contributing structures*.



These examples also illustrate the concomitant delocalization of charge in ionic conjugated systems. Analogously, delocalization of the spin of an unpaired electron occurs in conjugated *radicals*. See also *mesomerism*.

Denaturation : A process that changes the three-dimensional structure of a protein.

Denature : Denatured; denaturation. A loss of chemical function, usually due to some heat or chemically-induced structural change. For example, heating a protein causes it to lose its three dimensional form and it no longer functions correctly.

Density : (ρ, d) Compare with specific gravity. Mass of a substance per unit volume. Saying "the density of mercury is 13.55 g/cm^3 " is the same as saying "the mass of exactly 1 cm^3 of mercury is 13.55 g ".

An intensive property of a substance equal to the mass of a sample divided by the volume of the sample.

The mass per unit volume (e.g. g/cm^3).

Density functional : Density functional theory; density functional model. A model that describes the electronic structure of an atom or molecule by approximating the total energy as a function of electron density.

Dependent variable : Compare with independent variable. A dependent variable changes in response to changes in independent variables. For example, in an experiment where the vapor pressure of a liquid is measured at several different temperatures, temperature is the independent variable and vapor pressure is the dependent variable.

Derived unit : Derived units are units constructed from the SI system's base units. For example, the SI unit for density is kg/m^3 , derived from the base units kg and m.

Desalinisation : Removal of dissolved salts from seawater.

The removal of all the salts from sea water, by reverse osmosis or heating the water and collecting the distillate. It is a very energy-intensive process.

Desiccant : A substance that absorbs water vapour from the air.

Example: silica gel.

Desiccator : A glass bowl and lid containing a shelf. The apparatus is designed to store materials in dry air. A desiccant is placed below the shelf and the substance to be dried is placed on the shelf. The lid makes a gas-tight joint with the bowl.

Destructive distillation : the heating of a material so that it decomposes entirely to release all of its volatile components. Destructive distillation is also known as pyrolysis.

Destructive interference : Compare with constructive interference. When the peaks of one wave match the troughs of another, the waves interfere destructively. The amplitudes of the interfering waves cancel to give the resultant wave a lower amplitude.

Detachment : The reverse of an *attachment*.

Detailed balancing, principle of : When equilibrium is reached in a reaction system (containing an arbitrary number of components and reaction paths), as many atoms, in their respective *molecular entities*, will pass forward, as well as backwards, along each individual path in a given finite time interval. Accordingly, the reaction path in the reverse direction must in every detail be the reverse of the reaction path in the forward direction (provided always that the system is at equilibrium). The principle of detailed balancing is a consequence for macroscopic systems of the principle of *microscopic reversibility*.

Detergent : A chemical based on petroleum that removes dirt.

A synthetic analog of soap that contains a long, hydrophobic tail attached to a hydrophilic $-\text{SO}_3^-$ or $-\text{OSO}_3^-$ head.

Deuterium : (D, ^2H) An isotope of hydrogen that contains one neutron and one proton in its nucleus.

Devarda's alloy : Zinc with a trace of copper, which acts as a catalyst for reactions with the zinc.

Dextrorotatory : A compound that rotates plane-polarized light to the right (clockwise) when viewed in the direction of the light source.

Sextorotary. Compare with levorotatory. Having the property of rotating plane-polarized light clockwise.

Dialysis : Dialysis is the separation of components in a mixture by passing them across a semipermeable membrane.

Diamagnetic : A substance repelled by both poles of a magnet. A substance in which the electrons are all paired. See paramagnetic.

Substances having a negative magnetic susceptibility are diamagnetic. They are repelled out of a magnetic field. See also *paramagnetic*.

Diamagnetism : Diamagnetic. Compare with paramagnetism. Diamagnetic materials are very weakly repelled by magnetic fields. The atoms or molecules of diamagnetic materials contain no unpaired spins.

Diamond : A crystalline form of carbon, made of a network of covalent, tetrahedrally bound carbon atoms.

Diaphragm : A semipermeable membrane - a kind of ultrafine mesh filter - that allows only small ions to pass through. It is used in the electrolysis of brine.

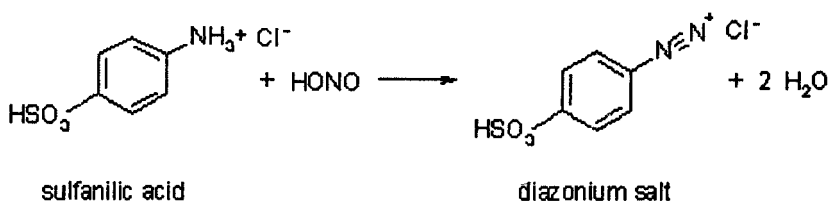
Diastereoisomerism : Stereoisomerism other than *enantiomerism*. Diastereoisomers (or diastereomers) are stereoisomers not related as mirror images. Diastereoisomers are characterized by differences in physical properties, and by some differences in chemical behaviour toward achiral as well as chiral reagents.

Diastereomer : diastereomeric. Compare with enantiomer. Stereoisomers which are not mirror images of each other. Diastereomers are chemically similar but distinguishable; they have different melting points and boiling points and they react at different rates.

Diatomic molecule : Compare with binary compound and polyatomic molecule. A molecule that contains only two atoms. All of the noninert gases occur as diatomic molecules; e. g. hydrogen, oxygen, nitrogen, fluorine, and chlorine are H_2 , O_2 , N_2 , F_2 , and Cl_2 , respectively. A molecule, such as H_2 or HCl , which contains two atoms.

Diazonium salt : A diazonium salt is a compound with general form $\text{Ar-N}\equiv\text{N}^+\text{X}^-$, where Ar represents a substituted benzene ring and X^- is a halide ion such as chloride. Diazonium salts are unstable and explosive in dry form. They are used to manufacture many different organic compounds, including azo dyes³². See also diazotization³³.

Diazotization : Diazotization is a reaction that converts an -NH_2 group connected to a phenyl ring to a diazonium salt. For example,



Diazotization reactions are extremely useful in organic synthesis. The nitrous acid provides NO^+ which replaces a hydrogen on the -NH_3^+ group to produce $\text{-NH}_2\text{NO}^+$ and water; a second water is eliminated to produce the -N_2^+ group.

Dichloromethane : (CH_2Cl_2) Dichloromethane (CH_2Cl_2) is an organic solvent often use to extract organic substances from samples. It is toxic but much less so than chloroform or carbon tetrachloride, which were previously used for this purpose.

Dielectric constant : A measure for the effect of a medium on the potential energy of interaction between two charges. It is measured by comparing the capacity of a capacitor with and without the sample present.

Dienophile : The olefin component of a Diels-Alder reaction.

Differential thermal analysis : (DTA) A technique that is often used to analyze materials that react or decompose at higher temperatures. The difference in temperature between the sample and an inert reference material is monitored as both are heated in a furnace. Phase transitions and chemical reactions taking place in the

sample on heating cause the temperature difference to become larger, at temperatures that are characteristic of the sample.

Diffraction : Diffract. Compare with effusion. The ability of a wave to bend around the edges of obstacles or holes. The effect is most noticeable when the obstacle or hole is comparable to the size of the wavelength.

Diffusion : Diffuse. Compare with effusion. The mixing of two substances caused by random molecular motions. Gases diffuse very quickly; liquids diffuse much more slowly, and solids diffuse at very slow (but often measurable) rates. Molecular collisions make diffusion slower in liquids and solids.

The movement of atoms, ions, or molecules through a gas, liquid, or solid.

The slow mixing of one substance with another until the two substances are evenly mixed. Mixing occurs because of differences in concentration within the mixture. Diffusion works rapidly with gases, very slowly with liquids.

Diffusion combustion : The form of combustion that occurs when two gases only begin to mix during ignition. As a result the flame is hollow and yellow in colour. *Example*: a candle flame.

Diffusion rate : Rate of diffusion. Compare with effusion. The number of randomly moving molecules that pass through a unit area per second. Diffusion rates are fastest when a large concentration difference exists on either side of the unit area. Diffusion rates increase with temperature, and decrease with increasing pressure, molecular weight, and molecular size.

Dilatometer : A device for measuring volume changes.

Dilute : Diluted; diluting. Compare with concentrate. Having a relatively low concentration.

Dilute acid : An acid whose concentration has been reduced in a large proportion of water.

Dilution : Adding solvent to a solution to lower its concentration.

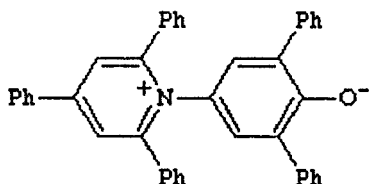
The process by which more solvent is added to decrease the concentration of a solution.

Dimensional analysis : An approach to solving problems that focuses on the way the units of the problem are used to set up the problem.

Dimer : Literally, two parts. A compound, such as N_2O_4 , produced by combining two smaller molecules, such as NO_2 .

Dimerization : The *transformation* of a *molecular entity* A to give a molecular entity A_2 . For example: $\text{CH}_3\cdot + \text{H}_3\text{C}\cdot \longrightarrow \text{CH}_3\text{CH}_3$
 $2 \text{CH}_3\text{COCH}_3 \longrightarrow (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_3$ $2 \text{RCOOH} \longrightarrow (\text{RCOOH})_2$.

Dimroth-Reichardt E_T parameter : A measure of the *ionizing power* (loosely *polarity*) of a solvent, based on the maximum wave number of the longest wavelength electronic absorption band of a



given solvent. E_T , called $E_T(30)$ by its originators, is given by $E_T = 2.859 \times 10^{-3} \nu = 2.859 \times 10^4 \lambda^{-1}$ where E_T is in kcal/mol, ν is in cm^{-1} and λ is in nm. The so-called normalized E_T^N scale is defined as $E_T^N = [E_T(\text{solvent}) - E_T(\text{SiMe}_4)]/[E_T(\text{water}) - E_T(\text{SiMe}_4)] = [E_T(\text{solvent}) - 30.7]/32.4$ See also *Grunwald-Winstein equation*, *Z-value*.

Dipolar aprotic solvent : A solvent with a comparatively high relative permittivity (or dielectric constant), greater than ca. 15, and a sizable permanent dipole moment, that cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds, e.g. dimethyl sulfoxide. The term (and its alternative "polar aprotic solvent") is a misnomer and is therefore discouraged. Such solvents are usually not *aprotic*, but *protophilic* (and at most weakly *protogenic*). In describing a solvent it is better to be explicit about its essential properties, e.g. dipolar and non-protogenic.

Dipolar bond : A *bond* formed (actually or conceptually) by *coordination* of two neutral moieties, the combination of which results in charge-separated structures, e.g., $R_3N: + O \longrightarrow R_3N^+-O^-$. The term is preferred to the obsolescent synonyms "coordinate link", "co-ordinate covalence", "dative bond", "semipolar bond".

Dipole : Anything with two equal but opposite electrical charges, such as the positive and negative ends of a polar bond or molecule.

Dipole-dipole interaction : Dipole-dipole force. Electrostatic attraction between oppositely charged poles of two or more dipoles.

Intermolecular or intramolecular interaction between molecules or groups having a permanent electric dipole moment. The strength of the interaction depends on the distance and relative orientation of the dipoles. The term applies also to intramolecular interactions between bonds having permanent dipole moments.

Diprotic acid : An acid, such as H_2SO_4 , that has the potential to lose two H^+ ions.

Diprotic base : A base, such as the S^{2-} ion, that can pick up two H^+ ions.

Disaccharide : A carbohydrate formed by linking a pair of monosaccharides.

Disinfectant : A chemical that kills bacteria and other microorganisms.

Disorder : A measure of the extent to which a system differs from a perfect crystal at 0 K, where there is no disorder.

Displacement : Displacement reaction; replacement reaction; replacement. A reaction in which a fragment of one reactant is replaced by another reactant (or by a fragment of another reactant). Displacement reactions have the same number of products as reactants, and are described by equations of the form $A + BC \rightarrow AB + C$ (single displacement) or $AB + CD \rightarrow AC + BD$ (double displacement).

Displacement reaction : A reaction that occurs because metals differ in their reactivity. If a more reactive metal is placed in a solution of a less reactive metal compound, a reaction occurs in which the more reactive metal displaces the metal ions in the solution. *Example*: when zinc metal is introduced into a solution of copper (II) sulphate (which thus contains copper ions), zinc goes into solution as zinc ions, while copper is displaced from the solution and forced to precipitate as metallic copper.

Disproportionation : A reaction in which an element or compound simultaneously undergoes both oxidation and reduction, such as the decomposition of H_2O_2 to form H_2O and O_2 .

Any *chemical reaction* of the type $\text{A} + \text{A} \longrightarrow \text{A}' + \text{A}''$, where A, A' and A'' are different chemical species. For example: $2 \text{ArH}^+ \longrightarrow \text{ArH} + \text{ArH}^{2+}$ The reverse of disproportionation is called *comproportionation*. A special case of disproportionation (or "dismutation") is "radical disproportionation", exemplified by $\cdot\text{CH}_2\text{CH}_3 + \cdot\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_2=\text{CH}_2 + \text{CH}_3\text{CH}_3$ Reactions of the more general type $\text{R}'\text{CHCH}_3 + \text{R}'\text{CHCH}_3 \longrightarrow \text{RCH}=\text{CH}_2 + \text{R}'\text{CH}_2\text{CH}_3$ are also loosely described as radical disproportionations. (A somewhat more restricted usage of the term prevails in inorganic chemistry.)

Disproportion; disproportionate; disproportionating. A reaction involving a substance that produces two different forms of the substance, one more oxidized and the other more reduced than the original.

Dissociate : To break bonds apart. In the case of acids, it means to break up, forming hydrogen ions. This is an example of ionisation. Strong acids dissociate completely. Weak acids are not completely ionised, and a solution of a weak acid has a relatively low concentration of hydrogen ions.

Dissociation : The separation of a *molecular entity* into two or more molecular entities (or any similar separation within a polyatomic molecular entity). Examples include *unimolecular heterolysis* and *homolysis*, and the separation of the constituents of an *ion pair* into free ions.

The separation of the constituents of any aggregate of molecular entities. In both senses dissociation is the reverse of *association*.

The process by which salts dissolve in water to give solutions that contain the corresponding ions.

Dissolve : Literally, to loosen. Used to describe the process in which one substance mixes with another. When a solid dissolves in a liquid, the particles that form the solid are released into solution. To break down a substance in a solution without causing a reaction.

Dissolved oxygen : DO. The amount of oxygen dissolved in a solvent (usually water). Dissolved oxygen levels are used as a general indicator of water quality.

Distillate : The vapor collected and condensed from a distillation.

A technique used to separate liquids with different boiling points.

Distillation is a technique for separating components of a mixture on the basis of differing boiling points. The mixture is heated, vaporizing some of the components. The vapor is collected and condensed to isolate the components with the lowest boiling points.

Distillation : The process of separating mixtures by condensing the vapours through cooling.

Distilled water : Distilled water is nearly pure water and is produced by distillation of tap water. Distilled water is used in the laboratory in preference to tap water because the distillation process removes many of the impurities in tap water that may influence the chemical reactions for which the water is used.

Distonic radical cation : A radical cation in which charge and radical sites are separated.

Disulfide linkage : The -S-S- linkage that can form between the -SH side chains on adjacent cysteine residues in a protein.

Divalent : Binds to two other things (which may be other atoms, molecules, ions, or electrons). See also divalent anion and divalent cation.

Divalent anion : An ion with a charge of -2.

Divalent cation : An ion with a charge of +2.

DNA : Deoxyribonucleic acid, the nucleic acid used to store the genetic information that codes for the synthesis of proteins. A nucleic acid with 2-deoxy-D-ribose as the sugar in its nucleotides. DNA contains encoded genetic information, specifically templates for the synthesis of all of an organism's proteins and enzymes.

Deoxyribonucleic acid.

Domoic acid : Domoic acid is a toxic amino acid produced by certain species of algae. Domoic acid binds to a receptor that helps nerve cells control the flow of ions across their cell membranes. The receptor no longer works correctly, and the uncontrolled flux of ions damages and eventually kills the nerve cell.

Donor number (DN) : A quantitative measure of *Lewis basicity* devised by GUTMANN .

Double displacement : double displacement reaction; double replacement; double replacement reaction; double exchange; exchange; metathesis. A double displacement or metathesis is a reaction in which two reactants trade fragments: $AB + CD = AC + BD$ Most commonly, the fragments are ions, e. g. $AgNO_3(aq) + NaCl(aq) = AgCl(s) + NaNO_3(aq)$

Dreschel bottle : a tall bottle with a special stopper, designed to allow a gas to pass through a liquid. The stopper contains both inlet and outlet tubes. One tube extends below the surface of the liquid so that the gas has to pass through the liquid before it can escape to the outlet tube.

Driving force (also called the affinity) of a reaction, A (SI unit: kJ mol^{-1}) The decrease in Gibbs energy on going from the reactants to the products of a *chemical reaction* ($-\Delta G$).

Dropper funnel : a special funnel with a tap to allow the controlled release of a liquid. Also known as a dropping funnel or tap funnel.

Drug : A biologically active compound or mixture used to cure, prevent, or detect disease, to control biological processes, or to alter mental state.

Dry cell : Leclanché cell. A electrolytic cell that uses a moist paste rather than a liquid as an electrolyte. Flashlight batteries are dry cells with a zinc cup for an anode, a carbon rod for a cathode, and a paste made of powdered carbon, NH_4Cl , ZnCl_2 , and MnO_2 for an electrolyte.

Dual substituent-parameter equation : In a general sense, this is any equation which expresses substituent effects in terms of two parameters. However, in practice the term is used more specifically for an equation for summarizing the effects of meta- or para-substituents ($i = m$ or p) X on chemical reactivity, spectroscopic properties, etc. of a probe site Y in benzene or other aromatic system. $P^i = \rho_I^i \sigma_I + \rho_R^i \sigma_R$ P is the magnitude of the property Y for substituent X, expressed relative to the property for $\text{X}=\text{H}$; σ_I and σ_R are inductive or polar and resonance substituent constants, respectively, there being various scales for σ_R ; ρ_I and ρ_R are the corresponding regression coefficients.

Ductile : Capable of being drawn into thin sheets or wires without breaking.

Ductility. Compare with malleable. Capable of being drawn into wire. Metals are typically ductile materials.

Dye : A coloured substance that will stick to another substance so that both appear coloured.

Dynamic equilibrium : Equilibrium. Compare with position of equilibrium. Dynamic equilibrium is established when two opposing processes are occurring at precisely the same rate, so that there is no apparent change in the system over long periods of time.

Dyne : (dyn) The unit of force in the obsolete cgs system of units. A dyne is the force required to accelerate a 1 g mass by 1 cm/s per second.

Dyotropic rearrangement : An uncatalyzed process in which two sigma bonds simultaneously migrate intramolecularly, e.g

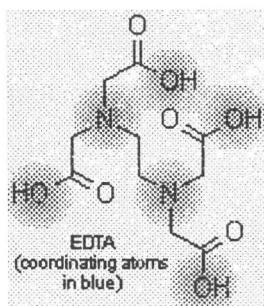


A plot of relative intensity of emitted radiation as a function of wavelength or frequency.

E

Ebulliometry : Ebulliometric. Determination of average molecular weight of a dissolved substance from the boiling point elevation of the solution.

EDTA : Ethylenediaminetetracetic acid; versine. A polydentate ligand that tightly complexes certain metal ions. EDTA is used as a blood preservative by complexing free calcium ion (which promotes blood clotting). EDTA's ability to bind to lead ions makes it useful as an antidote for lead poisoning.



Educt : Term used mainly in the German literature for starting material (reactant). It should be avoided in English, because there it means "something that comes out" and not "something that goes in". The German use of the term is in fact also incorrect.

Effective charge : Change in effective charge is a quantity obtained by comparison of the *polar effect* of substituents on the free energies of rate or equilibrium processes with that on a standard ionization equilibrium. Provided the effective charge on the states in the standard equilibrium are defined, then it is possible to measure

effective charges for states in the reaction or equilibrium under consideration.

Effective molarity (or effective concentration) : The ratio of the first-order rate constant of an *intramolecular* reaction involving two functional groups within the same *molecular entity* to the second-order *rate constant* of an analogous *intermolecular* elementary reaction. This ratio has the dimension of concentration. The term can also apply to an equilibrium constant.

Effective nuclear charge : (Z_{eff}) Compare with atomic number. The nuclear charge experienced by an electron when other electrons are shielding the nucleus.

Effervesce : Give off bubbles of gas.

To lose water and turn to a fine powder on exposure to the air. *Example:* Sodium carbonate on the rim of a reagent bottle stopper.

Efflorescent : Efflorescence; efflorescing. Compare with deliquescent and hygroscopic. Efflorescent substances lose water of crystallization to the air. The loss of water changes the crystal structure, often producing a powdery crust.

Effusion : Effuse. Compare with diffusion and diffraction. Gas molecules in a container escape from tiny pinholes into a vacuum with the same average velocity they have inside the container. They also move in straight-line trajectories through the pinhole.

Effusion : The process by which a gas escapes through a pinhole into a vacuum.

Eighteen-electron rule : An electron-counting rule to which an overwhelming majority of stable diamagnetic transition metal complexes adhere. The number of nonbonded electrons at the metal plus the number of electrons in the metal-ligand bonds should be 18. The 18 electron rule in transition metal chemistry is a full analogue of the "Lewis octet rule".

Elastic collision : A collision in which no kinetic energy is lost.

Elastomer : A polymer that snaps back to its original shape after being stretched to at least twice its original length.

Electric charge : Charge. A property used to explain attractions and repulsions between certain objects. Two types of charge are possible: negative and positive. Objects with different charge attract; objects with the same charge repel each other.

Electric current : Current; electrical current. A flow of electric charges. The SI unit of electric current is the ampere.

Electric dipole : Dipole. An object whose centers of positive and negative charge do not coincide. For example, a hydrogen chloride (HCl) molecule is an electric dipole because bonding electrons are on average closer to the chlorine atom than the hydrogen, producing a partial positive charge on the H end and a partial negative charge on the Cl end.

Electric dipole moment : (μ) dipole moment. A measure of the degree of polarity of a polar molecule*. Dipole moment is a vector with magnitude equal to charge separation times the distance between the centers of positive and negative charges. Chemists point the vector from the positive to the negative pole; physicists point it the opposite way. Dipole moments are often expressed in units called Debyes.

Electric field : A field of forces that act on any electric charge placed within it. The stronger the field, the stronger the force that acts on the charge. For example, the positive charge on an atomic nucleus creates an electric field that traps electrons.

Electrical conductivity : Conductivity; electric conductivity; electrical conductance; conductance. Compare with resistance. A measure of how easily an electric current can pass through a material. The conductivity is the reciprocal of the resistance. The SI unit of conductance is the siemens.

Electrical potential : The energy produced by an electrochemical cell and measured by the voltage or electromotive force (emf).

Electrical resistance : Resistance. Compare with conductivity.

Electrochemical cell : A cell consisting of two electrodes and an electrolyte. It can be set up to generate an electric current (usually known as a galvanic cell, an example of which is a battery), or an

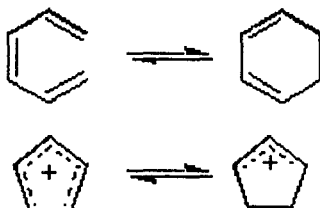
electric current can be passed through it to produce a chemical reaction (in which case it is called an electrolytic cell and can be used to refine metals or for electroplating).

Electric cell. A device that uses a redox reaction to produce electricity, or a device that uses electricity to drive a redox reaction in the desired direction.

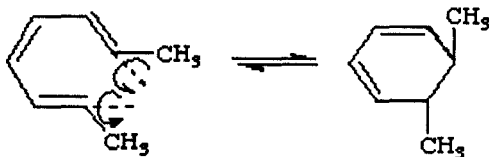
Electrochemical series : The arrangement of substances that are either oxidising or reducing agents in order of strength as a reagent, for example, with the strong oxidising agents at the top of the list and the strong reducing agents at the bottom.

Electrochemistry : The study of the interchange of chemical and electrical energy.

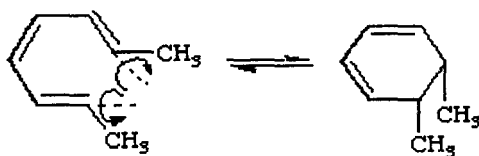
Electrocyclic reaction : A *molecular rearrangement* that involves the formation of a sigma bond between the termini of a fully *conjugated* linear pi-electron system (or a linear fragment of a pi-electron system) and a decrease by one in the number of pi bonds, or the reverse of that process. For example:



The stereochemistry of such a process is termed "conrotatory" or *antarafacial* if the substituents at the interacting termini of the conjugated system both rotate in the same sense, e.g. or "disrotatory"



(or *suprafacial*) if one terminus rotates in a clockwise and the other in a counter-clockwise sense, e.g.



Electrode : A conductor that forms one terminal of a cell.

An electrically conducting surface that allows electrons to be transferred between reactants in an electrochemical cell.

Any terminal that conducts an electric current into or away from various conducting substances in a circuit (such as the anode or cathode of a battery).

Electrofuge : A *leaving group* that does not carry away the bonding electron pair. For example, in the nitration of benzene by NO_2^+ , H^+ is the electrofuge. The adjective of electrofuge is electrofugal.

Electrolysis : A process in which an electric current is used to decompose a compound into its elements.

A process that involves forcing a current through a cell to cause a nonspontaneous chemical reaction to occur.

An electrical-chemical process that uses an electric current to cause the break-up of a compound and the movement of metal ions in a solution. The process happens in many natural situations (as for example in rusting) and is also commonly used in industry for purifying (refining) metals or for plating metal objects with a fine, even metal coating.

The process of driving a redox reaction in the reverse direction by passage of an electric current through the reaction mixture.

A substance that dissociates fully or partially into ions when dissolved in a solvent, producing a solution that conducts electricity. See strong electrolyte weak electrolyte.

An ionic solution that conducts electricity.

Electrolytic cell : A cell that uses electrical energy to produce a chemical change that would otherwise not occur spontaneously.

An electrochemical cell in which electrolysis is done.

Radiation (such as radiowaves, microwaves, infrared rays, light, ultraviolet rays, x-rays, or gamma-rays) that contains both electric and magnetic components and travels at the speed of light.

$$\begin{array}{c}
 \text{R}_2\text{N}-\text{C}=\text{C}-\text{C}=\text{O} \\
 | \quad | \quad | \\
 \text{---} \quad \text{---} \quad \text{---}
 \end{array}
 \xrightarrow{\text{---}}
 \begin{array}{c}
 \text{R}_2\text{N}^+=\text{C}-\text{C}=\text{C}-\text{O}^- \\
 | \quad | \quad | \\
 \text{---} \quad \text{---} \quad \text{---}
 \end{array}$$

The term has been deemed obsolescent or even obsolete (see *mesomeric effect*, *resonance effect*). It has long been custom to use phrases such as "enhanced substituent resonance effect" which imply the operation of the electromeric effect, without using the term, and various modern theoretical treatments parametrize the response of substituents to "electronic demand", which amounts to considering the electromeric effect together with the *inductomeric effect*.

Electromotive force (emf) : the force set up in an electric circuit by a potential difference.

Electron : (e^-) Compare with proton and neutron. A fundamental constituent of matter, having a negative charge of $1.602\,176\,462 \times 10^{-19}$ coulombs $\pm 0.000\,000\,063 \times 10^{-19}$ coulombs and a mass of $9.109\,381\,88 \times 10^{-31}$ kg $\pm 0.000\,000\,72 \times 10^{-31}$ kg

Electron : A subatomic particle with a charge of -1 and a mass of roughly 0.0005 amu.

A tiny, negatively charged particle that is part of an atom.
The flow of electrons through a solid material such as a wire produces an electric current.

Electron acceptor : A substance to which an electron may be transferred; for example 1,4-dinitrobenzene or the dication 1,1'-dimethyl-4,4'-bipyridylium.

A *Lewis acid*. This usage is discouraged.

Electron affinity (EA) : The energy given off when a neutral atom in the gas phase picks up an electron to form a negatively charged ion.

The energy released when an additional electron (without excess energy) attaches itself to a *molecular entity* (usually an electrically neutral molecular entity). (The direct measurement of this quantity involves molecular entities in the gas phase.)

The enthalpy change for the addition of one electron to an atom or ion in the gaseous state. For example, the electron affinity of hydrogen is ΔH in the reaction $H(g) + e^- \rightarrow H^-(g)$
 $\Delta H = -73$ kJ/mol.

Electron attachment : The transfer of an electron to a *molecular entity*, resulting in a molecular entity of (algebraically) increased negative charge.



Electron capture : A reaction in which the nucleus of an atom captures a $1s$ electron.

Electron configuration : electronic configuration. A list showing how many electrons are in each orbital or subshell^{**}. There are several notations. The subshell notation lists subshells in order of increasing energy, with the number of electrons in each subshell indicated as a superscript. For example, $1s^2 2s^2 2p^3$ means "2 electrons in the $1s$ subshell, 2 electrons in the $2s$ subshell, and 3 electrons in the $2p$ subshell."

Electron configuration : The arrangement of electrons in atomic orbitals; for example, $1s^2 2s^2 2p^3$.

The pattern in which electrons are arranged in shells around the nucleus of an atom. *Example*: chlorine has the configuration 2, 8, 7.

Electron density : If $P(x,y,z) dx dy dz$ is the probability of finding an electron in the volume element $dx dy dz$ at the point of a molecular entity with coordinates x,y,z , then $P(x,y,z)$ is the electron density at this point. For many purposes (e.g., X-ray scattering, forces on atoms) the system behaves exactly as if the electrons were spread out into a continuously distributed charge. The term has frequently been wrongly applied to negative *charge population*. See also *charge density*.

Electron detachment : The reverse of an *electron attachment*.

Electron donor : A *molecular entity* that can transfer an electron to another molecular entity, or to the corresponding *chemical species*.

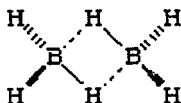
A Lewis base. This use is discouraged.

Electron emission : A nuclear reaction in which electrons, or β particles, are ejected from the nucleus of an atom. See beta decay.

Electron transfer : The transfer of an electron from one *molecular entity* to another, or between two localized sites in the same molecular entity. See also *inner sphere (electron transfer)*, *outer sphere (electron transfer)*, *Marcus equation*.

Electron volt : Energy required to move an electron through a potential difference of 1 volt. An electron volt is equivalent to 1.6×10^{-19} J.

Electron-deficient bond : A single bond between adjacent atoms that is formed by less than two electrons, as in B_2H_6 : The B-H-B bonds are called a "two-electron three-centre bonds".



Electron-donor-acceptor complex : A term sometimes employed instead of *charge-transfer complex* or *Lewis adduct*. See also *adduct*, *coordination*.

Electronegativity : A measure of the power of an atom or a group of atoms to attract electrons from other parts of the same *molecular entity*.

Compare with ionization energy and electron affinity. Electronegativity is a measure of the attraction an atom has for bonding electrons. Bonds between atoms with different electronegativities are polar, with the bonding electrons spending more time on average around the atom with higher electronegativity.

The tendency of an atom to draw the electrons in a bond toward itself.

Electroneutrality principle : The principle expresses the fact that all pure substances carry a net charge of zero.

Electronic effect of substituents: symbols and signs : The *inductive effect* has universally been represented by the symbol I. This is now commonly taken to include both through-bonds and through-space transmission, but I is also used specifically for through-bonds transmission; through-space transmission is then symbolized as F (for *field effect*). The symbols for the influence of substituents exerted through electron delocalization have variously been M (*mesomeric*), E (*electromeric*), T (*tautomeric*), C (*conjugative*), K (*konjugativ*), and R (*resonance*). Since the present fashion is to use the term *resonance effect*, R is the most commonly

used symbol, although M is still seen quite often. Both the possible sign conventions are in use. The Ingold sign convention associates *electronegativity* (relative to hydrogen atom) with a negative sign, electropositivity with a positive sign. Thus the nitro group is described as electron- withdrawing by virtue of its - I and - M effects; chloro is described as a - I, +M substituent, etc. For *correlation analysis* and *linear free-energy relationships* this convention has been found inconvenient, for it is in contradiction to the sign convention for polar substituent constants (σ -constants). Authors concerned with these fields often avoid this contradiction by adopting the opposite sign convention originally associated with Robinson, for electronic effects. This practice is almost always associated with the use of R for the electron delocalization effect: thus the nitro group is a +I, +R substituent; chloro a +I, - R substituent, etc.

Electron-pair acceptor : A synonym for *Lewis acid*.

Electron-pair donor : A synonym for *Lewis base*.

Electron-transfer catalysis : The term indicates a sequence of reactions such as shown in equations (1)-(3), leading from A to B : $A + e^- \longrightarrow A^{\cdot -}$ (1) $A^{\cdot -} \longrightarrow B^{\cdot -}$ (2) $B^{\cdot -} + A \longrightarrow B + A^{\cdot -}$ (3) An analogous sequence involving radical cations ($A^{\cdot +}$, $B^{\cdot +}$) is also observed. The most notable example of electron-transfer catalysis is the $S_{RN}1$ (or $T+D_N+A_N$) reaction of aromatic halides. The term has its origin in a suggested analogy to acid-base catalysis, with the electron instead of the proton. However, there is a difference between the two catalytic mechanisms, since the electron is not a true catalyst, but rather behaves as the initiator of a *chain reaction*. "Electron-transfer induced chain reaction" is a more appropriate term for the situation described by equations (1)-(3).

Electrophile : A species that *loves* electrons. Since the electrons are negatively charged, electrophiles are positively charged or bear a partial positive charge. Examples are carbocations or protons.

Literally, something that loves electrons. A Lewis acid that attacks a site rich in electron density.

An electrophile (or electrophilic reagent) is a reagent that forms a *bond* to its reaction partner (the *nucleophile*) by accepting both bonding electrons from that reaction partner. An "electrophilic *substitution reaction*" is a *heterolytic* reaction in which the reagent supplying the entering group acts as an electrophile. For example $\text{C}_6\text{H}_6 + \text{NO}_2^+$ (electrophile) $\longrightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}^+$ (electrofuge) Electrophilic reagents are *Lewis acids*. "Electrophilic catalysis" is catalysis by Lewis acids. The term "electrophilic" is also used to designate the apparent polar character of certain *radicals*, as inferred from their higher relative reactivities with reaction sites of higher electron density.

Electrophilicity : The property of being *electrophilic* (see *electrophile*).

The relative reactivity of an electrophilic reagent. (It is also sometimes referred to as "electrophilic power".) Qualitatively, the concept is related to *Lewis acidity*. However, whereas Lewis acidity is measured by relative equilibrium constants, electrophilicity is measured by relative *rate constants* for reactions of different electrophilic reagents towards a common *substrate* (usually involving attack at a carbon atom).

Electroplating : Depositing a thin layer of a metal on to the surface of another substance using electrolysis.

Electrorefining : Electrorefining is a method for purifying a metal using electrolysis. An electric current is passed between a sample of the impure metal and a cathode when both are immersed in a solution that contains cations of the metal. Metal is stripped off the impure sample and deposited in pure form on the cathode.

Element : A substance that cannot be decomposed into a simpler substance by a chemical reaction. A substance composed of only one kind of atom.

A substance that cannot be decomposed into simpler substance by chemical means. *Examples*: calcium, iron, gold.

Compare with compound and mixture. An element is a substance composed of atoms with identical atomic number. The older definition of element (*an element is a pure substance that can't be decomposed chemically*) was made obsolete by the discovery of isotopes.

Element effect : The ratio of the rate constants of two reactions that differ only in the identity of the element of the atom in the *leaving group*, e.g., k_{Br}/k_{Cl} . As for *isotope effects*, a ratio of unity is regarded as a "null effect".

Element symbol : An international abbreviation for element names, usually consisting of the first one or two distinctive letters in element name. Some symbols are abbreviations for ancient names.

Elemental analysis : The process by which the percent-by-mass of the elements in a compound are determined.

Elementary reaction : A reaction for which no reaction intermediates have been detected or need to be postulated in order to describe the chemical reaction on a molecular scale. An elementary reaction is assumed to occur in a single step and to pass through a single *transition state*. See also *stepwise reaction*.

Compare with net chemical reaction. A reaction that occurs in a single step. Equations for elementary reactions show the actual molecules, atoms, and ions that react on a molecular level.

Elementary Step : Reaction mechanisms are broken down into elementary steps. For each step the reactants are directly involved in forming the transition state. Therefore a rate law can be written from an elementary step but not from an overall reaction.

Elimination : The reverse of an *addition reaction* or *transformation*. In an elimination two groups (called eliminands) are lost most often from two different centres (1/2/elimination or 1/3/elimination, etc.) with concomitant formation of an unsaturation in the molecule (double bond, triple bond) or formation of a new ring. If the groups are lost from a single centre (α -elimination, 1/1/elimination) the resulting product is a *carbene* or a "carbene analogue".

Emission spectrum : Emission spectra. Compare with absorption spectrum.

The spectrum of bright lines against a dark background obtained when an atom or molecule emits radiation when excited by heat or an electric discharge.

Emollient : A substance added to a formulation that gives it softening ability. For example, oils that can soften skin are added as emollients in some skin creams.

Empirical formula : Simplest formula. Compare with molecular formula. Empirical formulas show which elements are present in a compound, with their mole ratios indicated as subscripts. For example, the empirical formula of glucose is CH_2O , which means that for every mole of carbon in the compound, there are 2 moles of hydrogen and one mole of oxygen.

The simplest formula for a compound. The ratio of the number of atoms of each element in the compound.

Empirical temperature : A property that is the same for any two systems that are in thermodynamic equilibrium with each other.

Empirical weight : The weight of the empirical formula, calculated from a table of atomic weights.

Emulsion : Compare with colloid. A colloid formed from tiny liquid droplets suspended in another, immiscible liquid. Milk is an example of an emulsion.

Tiny droplets of one substance dispersed in another. One common oil in water emulsion is called milk. Because the tiny droplets tend to come together, another stabilising substance is often needed. Soaps and detergents are such agents, wrapping the particles of grease and oil in a stable coat. Photographic film is an example of a solid emulsion.

Enantiomer : Enantiomeric. Compare with diastereomer. Two molecules that are nonsuperimposable mirror images of each other. One enantiomer rotates plane-polarized light to the left; the other rotates it to the right.

One of a pair of *molecular entities* which are mirror images of each other and non-superimposable.

Stereoisomers that are non-superimposable mirror images.

Encounter complex : A *complex of molecular entities* produced at an *encounter-controlled rate*, and which occurs as an intermediate in a reaction mechanism. When the complex is formed from two molecular entities it is called an "encounter pair". A distinction between encounter pairs and (larger) encounter complexes may be relevant in some cases, e.g. for mechanisms involving *pre-association*.

Encounter-controlled rate : A *rate of reaction* corresponding to the rate of encounter of the reacting *molecular entities*. This is also known as "diffusion-controlled rate" since rates of encounter are themselves controlled by diffusion rates (which in turn depend on the viscosity of the *medium* and the dimensions of the reactant molecular entities). For a *bimolecular* reaction between solutes in water at 25 °C an encounter-controlled rate is calculated to have a second-order *rate constant* of about $10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

End point : The stage in a titration when the reaction between the titrant (added from a burette) and the titrate (in the flask) is complete. The end point is normally recognised by use of an indicator which has been added to the titrate. In an acid-base reaction this is also called the neutralisation point.

The point at which the indicator of an acid-base titration changes color. See equivalence point.

End point. Compare with equivalence point. The experimental estimate of the equivalence point in a titration.

Endergonic : A process that leads to an increase in the free energy of a system and is therefore not spontaneous.

Refers to a reaction for which the free energy of the system increases; ΔG is positive for an endergonic reaction.

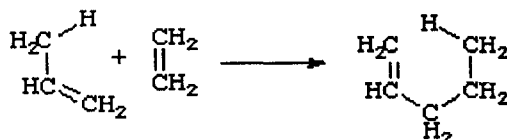
Endergonic : A process in which the system absorbs heat from the surroundings. See exothermic.

Endothermic reaction; endothermic process. Compare with exothermic. A process that absorbs heat. The enthalpy change for an endothermic process has a positive sign.

Refers to a reaction where energy (as heat) flows into the system; at constant pressure ΔH is positive for an endothermic reaction.

A reaction that takes in heat. *Example:* when ammonium chloride is dissolved in water.

Ene reaction : The addition of a compound with a double bond having an allylic hydrogen (the "ene") to a compound with a multiple bond (the "enophile") with transfer of the allylic hydrogen and a concomitant reorganization of the bonding, as illustrated below for propene (the "ene") and ethene (the "enophile"). The reverse is a "retro-ene" reaction.



Energy : Compare with heat and work. Energy is an abstract property associated with the capacity to do work.

The ability to do work or transfer heat.

Energy of activation (Arrhenius energy of activation; activation energy), E_a (SI unit: kJ mol^{-1}) An operationally defined quantity expressing the dependence of a rate constant on temperature according to $E_a = RT^2(\partial \ln k / \partial T)_p$ as derived from the "Arrhenius equation", $k = A \exp(-E_a/RT)$, where A (SI unit: as for the corresponding rate constant) is termed the "pre-exponential factor". See also *enthalpy of activation*.

Enforced concerted mechanism : Variation of reaction parameters in a series of reactions proceeding in non-concerted steps may lead to a situation, where the putative intermediate will possess a lifetime shorter than a bond vibration, so that the steps become concerted. The *transition state* structure will lie on the coordinate of the *More O'Ferrall-Jencks diagram* leading to that of the putative intermediate.

Enkephalin : Enkephalins are molecules produced naturally by the central nervous system to numb pain. Enkephalins lock into receptors on the surface of a nerve cell and open ion channels. Ions flow into the cell and the distribution of charge on either side of the cell membrane becomes such that the nerve cell cannot fire.

Ensemble : The set of atoms or molecules comprising the system.

Entering group : An atom or *group* that forms a *bond* to what is considered to be the main part of the *substrate* during a reaction. For example: the attacking *nucleophile* in a bimolecular nucleophilic *substitution reaction*.

Enthalpy (H) : The sum of the internal energy plus the product of the pressure times the volume of the gas in a system: $H = E + PV$.

(H) enthalpy change. Compare with heat. Enthalpy (H) is defined so that changes in enthalpy (ΔH) are equal to the heat absorbed or released by a process running at constant pressure. While changes in enthalpy can be measured using calorimetry, absolute values of enthalpy usually cannot be determined. Enthalpy is formally defined as $H = U + PV$, where U is the internal energy, P is the pressure, and V is the volume.

A property of a system equal to $E + PV$, where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system. At constant pressure the change in enthalpy equals the energy flow as heat.

Enthalpy of activation (standard enthalpy of activation), $\Delta^\ddagger H^\circ$ (SI unit: kJ mol^{-1}) The standard enthalpy difference between the *transition state* and the ground state of the reactants at the same temperature and pressure. It is related to the temperature coefficient of the rate constant according to the equation : $\Delta^\ddagger H = RT^2(\partial \ln k / \partial T)_p - RT = E_a - RT = -R(\partial \ln(k/T) / \partial (1/T))_p$ where E_a is the *energy of activation*, providing that the rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3} , measured at a fixed temperature and pressure). If $\ln k$ is expressed as $\ln k = (a/T) + b + c \ln T + dT$, then $\Delta^\ddagger H = -aR + (c - 1)RT + dRT^2$. If enthalpy of activation and

entropy of activation are assumed to be temperature independent, then $\Delta^\ddagger H = -aR$. If the concentration units are mol dm^{-3} , the true and apparent enthalpies of activation differ by $(n - 1)/(\alpha RT^2)$, where n is the *order of reaction* and α the thermal expansivity.

Enthalpy of atomization : (ΔH_{at}) atomization enthalpy; heat of atomization. The change in enthalpy that occurs when one mole of a compound is converted into gaseous atoms. All bonds in the compound are broken in atomization and none are formed, so enthalpies of atomization are always positive.

Enthalpy of combustion : (ΔH_c) heat of combustion. The change in enthalpy when one mole of compound is completely combusted. All carbon in the compound is converted to $\text{CO}_2(\text{g})$, all hydrogen to $\text{H}_2\text{O}(\ell)$, all sulfur to $\text{SO}_2(\text{g})$, and all nitrogen to $\text{N}_2(\text{g})$.

Enthalpy of formation (ΔH_f) : The change in the enthalpy that occurs during a chemical reaction that leads to the formation of a compound from its elements in their most thermodynamically stable states at 1 MPa.

Enthalpy of formation : The enthalpy change when 1 mole of a substance is formed from the elements in their standard states; represented by the symbol ΔH_f° ; also called heat of formation.

Enthalpy of fusion : (ΔH_{fus}) Heat of fusion; molar heat of fusion; molar enthalpy of fusion. The change in enthalpy when one mole of solid melts to form one mole of liquid. Enthalpies of fusion are always positive because melting involves overcoming some of the intermolecular attractions in the solid.

The enthalpy change that occurs to melt a solid at its melting point; also called the heat of fusion.

Enthalpy of hydration : (ΔH_{hyd}) hydration enthalpy; heat of hydration. The change in enthalpy for the process $\text{A}(\text{g}) \rightarrow \text{A}(\text{aq})$ where the concentration of A in the aqueous solution approaches zero. Enthalpies of hydration for ions are always negative because strong ion-water attractions are formed when the gas-phase ion is surrounded by water.

Enthalpy of neutralization : Heat of neutralization. The heat released by an acid-base neutralization reaction running at constant pressure.

Enthalpy of reaction (ΔH) : The change in the enthalpy that occurs during a chemical reaction. The difference between the sum of the enthalpies of the reactants and the products of the reaction.

(ΔH_{rxn}) Heat of reaction. The heat absorbed or released by a chemical reaction running at constant pressure.

Enthalpy of solution : (ΔH_{soln}) Heat of solution. Compare with integral enthalpy of solution.

Enthalpy of sublimation : (ΔH_{sub}) Heat of sublimation. The change in enthalpy when one mole of solid vaporizes to form one mole of gas. Enthalpies of sublimation are always positive because vaporization involves overcoming most of the intermolecular attractions in the sublimation.

Enthalpy of vaporization : (ΔH_{vap}) Heat of vaporization. The change in enthalpy^{*} when one mole of liquid evaporates to form one mole of gas. Enthalpies of vaporization are always positive because vaporization involves overcoming most of the intermolecular attractions in the liquid.

Entropy (S) : A measure of the disorder in a system.

(S) Entropy is a measure of energy dispersal. Any spontaneous change disperses energy and increases entropy overall. For example, when water evaporates, the internal energy of the water is dispersed with the water vapor produced, corresponding to an increase in entropy.

A thermodynamic function that measures randomness or disorder.

Entropy of activation, (standard entropy of activation), $\Delta^\ddagger S^\circ$ (SI unit: $\text{J mol}^{-1} \text{K}^{-1}$) The standard entropy difference between the *transition state* and the ground state of the reactants, at the same temperature and pressure. It is related to the *Gibbs energy of activation* and *enthalpy of activation* by the equations $\Delta^\ddagger S = (\Delta^\ddagger H - \Delta^\ddagger G)/T = \Delta^\ddagger H/T - R \ln (k_B/h) \mp R \ln (k/T)$ or, if $\ln k$ is expressed as $\ln k = a/T + b + c \ln T + dT$, $\Delta^\ddagger S = R [b - \ln (k_B/h) + (c - 1)(1 + \ln$

$T) + 2 dT]$ provided that rate constants for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3} , measured at a fixed temperature

and pressure). The numerical value of $\Delta^\ddagger S$ depends on the standard state (and therefore on the concentration units selected). If entropy of activation and *enthalpy of activation* are assumed to be temperature-independent, $\Delta^\ddagger S = R[b - \ln(k_B/h)]$ Strictly speaking, the quantity defined is the entropy of activation at constant pressure from which the entropy of activation at constant volume can be deduced. The information represented by the entropy of activation may alternatively be conveyed by the pre-exponential factor A .

Environmental chemistry. Chemical ecology. The study of natural and man-made substances in the environment, including the detection, monitoring, transport, and chemical transformation of chemical substances in air, water, and soil.

Enzyme : A protein that catalyzes a biochemical reaction.

Biological catalysts in the form of proteins in the body that speed up chemical reactions. Every living cell contains hundreds of enzymes that help the processes of life continue.

Protein or protein-based molecules that speed up chemical reactions occurring in living things. Enzymes act as catalysts for a single reaction, converting a specific set of reactants (called substrates) into specific products. Without enzymes life as we know it would be impossible.

Epimer : A *diastereoisomer* that has the opposite *configuration* at only one of two or more tetrahedral "stereogenic" centres present in the respective *molecular entity*.

Epimerization : Interconversion of epimers by reversal of the configuration at one of the "stereogenic" centres.

Equality : A symbolic representation of two quantities that are equivalent. For example, 12 inches = 1 foot.

Equation : A symbolic statement that can be used to do a calculation. For example, $x = 12y$, where x is the number of inches in y feet.

Equation of state : An equation, such as $PV = nRT$, which relates two or more of the quantities that describe the state of a system.

Equatorial : The three positions in a trigonal bipyramid that lie in the trigonal plane.

Equilibrium : The point at which there is no longer a change in the concentrations of the reactants and the products of a chemical reaction. The point at which the rates of the forward and reverse reactions are equal.

The point in a reaction at which the free energies of the reactants and products are equal; at this point $\Delta G = 0$. See also reversible process.

Equilibrium constant (K_c or K_p) : The product of the concentrations (or partial pressures) of the products of a reaction divided by the product of the concentrations (or partial pressures) of the reactants.

(K , K_{eq}) equilibrium constant expression; law of mass action. Compare with reaction quotient. The product of the concentrations of the products, divided by the product of the concentrations of the reactants, for a chemical reaction at equilibrium. For example, the equilibrium constant for $A + B = C + D$ is equal to $[C][D] / ([A][B])$, where the square brackets indicate equilibrium concentrations. Each concentration is raised to a power equal to its stoichiometric coefficient in the expression. The equilibrium constant for $A + 2B = 3C$ is equal to $[C]^3 / ([A][B]^2)$. For gas phase reactions, partial pressures can be used in the equilibrium constant expression in place of concentrations.

A constant represented by the symbol K which is defined as the product of the equilibrium concentrations of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the equilibrium concentrations of reactants, each raised to

the power that corresponds to its coefficient in the balanced equation. The magnitude of K is a measure of the extent to which a reaction occurs.

Equilibrium constant expression : The expression used to calculate the equilibrium constant for a reaction.

Equilibrium region : The portion of a plot of the concentration of a substance versus time in which the concentration does not change. The portion of this plot in which the reaction is at equilibrium.

Equilibrium, chemical : Reversible processes (processes which may be made to proceed in the forward or reverse direction by the (infinitesimal) change of one variable, ultimately reach a point where the rates in both directions are identical, so that the system gives the appearance of having a static composition at which the Gibbs energy, G , is a minimum. At equilibrium the sum of the chemical potentials of the reactants equals that of the products, so that $\Delta G_r = \Delta G_r^0 + RT \ln K = 0$ $\Delta G_r^0 = -RT \ln K$ The equilibrium constant, K , is given by the *mass-law effect*.

Equivalence point : Compare with end point. The equivalence point is the point in a titration when enough titrant has been added to react completely with the analyte.

The point in an acid-base titration at which equivalent amounts of acid and base have been added to the solution. See endpoint.

Equivalent : Compare with normality.

The amount of substance that gains or loses one mole of electrons in a redox reaction.

The amount of substances that releases or accepts one mole of hydrogen ions in a neutralization reaction.

The amount of electrolyte that carries one mole of positive or negative charge, for example, 1 mole of $\text{Ba}^{2+}(\text{aq})$ is 2 equivalents of $\text{Ba}^{2+}(\text{aq})$.

Ester : An ester is a compound formed from an acid and an alcohol. In esters of carboxylic acids, the $-\text{COOH}$ group and the $-\text{OH}$

group lose a water and become a -COO- linkage : $R\text{-COOH} + R'\text{-OH} = R\text{-COO-R}' + \text{H}_2\text{O}$ where R and R' represent organic groups.

Organic compounds formed by the reaction of an alcohol with an acid and which often have a fruity taste. *Example:* ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$).

Ethanol : ($\text{CH}_3\text{CH}_2\text{OH}$) Ethyl alcohol; grain alcohol. A colorless, flammable liquid produced by fermentation of sugars. Ethanol is the alcohol found in alcoholic beverages.

Ether : A compound in which an oxygen atom is attached to two carbon atoms, such as diethyl ether, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$.

Ethyl : (-Et, $-\text{CH}_2\text{CH}_3$) ethyl group. A molecular fragment produced by removing a hydrogen atom from ethane ($\text{CH}_3\text{-CH}_3$). For example, ethyl chloride is $\text{CH}_3\text{-CH}_2\text{-Cl}$.

Ethyl acetate : ($\text{CH}_3\text{COOCH}_2\text{CH}_3$) A flammable liquid with a fruity odor, used in flavorings and as a solvent.

Eutectic mixture : A mixture of two or more substances with melting point lower than that for any other mixture of the same substances.

Eutectic point : Eutectic temperature; eutectic composition. The composition and the melting point of a eutectic mixture. For example, the eutectic point of a mixture of NaCl and water occurs at 23.3% NaCl (by mass) and -21.1°C . That means that the lowest possible temperature at which a liquid NaCl solution can exist is -21.1°C ; below the eutectic point the solution will freeze into a mixture of ice and salt crystals.

Evaporate : To convert a liquid into a gas.

Evaporation : The change of state of a liquid to a gas. Evaporation happens below the boiling point and is used as a method of separating the materials in a solution.

Vaporization. Conversion of a liquid into a gas.

Excess reagent : In a limiting reagent problem, this is the reactant present in excess. The reaction will stop before all of the excess reagent is consumed.

Excess, to : If a reactant has been added to another reactant in excess, it has exceeded the amount required to complete the reaction.

Excimer : An excited dimer, "non-bonding" in the ground state. For example, a complex formed by the interaction of an excited *molecular entity* with a ground state counterpart of this entity.

Exciplex : An electronically excited complex of definite stoichiometry, "non-bonding" in the ground state. For example, a complex formed by the interaction of an excited *molecular entity* with a ground state counterpart of a different structure.

Excited state : Compare with ground state. An atom or molecule which has absorbed energy is said to be in an excited state. Excited states tend to have short lifetimes; they lose energy either through collisions or by emitting photons to "relax" back down to their ground states.

State of a system with energy higher than that of the ground state. This term is most commonly used to characterize a molecule in one of its electronically excited states, but can also refer to vibrational and/or rotational excitation in the electronic ground state.

Excitotoxin : An excitotoxin is a toxic molecule that stimulates nerve cells so much that they are damaged or killed. Domoic acid and glutamate are examples of excitotoxins.

Excluded volume : The fraction of the volume of a gas that is not empty space. The volume of the gas actually occupied by gas particles. At room temperature and atmosphere pressure, the excluded volume of a gas is approximately 0.12% of the total volume.

Exergonic : A process that leads to a decrease in the free energy of the system and is therefore spontaneous.

Refers to a reaction for which the free energy of the system decreases; ΔG is negative for an exergonic reaction.

Exothermic : A process in which a system gives off heat to the surroundings.

Exothermic : Exothermic reaction; exothermic process. Compare with endothermic. A process that releases heat. The enthalpy change for an exothermic process is negative. Examples of exothermic processes are combustion reactions and neutralization reactions.

Refers to a reaction where energy (as heat) flows out of the system; at constant pressure ΔH is negative for an exothermic reaction.

Exothermic reaction : A reaction that gives out substantial amounts of heat. *Example*: sucrose and concentrated sulphuric acid.

Expandibility : A measure of the ability to expand. A characteristic of substances, such as gases, that can expand to fill their containers.

Experiment : An experiment is direct observation under controlled conditions. Most experiments involve carefully changing one variable and observing the effect on another variable (for example, changing temperature of a water sample and recording the change volume that results).

Experimental yield : Actual yield. Compare with theoretical yield and percent yield. The measured amount of product produced in a chemical reaction.

Explosive : A substance which, when a shock is applied to it, decomposes very rapidly, releasing a very large amount of heat and creating a large volume of gases as a shock wave.

Extended Hammett equation : This term applies in a general way to any multiparametric extension of the *Hammett equation*. It is sometimes used specifically for a form of *dual substituent-parameter equation* in which the actual value of the correlated property P under the influence of the substituent X is used, rather than the value relative to that for $X = H$. An intercept term h corresponding to the value of P for $X = H$ is introduced, e.g. $P = \alpha \sigma_I + \beta \sigma_R + h$. The equation may be applied to systems for which the inclusion of further terms to represent other effects, e.g. steric, is appropriate.

Extensive properties : Properties which are dependent on the amount of the substance.

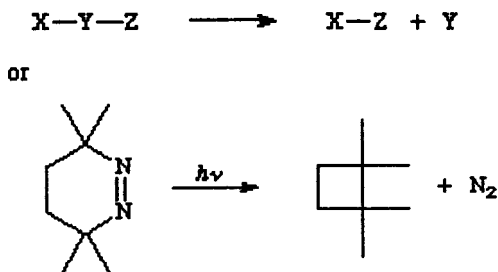
Extensive property : A quantity that depends on the size of the sample, such as mass, weight, length, height, and width. See *intensive property*.

Extensive; extensive properties. Compare with *intensive property*. A property that changes when the amount of matter in a sample changes. Examples are mass, volume, length, and charge.

Extraction : A method of separating mixtures based on differences in the solubility of their components in polar versus nonpolar solvents.

A technique for separating components in a mixture that have different solubilities. For example, caffeine can be separated from coffee beans by washing the beans with supercritical fluid carbon dioxide; the caffeine dissolves in the carbon dioxide but flavor compounds do not. Vanillin can be extracted from vanilla beans by shaking the beans with an organic solvent, like ethanol.

Extrusion transformation : A *transformation* in which an atom or *group* Y connected to two other atoms or groups X and Z is lost from a molecule, leading to a product in which X is bonded to Z, e.g., The reverse of an extrusion is called *insertion*. See *cheletropic reaction*. η -symbol ("eta") See *hapto*.



The ability of a material to oppose the flow of an electric current, converting electrical energy into heat. The SI unit of resistance is the ohm.

The heat absorbed or released when a solute is dissolved in a solvent. The heat of solution depends on the nature of the solute and on its concentration in the final solution.

F

F orbital : f-orbital. An orbital with angular momentum quantum number $\ell = 2$. The f orbitals generally have 3 nuclear nodes and rather complex shapes.

Face-centered cubic : A structure in which the simplest repeating unit consists of fourteen equivalent lattice points, eight of which are at the corners of a cube and another six in the centers of the faces of the cube. Found in cubic closest-packed structures.

Fahrenheit : ($^{\circ}\text{F}$) Fahrenheit temperature scale; Fahrenheit scale. Compare with Celsius. A temperature scale proposed by Daniel Gabriel Fahrenheit (1686-1736) which uses the melting point of ice (32°F) and the boiling point of water at one atmosphere (212°F) as calibration points. More...

Family : A vertical column of elements in the periodic table, such as the elements H, Li, Na, K, and so on.

Faraday : a constant representing the charge on one mole of electrons; 96,500 coulombs.

Faraday's constant : The charge on a mole of electrons: 96,484.56 C.

Faraday's law : A statement of the relationship between the amount of product formed during electrolysis and the amount of electric current that passes through the electrolytic cell.

Fast-atom bombardment (FAB) mass spectroscopy : A method in which ions are produced in a mass spectrometer from nonvolatile or thermally fragile organic molecules by bombarding

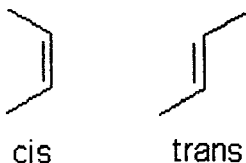
the compound in the condensed phase with energy-rich neutral particles.

Fat : A solid triester of glycerol and fatty acids. See oil.

Fats : semisolid, energy-rich compounds derived from plants or animals, made of carbon, hydrogen and oxygen. These are examples of esters.

Fatty acid : A carboxylic acid that contains a long, hydrophobic hydrocarbon chain.

Fatty acids are carboxylic acids with long hydrocarbon side chains. Most natural fatty acids have hydrocarbon chains that don't branch; any double bonds occurring in the chain are *cis* isomers (side chains are attached on the same side of the double bond).



Femto- : (f) Prefix used in the SI system meaning "multiply by 10^{-15} ". For example 22 fg means 22×10^{-15} g.

Ferment : To break down a substance by microorganisms in the absence of oxygen. *Example*: fermentation of sugar to ethanol during the production of alcoholic drinks.

Fermentation : A class of biochemical reactions that break down complex organic molecules (such as carbohydrates) into simpler materials (such as ethanol, carbon dioxide, and water). Fermentation reactions are catalyzed by enzymes.

Ferric : Ferric ion. *Deprecated*. The iron(III) ion, Fe^{3+} .

A compound that contains iron in the +3 oxidation state.

Ferroin : A blood-red complex of Fe^{2+} ion with 1,10-phenanthroline, used as a redox indicator. Ferroin changes from red to pale blue when oxidized.

Ferromagnetism : ferromagnetic. Compare with paramagnetic and diamagnetic. Ferromagnetic materials exhibit magnetism even in the absence of an external magnetic field. Ferromagnetic materials contain regions where many paramagnetic atoms or ions have magnetic moments that are aligned in the same direction. Iron, cobalt, nickel, and gadolinium are elements that can exhibit ferromagnetic behavior.

Ferrous : ferrous ion. *Deprecated.* The iron(II) ion, Fe^{2+} .

A compound that contains iron in the +2 oxidation state.

Fertile nuclide : A nuclide that can be converted into one that undergoes spontaneous fission, such as ^{238}U , which can be converted into ^{239}Pu .

Field effect : An experimentally observable effect symbolized by F (on reaction rates, etc.) of *intramolecular* coulombic interaction between the centre of interest and a remote unipole or dipole, by direct action through space rather than through bonds. The magnitude of the field effect (or "direct effect") depends on the unipolar charge/dipole moment, orientation of dipole, shortest distance between the centre of interest and the remote unipole or dipole, and on the effective dielectric constant.

Filled-shell configuration : An electron configuration in which a shell of atomic orbitals is filled, such as $1s^2 2s^2 2p^6$.

Filtrate : The liquid that has passed through a filter.

Filtration : The separation of a liquid from a solid using a membrane with small holes (i.e. a filter paper).

First ionization energy : (IE, IP) First ionization potential. Compare with second ionization energy, adiabatic ionization energy, vertical ionization energy, electronegativity, and electron affinity. The energy needed to remove an electron from an isolated, neutral atom.

The energy needed to remove the outermost, or highest-energy, electron from a neutral atom in the gas phase.

First law : First law of thermodynamics. The first law states that energy cannot be created or destroyed. Many equivalent statements are possible, including: Internal energy changes depend

only on the initial and final states of the system, not on the path taken. The work done during an adiabatic process depends only on the initial and final states of the system, and not on the path taken. The internal energy change for any cyclic process is zero.

A statement of the relationship between the internal energy of a system and the heat and work transferred from the system to its surroundings, or vice versa: $\Delta E_{\text{sys}} = q + w$.

The energy of the universe is constant; same as the law of conservation of energy.

First order reaction : Compare with zero order reaction and second order reaction. The sum of concentration exponents in the rate law for a first order reaction is one. Many radioactive decays are first order reactions.

A reaction whose rate is proportional to the concentration of a single reactant raised to the first power: $\text{rate} = k(X)$

Fission : A nuclear reaction in which a nuclide splits into two smaller nuclides. See fusion.

Nuclear fission. A nuclear reaction in which an atomic nucleus breaks into smaller nuclei of comparable mass, releasing a large amount of energy.

Flame : A mixture of gases undergoing burning. A solid or liquid must produce a gas before it can react with oxygen and burn with a flame.

Flammable (also inflammable) : Able to burn (in air).
Opposite: non-flammable.

Flash point : Compare with auto-ignition temperature. The temperature when vapor pressure[‡] of a substance becomes high enough to allow the air/vapor layer over the substance to be ignited. Ether and acetone have flash points below room temperature, which makes them very dangerous.

Flash vacuum pyrolysis (FVP) : Thermal reaction of a molecule by exposing it to a short thermal shock at high temperature, usually in the gas phase.

Flocculation : The grouping together of small particles in a suspension to form particles large enough to settle out as a precipitate. Flocculation is usually caused by the presence of a flocculating agent. *Example*: calcium ions are the flocculating agent for suspended clay particles.

Fluid : Able to flow; either a liquid or a gas.

Fluorescence : A process in which a compound emits light at one wavelength while being excited by radiation with a shorter wavelength.

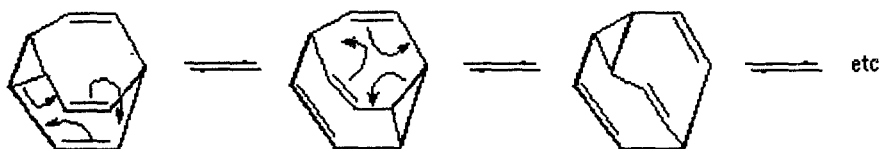
Fluorescent; fluorescent compound. A fluorescent substance absorbs short wavelength radiation and re-emits it as radiation with a longer wavelength in a very short time.

Fluorescent : A substance that gives out visible light when struck by invisible waves, such as ultraviolet rays.

Fluoride : Any compound that contains either the F^- ion or fluorine with an oxidation state of -1, such as CaF_2 .

Flux : A material used to make it easier for a liquid to flow. A flux dissolves metal oxides and so prevents a metal from oxidising while being heated.

Fluxional : A *chemical species* is said to be fluxional if it undergoes rapid *degenerate rearrangements* (generally detectable by methods which allow the observation of the behaviour of individual nuclei in a rearranged chemical species, e.g. NMR, X-ray). *Example*: Bullvalene (1 209 600 interconvertible arrangements of the ten CH groups).



The term is also used to designate positional change among ligands of complex compounds and organometallics. In these cases, the change is not necessarily degenerate.

Foam : A substance that is sufficiently gelatinous to be able to contain bubbles of gas. The gas bulks up the substance, making it behave as though it were semirigid.

Compare with colloid. A colloid in which bubbles of gas are suspended in a solid or liquid. Aerogel (solid smoke) and Styrafoam are examples of solid foams; whipped cream is an example of a liquid foam.

Force : The product of the mass of an object times its acceleration.

Formal charge : The charge on an atom in its Lewis structure. Formal charge is calculated by dividing the electrons in each covalent bond between the atoms in the bond, and then comparing the number of electrons that can be formally assigned to each atom with the number of electrons on a neutral atom of the element.

Formation : Formation reaction. A reaction that forms one mole of a compound from its elements in their most stable forms. For example, the formation reaction for water is $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}(\ell)$.

Formula unit : Compare with empirical formula. One formula weight of a compound.

Formula weight : Formula mass. Compare with molecular weight and empirical formula. The formula weight is the sum of the atomic weights of the atoms in an empirical formula. Formula weights are usually written in atomic mass units (u).

Fossil fuels : Hydrocarbon compounds that have been formed from buried plant and animal remains. High pressures and temperatures lasting over millions of years are required. *Examples*: The fossil fuels are coal, oil and natural gas.

Fraction : A group of similar components of a mixture. *Example*: In the petroleum industry the light fractions of crude oil are those with the smallest molecules, while the medium and heavy fractions have larger molecules.

Fractional distillation : Compare with distillation. A technique for separation of liquid mixtures by distillation that uses a tower attached to a flask containing the mixture to perform multiple distillations. Vapor moving up the column condenses on packing

material inside the column, trickles down the column, and again vaporises. The more volatile component can then be drawn off at the top of the component, while the less volatile component remains at the bottom.

The separation of the components of a liquid mixture by heating them to their boiling points.

Fractionating column : A glass column designed to allow different fractions to be separated when they boil. In industry, it may be called a fractionating tower.

Fractionation factor, isotopic : The ratio $(x_1/x_2)_A/(x_1/x_2)_B$, where x is the abundance, expressed as the atom fraction of the isotope distinguished by the subscript numeral, when the two isotopes are equilibrated between two different *chemical species* A and B (or between specific sites A and B in the same or different chemical species). The term is most commonly met in connection with deuterium solvent *isotope effects*, when the fractionation factor ϕ expresses the ratio $\phi = (x_D/x_H)_{\text{solute}}/(x_D/x_H)_{\text{solvent}}$ for the exchangeable hydrogen atoms in the chemical species (or sites) concerned. The concept is also applicable to *transition states*.

Fragmentation : The *heterolytic* cleavage of a molecule according to the general reaction $a-b-c-d-X \longrightarrow (a-b)^+ + c=d + X^-$ where $a-b$ is an *electrofuge* and X is a *nucleofuge* (which may emerge from the reaction in combined form), and the middle group affords the unsaturated fragment $c=d$. For example, $\text{Ph}_3\text{C}-\text{CO}_2\text{H} + \text{H}^+ \longrightarrow \text{Ph}_3\text{C}^+ + \text{C}=\text{O} + \text{H}_2\text{O}$.

The breakdown of a *radical* into a diamagnetic molecule or ion and a smaller radical, e.g., $(\text{CH}_3)_3\text{C}-\text{O}^\bullet \longrightarrow (\text{CH}_3)_2\text{C}=\text{O} + \text{H}_3\text{C}^\bullet$ $[\text{ArBr}]^- \longrightarrow \text{Ar}^\bullet + \text{Br}^-$ (solution)

The breakdown of a *radical ion* in a mass spectrometer or in solution, forming an ion of lower molar mass and a radical, e.g., $[(\text{CH}_3)_3\text{C}-\text{OH}]^+ \longrightarrow (\text{CH}_3)_2\text{C}=\text{OH}^+ + \text{H}_3\text{C}^\bullet$ (mass spectrometer)

Free energy (G) : The energy associated with a chemical reaction that can be used to do work. The free energy of a system is the sum of its enthalpy plus the product of the temperature times the entropy of the system: $G = H - TS$.

Energy that is actually available to do useful work. A decrease in free energy accompanies any spontaneous process. Free energy does not change for systems that are at equilibrium.

Free radical : A free radical is a molecule with an odd number of electrons. Free radicals do not have a completed octet and often undergo vigorous redox reactions. Free radicals produced within cells can react with membranes, enzymes, and genetic material, damaging or even killing the cell. Free radicals have been implicated in a number of degenerative conditions, from natural aging to Alzheimer's disease.

A neutral atom or molecule that contains an unpaired electron.

A very reactive atom or group with a 'spare' electron.
Example: methyl, $\text{CH}_3\cdot$

Freezing point : (mp) Standard melting point; normal melting point; melting point. The temperature at which the vapor pressure of a liquid is equal to the vapor pressure of the corresponding solid form. The liquid and solid forms can coexist at equilibrium at the freezing point. The standard melting point is the melting point at standard pressure.

The temperature at which a substance undergoes a phase change from a liquid to a solid. It is the same temperature as the melting point.

The temperature at which the solid and liquid phases of a substance are in equilibrium at atmospheric pressure. See melting point.

Freezing point depression : (ΔT_{fp}) The freezing point of a solution is always lower than the freezing point of the pure solvent. The freezing point depression is roughly proportional to the molality of solute particles in the solution. Freezing point depression is an example of a colligative property of a solution.

The decrease in the freezing point of a solvent that occurs when a solute is added to form a solution.

Frequency : (ν) Compare with wavelength. The number of cycles of a wave that move past a fixed observation point per second. The SI unit of frequency is the Hertz (Hz).

The number of wave crests or troughs that pass a fixed point per unit time.

Frontier orbitals : The Highest-energy Occupied Molecular Orbital (HOMO) (filled or partly filled) and Lowest-energy Unoccupied Molecular Orbital (LUMO) (completely or partly vacant) of a *molecular entity*. Examination of the mixing of frontier molecular orbitals of reacting molecular entities affords an approach to the interpretation of reaction behaviour; this constitutes a simplified perturbation *molecular orbital* theory of chemical behaviour. See also *SOMO*, *subadjacent orbital*.

Fuel : A concentrated form of chemical energy. The main sources of fuels (called fossil fuels because they were formed by geological processes) are coal, crude oil and natural gas.

Fuel cell : A device that converts the chemical energy obtained from a redox reaction directly into electrical energy.

Fuel rods : The rods of uranium or other radioactive material used as a fuel in nuclear power stations.

Fume chamber or fume cupboard : A special laboratory chamber fitted with a protective glass shield and containing a powerful extraction fan to remove toxic fumes.

Fuming : An unstable liquid that gives off a gas. Very concentrated acid solutions are often

Functional group : A substructure that imparts characteristic chemical behaviors to a molecule, for example, a carboxylic acid group.

An atom or group of atoms in an organic compound that gives the compound some of its characteristic properties, such as the C=O functional group in aldehydes and ketones.

Organic compounds are thought of as consisting of a relatively unreactive backbone, for example a chain of sp^3 hybridized carbon atoms, and one or several functional groups. The functional group is an atom, or a group of atoms

that have similar chemical properties whenever it occurs in different compounds. It defines the characteristic physical and chemical properties of families of organic compounds.

Furanose ring : A five-membered cyclic hemiacetal or hemiketal of a carbohydrate.

Fusion : The formation of heavier nuclides by the fusing of two light nuclides.

The melting of a solid to form a liquid. See latent heat of fusion



A naturally occurring aliphatic amino acid, found in large quantities in gelatin.

Galvanic cell : An electrochemical cell that uses a spontaneous chemical reaction to do work. Also known as a voltaic cell.

Galvanic corrosion : Corrosion that occurs when two metals are in contact with each other and with water.

Galvanising : Applying a thin zinc coating to protect another metal.

Gamma ray (γ) : A high-energy, short wavelength form of electromagnetic radiation emitted by the nucleus of an atom that carries off some of the energy released in a nuclear reaction.

(γ -rays) gamma radiation. A very high energy form of electromagnetic radiation, typically with wavelengths of less than 3 pm. Gamma rays are produced by certain nuclear decay processes, and are used to sterilize food.

Waves of radiation produced as the nucleus of a radioactive element rearranges itself into a tighter cluster of protons and neutrons. Gamma rays carry enough energy to damage living cells.

Gangue : The unwanted material in an ore.

Gas : A substance that flows freely, expands to fill its container, and can be compressed to fit into a smaller container.

Gases; vapor. Matter in a form that has low density, is easily compressible and expandable, and expands spontaneously when placed in a larger container. Molecules in a gas move freely and are relatively far apart. "Vapor" often refers to a

gas made of a substance that is usually encountered as a liquid or solid; for example, gaseous H_2O is called "water vapor".

Gas syringe : A glass syringe with a graduated cylinder designed to collect and measure small amounts of gases produced during an experiment.

Gas/gaseous phase : A form of matter in which the molecules form no definite shape and are free to move about to uniformly fill any vessel they are put in. A gas can easily be compressed into a much smaller volume.

Gas-phase chromatography : Chromatography in which the components of a gas are separated as they pass over a solid support.

Gas-phase reaction : A reaction in which the reactants and products are all gases.

Gay-Lussac's law : A statement of the fact that the ratio of the volumes of gases consumed or produced in a gas-phase reaction is equal to the ratio of two simple whole numbers. Also known as the law of combining volumes.

Gel : Compare with colloid. A gell is a sol in which the solid particles fuse or entangle to produce a rigid or semirigid mixture. For example, gelatin dissolved in water produces a sol of protein molecules. When the gelatin is cooked, the protein chains entangle and crosslink, forming a gel which is a mesh of solid protein with trapped pockets of liquid inside. Fruit jellies are also gels

Gelatinous precipitate : a precipitate that has a jelly-like appearance. *Example:* iron(iii) hydroxide. Because a gelatinous precipitate is mostly water, it is of a similar density to water and will float or lie suspended in the liquid.

Geochemistry : geological chemistry. The study of materials and chemical reactions in rocks, minerals, magma, seawater, and soil.

Geometric isomer : Geometric isomers are molecules that have the same molecular formula and bond connections, but distinctly different shapes.

Geometric isomers : Geometric or also called cis-trans isomers are stereoisomers in molecules with restricted rotation about a bond. Cycloalkanes and alkenes form cis-trans isomers due to the restriction of rotation about the double bond or due to the restriction in a ring. In order for an alkene to freely rotate, the pi bond must be broken. This process has a high activation energy and does not occur at room temperature. Cis isomers have the two substituents on each of the carbons of the double bond on the same side, whereas in the trans isomer they are on opposite sides. The expression cis and trans only applies to alkenes or cycloalkanes if one of the substituents on each of the carbons are the same. If there are three or four different substituents, E,Z or R,S nomenclature must be used.

Gibbs free energy : (G) Gibbs' free energy. A thermodynamic property devised by Josiah Willard Gibbs in 1876 to predict whether a process will occur spontaneously at constant pressure and temperature. Gibbs free energy G is defined as $G = H - TS$ where H , T and S are the enthalpy, temperature, and entropy. Changes in G correspond to changes in free energy for processes occurring at constant temperature and pressure; the Gibbs free energy change corresponds to the maximum nonexpansion work that can be obtained under these conditions. The sign of ΔG is negative for all spontaneous processes and zero for processes at equilibrium.

A function of the system related to ΔS_{univ} . It is used to determine the spontaneity of a reaction. It is represented by the symbol G .

The thermodynamic function as defined by the equation: $G = H - TS$.

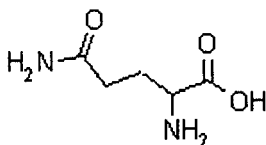
Gibbs free energy of formation : (ΔG_f°) Gibbs' free energy of formation. The change in Gibbs free energy that accompanies the formation of one mole of a compound from its elements in their most stable form.

Glass : a transparent silicate without any crystal growth. It has a glassy lustre and breaks with a curved fracture. Note that some minerals have all these features and are therefore natural glasses. Household glass is a synthetic silicate.

Glucose : the most common of the natural sugars ($C_6H_{12}O_6$). It occurs as the polymer known as cellulose, the fibre in plants. Starch is also a form of glucose.

Glutamate : Ionic salts of glutamic acid used as flavor enhancers in many foods. Glutamate is usually manufactured by acid hydrolysis of vegetable proteins. Besides being a basic building block of proteins, glutamate functions as a neurotransmitter that helps neurons grow new connections; as such, glutamate plays an important role in learning and memory. At high concentrations, glutamate can function as an excitotoxin. -aminoglutaric-20 acid">**glutamic acid**. Glu; α -aminoglutaric acid. Compare with glutamate and glutamine. A naturally occurring amino acid that has a carboxylic acid group on its side chain. In proteins, glutamic acid residues can occur with the side-chain carboxylic acid group converted to an amide; the residue is then called glutamine.

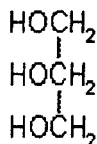
Glutamate receptors : Glutamate receptors are protein molecules that helps gate the flow of ions across a nerve cell's membrane. They play a role in the formation of new connections between nerve cells (and so, in learning and memory). The receptors are normally activated by aspartate and glutamate. In amnesic shellfish poisoning, domoic acid acts as an excitotoxin that very strongly activates some of these receptors, preventing their proper functioning.



Glutamine : Gln. The amide of the amino acid glutamic acid. Glutamic acid often occurs as glutamine when built into proteins.

Glyceride : Monoglyceride; diglyceride; triglyceride. Glycerides are fats and oils that are esters of glycerol with one or more fatty acids. Monoglycerides, diglycerides, and triglycerides contain one, two, and three fatty acids linked to the glycerol, respectively.

Glycerol : $(\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH})$ Glycerol is a small molecule with three alcohol groups. It is a basic building block of fats and oils.



Glycine : $(\text{NH}_2\text{CH}_2\text{COOH})$ Gly; aminoacetic acid.

Glycogen : A polymer of glucose that is built like amulopectin except that it is larger and even more branched. Branching occurs at every 10th to 18th glucose molecule.

Graham's law : The relationship between the rate at which a gas diffuses or effuses and its molecular weight: $\text{rate} \propto (\text{MW})^{1/2}$.

Gram : A metric unit of mass, equal to 1/1000 of a kilogram. Kilograms are the base SI units for mass, not grams.

The basic unit of mass in the metric system. A penny weighs roughly 2.5 grams.

Granular precipitate : A precipitate that has a grain-like appearance. *Example*: lead(ii) hydroxide.

Graphite : An amorphous form of carbon, made of carbon atoms bound hexagonally in sheets (like chickenwire).

Gravimetric analysis : A quantitative form of analysis in which the mass (weight) of the reactants and products is measured.

Greenhouse effect : An increase in the global air temperature as a result of heat released from burning fossil fuels being absorbed by carbon dioxide in the atmosphere.

Greenhouse gas : Any of the various gases that contribute to the Greenhouse Effect. *Example*: carbon dioxide.

Grignard reagent : An alkylmagnesium halide, such as CH_3MgBr . A source of a carbanion (such as the CH_3^- ion) for use in organic synthesis.

Gross error : Compare with systematic error, random error and mistake. Gross errors are undetected mistakes that cause a

measurement to be very much farther from the mean measurement than other measurements.

Ground state : Compare with excited state. The lowest energy state for an atom or molecule. When an atom is in its ground state, its electrons fill the lowest energy orbitals completely before they begin to occupy higher energy orbitals, and they fill subshells in accordance with Hund's rule (usually!)

Group : A substructure that imparts characteristic chemical behaviors to a molecule, for example, a carboxylic acid group. (also: functional group).

A vertical column on the periodic table, for example, the halogens. Elements that belong to the same group usually show chemical similarities, although the element at the top of the group is usually atypical.

A vertical column in the Periodic Table. There are eight groups in the table. Their numbers correspond to the number of electrons in the outer shell of the atoms in the group. *Example*: Group 2 contains beryllium, magnesium, calcium, strontium, barium and radium.

A vertical column, or family, of elements in the periodic table.

Group number : A number that identifies a group of elements in the periodic table. Until recently, groups were labeled IA, IIA, and so on. A new system has been proposed in which the columns or groups of the periodic table are numbered 1, 2, 3 ... sequentially from right to left.



Haber process : The industrial process used to make NH_3 from N_2 and H_2 .

Half life : The half life of a reaction is the time required for the amount of reactant to drop to one half its initial value.

The time it takes for the radiation coming from a sample of a radioactive element to decrease by half.

The time required for the amount of a reactant to decrease to half its initial value.

$t_{1/2}$ (SI unit: s) In a kinetic experiment, the time required for the concentration of a particular reacting *species* to fall to one-half of its initial value. (Its dependence on initial concentration depends upon the *order of reaction*. It is independent of initial concentration only for a first-order process.).

Half-cell : One half of a voltaic cell.

Half-reaction : The reaction that takes place in a half-cell.

Half reactions : The two parts of an oxidation-reduction reaction, one representing oxidation, the other reduction.

Halide : Halide ion. A compound or ion containing fluorine, chlorine, bromine, iodine, or astatine.

A F^- , Cl^- , Br^- , or I^- ion. 3. A salt of one of the halogens.

Halochromism : Halochromism means the colour change which occurs on addition of *acid* (or *base*, or a salt) to a solution of a compound. A chemical reaction (e.g. ion formation) transforms a colourless compound into a coloured one.

Halogen : Group VIIA; group 18. An element of group VIIA (a. k. a. Group 18). The name means "salt former"; halogens react with metals to form binary ionic compounds. Fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At) are known at this time.

One of a group of elements including chlorine, bromine, iodine and fluorine in Group 7 of the Periodic Table. F_2 , Cl_2 , Br_2 , or I_2 .

Hammett equation (or Hammett relation) : The equation in the form $\lg(k/k_0) = \rho \sigma$ or $\lg(K/K_0) = \rho \sigma$ applied to the influence of meta- or para-substituents X on the reactivity of the functional group Y in the benzene derivative *m*- or *p*-XC₆H₄Y. *k* or *K* is the rate or equilibrium constant, respectively, for the given reaction of *m*- or *p*-XC₆H₄Y; *k*₀ or *K*₀ refers to the reaction of C₆H₅Y, i.e. X = H; σ is the *substituent constant* characteristic of *m*- or *p*-X; ρ is the *reaction constant* characteristic of the given reaction of Y. The equation is often encountered in a form with $\lg k_0$ or $\lg K_0$ written as a separate term on the right hand side, e.g. $\lg k = \rho \sigma + \lg k_0$ or $\lg K = \rho \sigma + \lg K_0$. It then signifies the intercept corresponding to X = H in a regression of $\lg k$ or $\lg K$ on σ . See also ρ -value, σ -constant, Taft equation, Yukawa-Tsuno equation.

Hammond principle (or Hammond postulate) : The hypothesis that, when a *transition state* leading to an unstable *reaction intermediate* (or product) has nearly the same energy as that intermediate, the two are interconverted with only a small reorganization of molecular structure. Essentially the same idea is sometimes referred to as "Leffler's assumption", namely, that the transition state bears the greater resemblance to the less stable species (reactant or reaction intermediate/product). Many text books and physical organic chemists, however, express the idea in Leffler's form, but attribute it to Hammond. As a corollary, it follows that a factor stabilising a reaction *intermediate* will also stabilize the *transition state* leading to that *intermediate*. The acronym "Bemahapothle" (Bell, Marcus, Hammond, Polanyi, Thornton, Leffler) is sometimes used in recognition of the principal contributors towards expansion of the original idea of the Hammond postulate.

Hansch constant : A measure of the capability of a solute for *hydrophobic (lipophilic)* interaction based on the partition coefficient P for distribution of the solute between octan-1-ol and water. The most general way of applying P in *correlation analysis*, QSAR, etc. is as $\log P$, but the behaviour of substituted benzene derivatives may be quantified by a substituent constant scale, π , which is defined in a way analogous to the Hammett σ scale. There are various π scales, depending on the substrate series used as reference.

Hapto : The hapto symbol, η with numerical superscript, provides a topological description for the bonding of hydrocarbons and other pi-electron systems to metals, by indicating the connectivity between the ligand and the central atom. For example, η^3 indicates that three atoms of the *ligand* are bonded to the central atom.

Hard acid : A *Lewis acid* with an acceptor centre of low *polarizability*. Other things being approximately equal, complexes of hard acids and bases or *soft acids* and *bases* have an added stabilization (sometimes called "HSAB" rule). For example the hard O- (or N-) bases are preferred to their S- (or P-) analogues by hard acids. Conversely a "soft acid" possesses an acceptor centre of high polarizability and exhibits the reverse preference for coordination of a soft base. These preferences are not defined in a quantitative sense. See PEARSON (1963, 1973); HO (1977).

Hard base : A *Lewis base* with a donor centre (e.g. an oxygen atom) of low *polarizability*, the converse applies to "soft bases". See also *hard acid*.

Hard water : Water with a high concentration of the Ca^{2+} , Mg^{2+} , and/or Fe^{3+} ions.

Hartree : (E_h) Compare with atomic unit. The atomic unit of energy, equal to $4.359\,743\,81 \times 10^{-18} \text{ J} \pm 0.000\,000\,34 \times 10^{-18} \text{ J}$

Heat (q) : A form of energy associated with the random motion of the elementary particles in matter. Compare with work, energy, enthalpy, and temperature. Heat is a transfer of energy that occurs when objects with different temperatures are placed into contact. Heat is a process, not a property of a material.

Energy transferred between two objects because of a temperature difference; the thermal motion of atoms and molecules. For chemical systems the sign for heat flow into the system is positive, because this process increases the internal energy of the system. Heat flowing out of the system is defined to be negative, since this process decreases the internal energy of the system.

The energy that is transferred when a substance is at a different temperature to that of its surroundings.

Heat capacity : Compare with molar heat capacity and specific heat. The heat required to raise the temperature of an object by 1°C is called the heat capacity of the object. Heat capacity is an extensive property with units of J K⁻¹.

The amount of energy required to raise the temperature of an object by one degree Celsius (or Kelvin); it is represented by the symbol C and is given in units of J/K.

The amount of heat required to raise the temperature of a defined amount of a pure substance by one degree. See Btu, calorie, molar heat capacity, and specific heat.

The ratio of the heat supplied to a substance, compared with the rise in temperature that is produced.

Heat capacity of activation, $\Delta^\ddagger C_p^\circ$ (SI unit: J mol⁻¹ K⁻¹) A quantity related to the temperature coefficient of $\Delta^\ddagger H$ (*enthalpy of activation*) and $\Delta^\ddagger S$ (*entropy of activation*) according to the equations : $\Delta^\ddagger C_p = (\partial \Delta^\ddagger H / \partial T)_p = T(\partial \Delta^\ddagger S / \partial T)_p$ If the rate constant is expressible in the form $\ln k = a/T + b + c \ln T + dT$, then $\Delta^\ddagger C_p = (c - 1)R + 2dRT$

Heat of combustion : The amount of heat given off by a mole of a substance during combustion. This heat is a property of the substance and is the same no matter what kind of combustion is involved. *Example:* heat of combustion of carbon is 94.05 kcal (x 4.18 = 393.1 kJ).

Heat of fusion : The enthalpy change that occurs to melt a solid at its melting point.

The heat that must be absorbed to melt a mole of a solid.

Heat of hydration : the enthalpy change associated with placing gaseous molecules or ions in water.

Heat of reaction : The change in the enthalpy of the system that occurs when a reaction is run at constant pressure.

Heat of solution : The enthalpy change associated with dissolving a solute in a solvent.

Heat of vaporization : The energy required to vaporize one mole of a liquid at a pressure of one atmosphere.

The heat that must be absorbed to boil a mole of a liquid.

Heating curve : a plot of temperature verses time for a substance where energy is added at a constant rate.

Heavy water : (D_2O) Water that contains 2H , rather than 1H . Heavy water is about 11% denser than ordinary water.

Helium : He. Element 2, atomic weight 4.0026. A colorless, odorless, inert gas, first discovered in the emission spectrum of the sun in 1868.

Helmholtz free energy : (A) *Arbeitsfunktion*. A thermodynamic property that can be used to predict whether a process will occur spontaneously at constant volume and temperature. Helmholtz free energy A is defined as $A = U - TS$ where U , T and S are the internal energy, temperature, and entropy. Changes in A correspond to changes in free energy for processes occurring at constant temperature and volume. The sign of ΔA is negative for spontaneous processes and zero for processes at equilibrium.

Henderson-Hasselbach equation : An equation of the form $pH = pK_a - \lg([HA]/[A^-])$ for the calculation of the pH of solutions where the ratio $[HA]/[A^-]$ is known.

Henry's Law : Henry's law constant. Henry's law predicts that the solubility (C) of a gas or volatile substance in a liquid is proportional to the partial pressure (P) of the substance over the liquid : $P = k C$ where k is called the Henry's law constant and is characteristic of the solvent and the solute.

Hertz : (Hz, s^{-1}) frequency. The SI unit of frequency, equal to one cycle of the wave per second (s^{-1}).

Hess's law : A law stating that the heat given off or absorbed in a chemical reaction is the same regardless of whether the reaction occurs in a single step or in many steps.

In going from a particular set of reactants to a particular set of products, the enthalpy change is the same whether the reaction takes place in one step or a series of steps; in other words, enthalpy is a state function.

Law of constant heat summation; Hess's law of heat summation. The heat released or absorbed by a process is the same no matter how many steps the process takes. For example, given a reaction $A \rightarrow B$, Hess's law says that ΔH for the reaction is the same whether the reaction is written as $A \rightarrow C \rightarrow B$ or as $A \rightarrow B$. This is the same as writing that $\Delta H(A \rightarrow B) = \Delta H(A \rightarrow C) + \Delta H(C \rightarrow B)$.

Heterobimetallic complex : A metal complex having two different metal atoms.

Heteroconjugation : Association between a base and the conjugate acid of a different base through a *hydrogen bond* ($B' \cdots HB^+$ or $A'H \cdots A$). The term has its origin in the *conjugate acid-base pair* and is in no way related to *conjugation of orbitals*. Heteroassociation is a more appropriate term.

Some authors refer to *conjugated systems* containing a heteroatom, e.g. pyridine, as "heteroconjugated systems". This usage is discouraged since it inappropriately suggests an analogy to *homoconjugation*, and conflicts with the currently accepted definition of that term.

Heterocyclic : Heterocycle; heterocyclic ring. An organic group or molecule containing rings with at least one noncarbon atom on the ring.

Heterogeneous catalysis : a form of catalysis in which the catalyst is in different physical state than the reactants.

Heterogeneous mixture : Heterogeneous. Compare with homogeneous mixture, solution, element, and compound. A sample of matter consisting of more than one pure substance and more than

one phase. Blood, protoplasm, milk, chocolate, smoke, and chicken soup are examples of heterogeneous mixtures.

Heterogenous. A common misspelling of heterogeneous.

Heteroleptic : Transition metal or Main Group compounds having more than one type of *ligand*. See also *homoleptic*.

Heterolysis, heterolytic : The cleavage of a *covalent bond* so that both bonding electrons remain with one of the two fragments between which the bond is broken, e.g.



Heterolytic bond fission is a feature of many *bimolecular reactions* in solution (e.g., *electrophilic substitution*, *nucleophilic substitution*).

Heterolytic bond-dissociation energy : The energy required to break a given *bond* of some specific compound by *heterolysis*. For the *dissociation* of a neutral molecule AB in the gas phase into A^+ and B^- the heterolytic *bond-dissociation energy* $D(\text{A}^+\text{B}^-)$ is the sum of the bond dissociation energy, $D(\text{A-B})$, and the adiabatic ionization energy of the radical A^\cdot minus the electron affinity of the radical B^\cdot .

Hexadentate : Used to describe a ligand that can bind to a transition metal six times. See *chelating ligand*.

Hexagonal closest-packed : A structure formed by the stacking of closest-packed planes of atoms in an ABABAB ... repeating pattern. See *cubic closest-packed*.

High performance liquid chromatography : HPLC. An efficient form of column chromatography that pumps a liquid solution of the sample at very high pressure through a column packed with a stationary phase made of very tiny particles. The high pressure pumps required make HPLC an expensive technique.

High spin complex : High-spin complex. A metal-ligand complex with the same number of unpaired electrons as the uncomplexed metal ion. When a weak ligand complexes the metal ion, the crystal field splitting is small and the electrons can still occupy all of the d orbitals without pairing.

High-spin complex : A transition-metal complex in which the difference between the energies of the t_{2g} and e_g sets of orbitals is smaller than the energy it takes to pair two electrons. As a result, the valence-shell d electrons on the metal are placed in both the t_{2g} and e_g sets of orbitals.

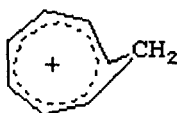
Hildebrand parameter : A parameter measuring the cohesion of a solvent (energy required to create a cavity in the solvent).

Hofmann rule : "The principal alkene formed in the decomposition of quaternary ammonium hydroxides that contain different primary alkyl groups is always ethylene, if an ethyl group is present." Originally given in this limited form by A.W. Hofmann, the rule has since been extended and modified as follows: "When two or more alkenes can be produced in a β -elimination reaction, the alkene having the smallest number of alkyl groups attached to the double bond carbon atoms will be the predominant product." This orientation described by the Hofmann rule is observed in elimination reactions of quaternary ammonium salts and tertiary sulfonium salts, and in certain other cases.

Homo : An acronym for Highest Occupied Molecular Orbital. See *frontier orbitals*.

A prefix (consisting of lower case letters, homo,) used to indicate a higher homologue of a compound.

Homoaromatic : Whereas in an *aromatic* molecule there is continuous overlap of p-orbitals over a cyclic array of atoms, in a homoaromatic molecule there is a formal discontinuity in this overlap resulting from the presence of a single sp^3 hybridized atom at one or several positions within the ring; p-orbital overlap apparently bridges these sp^3 centres, and features associated with aromaticity are manifest in the properties of the compound. Pronounced homoaromaticity is not normally associated with neutral molecules, but mainly with species bearing an electrical charge, e.g., the "homotropylium" cation, $C_8H_9^+$,



In bis, tris, (etc.) homoaromatic species, two, three, (etc.) single sp^3 centres separately interrupt the π -electron system.

Homoconjugation : Association between a base and its *conjugate acid* through a *hydrogen bond* ($B \cdots HB^+$ or $AH \cdots A^-$). Homoassociation is a more appropriate term for this phenomenon.

The orbital overlap of two π systems separated by a non-conjugating group, such as CH_2 .

Homogeneous : Compare with heterogeneous. Having uniform properties or composition.

A common misspelling of homogeneous. Homogeneous mixture. solution. Compare with heterogeneous mixture, element and compound. A sample of matter consisting of more than one pure substance with properties that do not vary within the sample.

Homogeneous catalysis : A form of catalysis in which the catalyst is in the same physical state than the reactants, for example reactants and catalyst are all gases.

Homoleptic : Transition metal or Main Group compounds having only one type of *ligand* are said to be homoleptic, e.g. $TaMe_5$. See also *heteroleptic*.

Homolog : Homologue; homologous; homologous series. A compound belonging to a series of compounds that differ by a repeating group. For example, propanol ($CH_3CH_2CH_2OH$), n-butanol ($CH_3CH_2CH_2CH_2OH$), and n-pentanol ($CH_3CH_2CH_2CH_2CH_2OH$) are homologs; they belong to a homologous series $CH_3(CH_2)_nOH$.

Homolysis, homolytic : The cleavage of a *bond* ("homolytic cleavage" or "homolytic fission") so that each of the molecular fragments between which the bond is broken retains one of the bonding electrons. A *unimolecular* reaction involving homolysis of a bond (not forming part of a cyclic structure) in a *molecular entity* containing an even number of (paired) electrons results in the formation of two radicals :



It is the reverse of *colligation*. Homolysis is also commonly a feature of bimolecular substitution reactions (and of other reactions) involving radicals and molecules.

Homonuclear diatomic molecule : A molecule, such as O_2 or F_2 , that contains two atoms of the same element.

Hormone : A molecule produced by endocrine glands that controls specific biological processes like growth and metabolism.

Host : A *molecular entity* that forms *complexes* with organic or inorganic guests, or a chemical species that can accommodate guests within cavities of its crystal structure. Examples include *cryptands* and *crowns* (where there are ion-dipole attractions between heteroatoms and positive ions), *hydrogen-bonded* molecules that form "clathrates" (e.g. hydroquinone and water), and host molecules of *inclusion compounds* (e.g. urea or thiourea). *van der Waals forces* and *hydrophobic interactions* bind the guest to the host molecule in clathrates and inclusion compounds.

Hückel ($4n + 2$) rule : Monocyclic planar (or almost planar) systems of trigonally (or sometimes digonally) hybridized atoms that contain $(4n + 2)$ π electrons (where n is a non-negative integer) will exhibit *aromatic* character. The rule is generally limited to $n = 0-5$. This rule is derived from the Hückel MO calculation on planar monocyclic conjugated hydrocarbons $(CH)_m$ where m is an integer equal to or greater than 3 according to which $(4n + 2)$ π electrons are contained in a closed-shell system. Examples of systems that obey the Hückel rule include :



Cyclopropenyl cation
($m = 3, n = 0$)



Cyclopentadienide
($m = 5, n = 1$)



Benzene
($m = 6, n = 1$)

Systems containing $4n$ π electrons (such as cyclobutadiene and the cyclopentadienyl cation) are "antiaromatic".

Humectant : A substance that absorbs or retains moisture, added to a product to keep it from drying out.

Hund's rule : Rule of maximum multiplicity. A rule of thumb stating that subshells fill so that the number of unpaired spins is maximized, or "spread them out and line them up."

Rules for adding electrons to degenerate orbitals, which assumes that electrons are added with parallel spins until each of the orbitals has one electron before a second electron is placed in one of these orbitals.

Hybrid atomic orbitals : Orbitals formed by mixing two or more atomic orbitals.

Hybridization : A process in which things are mixed. A resonance hybrid is a mixture, or average, of two or more Lewis structures. Hybrid orbitals are formed by mixing two or more atomic orbitals.

Hybrid orbitals; hybridized orbitals. The combination of a set of atomic orbitals to produce a new set of "hybrid" orbitals. Hybridized orbitals are theoretical constructions that make molecular structures easier to explain. For example, combining the valence s and p orbitals of carbon produces a set of four " sp^3 " hybrid orbitals that can be used to explain the tetrahedral bonding in CH_4 .

Linear combination of *atomic orbitals* on an atom. Hybrid orbitals are often used in organic chemistry to describe the bonding molecules containing tetrahedral (sp^3), trigonal (sp^2), and digonal (sp) atoms.

Hydrate : A solid compound in crystalline form that contains water molecules. Hydrates commonly form when a solution of a soluble salt is evaporated. The water that forms part of a hydrate crystal is known as the 'water of crystallisation'. It can usually be removed by heating, leaving an anhydrous salt.

Compare with addition compound. A hydrate is an addition compound that contains water in weak chemical combination with another compound. For example, crystals of $CuSO_4 \cdot 5 H_2O$ (copper sulfate pentahydrate) are made of regularly

repeating units, each containing 5 molecules of water weakly bound to a copper(II) ion and a sulfate ion.

Hydration : *Addition of water or of the elements of water (i.e. H and OH) to a molecular entity.* For example, hydration of ethene : $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \longrightarrow \text{CH}_3\text{CH}_2\text{OH}$ The term is also used in a more restricted sense for the process : $\text{A (gas)} \longrightarrow \text{A (aqueous solution)}$ cf. the use of the term in inorganic/physical chemistry to describe the state of the ions of an electrolyte in aqueous solution.

The process of absorption of water by a substance. In some cases hydration makes the substance change colour; in many other cases there is no colour change, simply a change in volume. *Example:* dark blue hydrated copper(II) sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) can be heated to produce white anhydrous copper(II) sulphate (CuSO_4).

Combination with water.

Hydrazine : (NH_2NH_2) A colorless, fuming, corrosive liquid that is a powerful reducing agent. NH_2NH_2 is used in jet and rocket fuels, and as an intermediate in the manufacture of agricultural, textile, photographic, and industrial chemicals.

Hydride : A compound containing just hydrogen and another element, most often a metal. *Examples:* water (H_2O), methane (CH_4) and phosphine (PH_3).

Literally, a salt containing the H^- ion, such as NaH . Also used to describe compounds such as HCl that contain hydrogen.

Hydride ion : (H^-) hydride. A -1 ion formed from hydrogen. Hydride ions and hydride ionic compounds react instantly and sometimes violently with water.

Hydrocarbon : A compound in which only hydrogen and carbon atoms are present. Most fuels are hydrocarbons, as is the simple plastic, polyethene. *Example:* methane CH_4 .

Hydrocarbon : A compound, such as CH_4 , that contains only carbon and hydrogen.

Compare with alkane, alkene, alkyne, and organic. Hydrocarbons are organic compounds that contain only hydrogen and carbon. The simplest hydrocarbons are the alkanes.

Hydrogen : (H) H; protium. Element 1, atomic weight 1.00797. The most abundant element in the universe. Hydrogen occurs as H₂ at ambient temperature and pressure, a colorless, odorless, and extremely flammable gas. Discovered in 1766 by Cavendish.

Hydrogen bond : A type of attractive force that holds one molecule to another. It is one of the weaker forms of intermolecular attractive force. *Example:* hydrogen bonds occur in water.

Hydrogen bonding. An especially strong dipole-dipole force between molecules X-H...Y, where X and Y are small electronegative atoms (usually F, N, or O) and ... denotes the hydrogen bond. Hydrogen bonds are responsible for the unique properties of water and they loosely pin biological polymers like proteins and DNA into their characteristic shapes.

The bond formed when the positive end of one polar molecule, such as water, is attracted to the negative end of another polar molecule.

The hydrogen bond is a form of *association* between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. Both electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e., N, O, or F. Hydrogen bonds may be *intermolecular* or *intramolecular*. With a few exceptions, usually involving fluorine, the associated energies are less than 20-25 kJ mol⁻¹ (5-6 kcal mol⁻¹).

Hydrolysis : A catch-all term for any reaction in which the water molecule is split.

Solvolysis by water.

Hydrometer : An instrument for measuring the specific gravity of liquids. A hydrometer is a weight with a vertical scale attached. When placed into a liquid, the hydrometer bobs upright, and sinks to a certain level. The specific gravity or solution composition can be read from the liquid level on the vertical scale. Hydrometers are often calibrated in degrees Baume.

Hydron : General name for the ion H^+ either in natural abundance, or where it is not desired to distinguish between the isotopes, as opposed to proton for $^1\text{H}^+$, deuteron for $^2\text{H}^+$ and triton for $^3\text{H}^+$.

Hydronium ion : (H_3O^+) hydronium. The H_3O^+ ion, formed by capture of a hydrogen ion by a water molecule. A strong covalent bond is formed between the hydrogen ion and water oxygen; all hydrogen ions in aqueous solution are bound inside hydronium ions.

Hydrophilic : "Water loving". The capacity of a *molecular entity* or of a *substituent* to interact with polar solvents, in particular with water, or with other polar groups.

Hydrophilicity; hydrophilic group. A polar molecule or group that can form strong hydrogen bonds with water.

Literally, water-loving. Describes polar groups that attract water molecules.

Hydrophobic : Hydrophobicity; hydrophobic group. A nonpolar molecule or group that has little affinity for water. Hydrophobic groups on molecules in solution tend to turn in on themselves or clump together with other hydrophobic groups because they are unable to disrupt the network of strong hydrogen bonds in the water around them.

Literally, water-hating. Describes nonpolar groups that repel water molecules.

Hydrophobic interaction : The tendency of hydrocarbons (or of *lipophilic* hydrocarbon-like groups in solutes) to form *intermolecular aggregates* in an aqueous *medium*, and analogous intramolecular interactions. The name arises from the attribution of the phenomenon to the apparent repulsion between water and hydrocarbons. However, the phenomenon ought to be attributed to

the effect of the hydrocarbon-like groups on the water-water interaction. The misleading alternative term "hydrophobic *bond*" is discouraged.

Hydrous : Hydrated with water.

Hydroxide : (OH⁻) hydroxide ion. Compare with hydroxyl. The OH⁻ ion.

Compounds containing the OH⁻ ion. See also: hydroxide compounds.

Hydroxide : A compound that contains an -OH group.

Hydroxyl : Compare with hydroxide. An -OH group within a molecule.

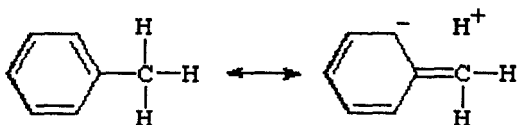
A free radical formed by abstraction of a hydrogen atom from water.

Hygroscopic : Able to absorb moisture from air. For example, sodium hydroxide pellets are so hygroscopic that they dissolve in the water they absorb from the air.

Hygroscopically : By absorbing moisture from air.

Hygroscopicity : The ability of a substance to absorb moisture from air. For example, sodium hydroxide pellets are so hygroscopic that they dissolve in the water they absorb from the air.

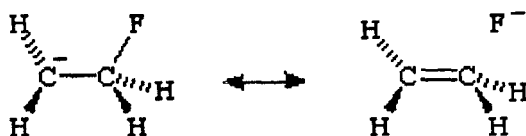
Hyperconjugation : In the formalism that separates bonds into σ and π types, hyperconjugation is the interaction of σ -bonds (e.g. C-H, C-C, etc.) with a π network. This interaction is customarily illustrated by *contributing structures*, e.g. for toluene (below), sometimes said to be an example of "heterovalent" or "sacrificial hyperconjugation", so named because the contributing structure contains one two-electron bond less than the normal *Lewis formula* for toluene



At present, there is no evidence for sacrificial hyperconjugation in neutral hydrocarbons. The concept of hyperconjugation is also applied to *carbenium ions* and *radicals*, where the interaction is now between σ -bonds and an unfilled or partially filled π or p-orbital. A contributing structure illustrating this for the *tert*-butyl cation is :



This latter example is sometimes called an example of "isovalent hyperconjugation" (the contributing structure containing the same number of two-electron bonds as the normal Lewis formula). Both structures shown on the right hand side are also examples of "double bond- no-bond resonance". The interaction between filled π or p orbitals and adjacent antibonding σ^* orbitals is referred to as "negative hyperconjugation", as for example in the fluoroethyl anion :



Hypergolic mixture : Hypergolic fuel; hypergolic. An oxidizing agent and a fuel that react or ignite instantly and spontaneously on contact. Methylhydrazine and dinitrogen tetroxide is a hypergolic mixture used as a propellant in the space shuttle's orbital maneuvering engines.

Hypertonic : Compare with osmotic pressure. Describes a solution which has higher osmotic pressure than some other solution (usually, higher osmotic pressure than cell or body fluids).

Freshwater fish die if placed in seawater because the seawater is hypertonic, and causes water to leave the cells in fish's body.

Hypothesis : Hypotheses. A hypothesis is a conjecture designed to guide experimentation. Hypotheses are extremely useful in problem solving, and are essential in developing new theories.

Hypotonic : Compare with osmotic pressure. Describes a solution which has lower osmotic pressure than some other solution (usually, lower osmotic pressure than cell or body fluids). Washing your contact lenses with distilled water rather than saline is painful because distilled water is hypotonic; it causes water to move into cells, and they swell and burst.

Hypsochromic shift : Shift of a spectral band to higher frequency or shorter wavelength upon substitution or change in medium. It is informally referred to as blue shift.

I

Ideal gas : A gas that obeys all the postulates of the kinetic molecular theory. Real gases differ from the expected behavior of an ideal gas for two reasons: (1) the force of attraction between the particles in a gas is not quite zero, and (2) the volume of the particles in a gas is not quite zero.

Ideal gases; perfect gas; ideal gas law. A gas whose pressure P , volume V , and temperature T are related by $PV = nRT$, where n is the number of moles of gas and R is the ideal gas law constant. Ideal gases have molecules with negligible size, and the average molar kinetic energy of an ideal gas depends only on its temperature. Most gases behave ideally at sufficiently low pressures.

Ideal gas equation : The relationship between the pressure, volume, temperature, and amount of an ideal gas: $PV = nRT$. See equation of state.

Ideal gas law constant : (R) ideal gas constant; universal gas constant. A constant R equal to $PV/(nT)$ for ideal gases, where the pressure, volume, moles, and temperature of the gas are P , V , n , and T , respectively. The value and units of R depend on the units of P , V , and T . Commonly used values and units of R include: $82.055 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$; $0.082055 \text{ L atm mol}^{-1} \text{ K}^{-1}$; $8.31434 \text{ J mol}^{-1} \text{ K}^{-1}$; $1.9872 \text{ cal K}^{-1} \text{ mol}^{-1}$; $8314.34 \text{ L Pa mol}^{-1} \text{ K}^{-1}$; $8.31434 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$.

Ideal solution : All molecules in an "ideal solution" interact in exactly the same way; the solvent-solvent, solvent-solute, and solute-solute intermolecular forces are all equivalent. Ideal solutions obey

Raoult's law exactly. Real solutions behave ideally only when they are very dilute.

Identity reaction : A *chemical reaction* whose products are chemically identical with the reactants, for example the bimolecular self exchange reaction of CH_3I with I^- . See also *degenerate rearrangement*.

Ignition temperature : The temperature at which a substance begins to burn.

Imbalance : The situation in which *reaction* parameters that characterize different bond forming or bond breaking processes in the same reaction have developed to different extents as the *transition state* is approached along some arbitrarily defined reaction coordinate. For example, in the nitroalkane anomaly, the Brønsted β exponent for proton removal is smaller than the Brønsted α for the nitroalkane, because of imbalance between the amount of bond breaking and resonance delocalization in the transition state. Imbalance is common in reactions such as elimination, addition and other complex reactions that involve proton (hydron) transfer.

Immiscible : Immiscibility. Compare with miscible and partial miscibility. Two liquids are considered "immiscible" or unmixable if shaking equal volumes of the liquids together results in a meniscus visible between two layers of liquid. If the liquids are completely immiscible, the volumes of the liquid layers are the same as the volumes of liquids originally added to the mixture.

Liquids, such as gasoline and water, that are not soluble in each other.

Will not mix with another substance. e.g. oil and water.

Incandescent : Glowing or shining with heat. *Example*: tungsten filament in an incandescent light bulb.

Inclusion compound (or inclusion complex) : A *complex* in which one component (the *host*) forms a cavity or, in the case of a crystal, a crystal lattice containing spaces in the shape of long tunnels or channels in which molecular entities of a second *chemical species* (the *guest*) are located. There is no covalent bonding between guest and host, the attraction being generally due to *van der Waals*

forces. If the spaces in the host lattice are enclosed on all sides so that the guest species is "trapped" as in a *cage*, such compounds are known as "clathrates" or "cage" compounds".

Incomplete combustion : A combustion reaction or process that does not convert all of the fuel's carbon and hydrogen into carbon dioxide and water, respectively. For example, incomplete combustion of carbon produces carbon monoxide.

Combustion in which only some of the reactant or reactants combust, or the products are not those that would be obtained if all the reactions went to completion. It is uncommon for combustion to be complete and incomplete combustion is more frequent. *Example*: incomplete combustion of carbon in oxygen produces carbon monoxide and not carbon dioxide.

Incomplete octet : An atom with less than eight electrons in its valence shell.

An atom with less than eight total bonding and nonbonding electrons in a Lewis structure, for example, B in BH_3 has an incomplete octet.

Independent variable : An independent variable that can be set to a known value in an experiment. Several independent variables may be controlled in an experiment. For example, in an experiment where the vapor pressure of a liquid is measured at several different temperatures, temperature is the independent variable and vapor pressure is the dependent variable.

Indicator (acid-base indicator) : A substance or mixture of substances used to test the acidity or alkalinity of a substance. An indicator changes colour depending on the acidity of the solution being tested. Many indicators are complicated organic substances. Some indicators used in the laboratory include Universal Indicator, litmus, phenolphthalein, methyl orange and bromothymol.

A compound, such as phenolphthalein, that changes color at the endpoint of a titration.

A substance that undergoes an sharp, easily observable change when conditions in its solutions change.

Indicator diagram : PV diagram. A plot of pressure vs. volume. Lines or curves on the indicator diagram represent processes. The areas under curves on the indicator diagram are equal to the work released by the process.

Induced dipole : A short-lived separation of charge, or dipole, created by polarization of a nonpolar atom or molecule.

Induced fission : Fission of a nuclide that occurs after the nuclide has absorbed another particle. See spontaneous fission.

Induction period : The initial slow phase of a *chemical reaction* which later accelerates. Induction periods are often observed with radical reactions, but they may also occur in other systems (for example before steady-state concentration of the reactants is reached).

The time taken for a reaction to reach ignition temperature. During this period, no apparent reaction occurs, then the materials appear to undergo spontaneous combustion.

Inductive effect : In strict definition, an experimentally observable effect (on rates of reaction, etc.) of the transmission of charge through a chain of atoms by electrostatic induction. A theoretical distinction may be made between the *field effect*, and the inductive effect as models for the Coulomb interaction between a given site within a *molecular entity* and a remote unipole or dipole within the same entity. The experimental distinction between the two effects has proved difficult, except for molecules of peculiar geometry, which may exhibit "reversed field effects". Ordinarily the inductive effect and the field effect are influenced in the same direction by structural changes in the molecule and the distinction between them is not clear. This situation has led many authors to include the field effect in the term "inductive effect". Thus the separation of σ values into inductive and *resonance* components does not imply the exclusive operation of a through-bonds route for the transmission of the non-conjugative part of the substituent effect. To indicate the all-inclusive use of the term inductive, the phrase "so-called inductive effect" is sometimes used. Certain modern theoretical approaches suggest that the "so-called inductive effect" reflects a field effect rather than through-bonds transmission.

Inductance effect. An inductive effect is the polarization of a chemical bond caused by the polarization of an adjacent bond. (Field effects are polarization caused by nonadjacent bonds).

Inductomeric effect : A molecular polarizability effect occurring by the inductive mechanism of electron displacement. The consideration of such an effect and the descriptive term have been regarded as obsolescent or even obsolete, but in recent years theoretical approaches have reintroduced substituent polarizability as a factor governing reactivity, etc. and its parametrization has been proposed.

Inelastic collision : A collision in which at least a portion of the kinetic energy of the colliding particles is lost.

Inert : *Stable* and *unreactive* under specified conditions.

Inert : Unreactive. Used to describe compounds that do not undergo chemical reactions.

Inert gas : Inert gases; noble gas; noble gases. Any of the elements of Group 18, which includes helium, neon, argon, krypton, xenon, radon, and element 118. These elements are referred to as "inert" or "noble" because they do not easily form compounds with other elements.

Inert pair : Inert pair effect. Valence electrons in an *s* orbital penetrate to the nucleus better than electrons in *p* orbitals, and as a result they're more tightly bound to the nucleus and less able to participate in bond formation. A pair of such electrons is called an "inert pair". The inert pair effect explains why common ions of Pb are Pb^{4+} and Pb^{2+} , and not just Pb^{4+} as we might expect from the octet rule.

Inertia : The tendency of a body to stay at rest or to continue to move at the same velocity, unless acted on by an outside force. A tractor trailer has more inertia than a bicycle. A bowling ball has more inertia than a tennis ball.

Infrared radiation : (IR) Infrared. Electromagnetic radiation with wavelength longer than visible light but shorter than that of

microwaves. Infrared radiation is produced by hot objects; absorption of infrared radiation causes chemical bonds to vibrate.

Infrared spectroscopy : IR spectroscopy. A technique for determining the structure (and sometimes concentration) of molecules by observing how infrared radiation is absorbed by a sample.

Inhibition : The decrease in *rate of reaction* brought about by the addition of a substance (inhibitor), by virtue of its effect on the concentration of a reactant, *catalyst* or reaction *intermediate*. For example, molecular oxygen and *p*-benzoquinone can react as "inhibitors" in many reactions involving *radicals* as intermediates by virtue of their ability to act as *scavengers* toward these radicals. If the rate of a reaction in the absence of inhibitor is v_0 and that in the presence of a certain amount of inhibitor is v , the degree of inhibition (*i*) is given by $i = (v_0 - v)/v_0$.

Inhibitor : A substance that prevents a reaction from occurring.

Initial concentration : The concentration of a reactant before it reacts with either the solvent or another reactant.

Initial rate of reaction : The rate of a chemical reaction extrapolated back to the instant the reactants were mixed.

Initiation : A reaction or process generating free *radicals* (or some other *reactive* reaction intermediates) which then induce a *chain reaction*. For example, in the chlorination of alkanes by a radical mechanism the initiation step is the *dissociation* of molecular chlorine.

Inner transition metal : Used to describe the elements in the two rows at the bottom of the periodic table.

Inner-sphere (electron transfer) : Historically an electron transfer between two metal centres sharing a ligand or atom in their respective coordination shells. The definition has more recently been extended to any situation in which the interaction between the donor and acceptor centres in the *transition state* is significant ($>20 \text{ kJ mol}^{-1}$).

Inorganic : Used to describe compounds that do not contain C-H bonds.

Inorganic chemistry : The study of inorganic compounds, specifically their structure, reactions, catalysis, and mechanism of action.

Inorganic compound : Inorganic. Compare with organic. A compound that does not contain carbon chemically bound to hydrogen. Carbonates, bicarbonates, carbides, and carbon oxides are considered inorganic compounds, even though they contain carbon.

Inorganic substance : A substance that does not contain carbon and hydrogen. *Examples*: NaCl, CaCO₃.

Insertion : A *chemical reaction* or *transformation* of the general type $X-Z + Y \longrightarrow X-Y-Z$ in which the connecting atom or *group* Y replaces the bond joining the parts X and Z of the reactant XZ. An example is the *carbene* insertion reaction $R_3C-H + H_2C: \longrightarrow R_3C-CH_3$. The reverse of an insertion is called an *extrusion*.

Insoluble : A substance that will not dissolve.

Insolubility. Compare with soluble. Refers to a substance that does not dissolve in a solvent to any significant degree. Compounds with solubilities of less than 1 g per liter of water are often referred to as 'insoluble', even though they *do* dissolve to a small extent.

Use to describe a substance that does not dissolve in a solvent to give a reasonable concentration.

Instantaneous rate of reaction : The rate of a chemical reaction at an instant in time. The infinitesimally small change in the concentration of one of the reactants (or products) that occurs over an infinitesimally small length of time: $d(X)/dt$.

Integral enthalpy of solution : (ΔH_{soln}) integral heat of solution; integrated heat of solution; integrated enthalpy of solution. Compare with enthalpy of solution. The heat absorbed or released when a solute is dissolved in a definite amount of solvent. The heat of solution depends on the nature of the solute and on its concentration in the final solution. The integral heat of solution when one mole of solute is added to an infinite amount of solvent is sometimes written as $\Delta H_{\infty, \text{soln}}$.

Integrated form of the rate law : An alternative form of the rate law for a chemical reaction that can be used to predict the concentrations of the reactants (or products) at some moment in time.

Integrated rate law : Rate laws like $d[A]/dt = -k[A]$ give instantaneous concentration changes. To find the change in concentration over time, the instantaneous changes must be added (integrated) over the desired time interval. The rate law $d[A]/dt = -k[A]$ can be integrated from time zero to time t to obtain the integrated rate law $\ln([A]/[A]_0) = -kt$, where $[A]_0$ is the initial concentration of A.

Intensive property : A quantity, such as temperature, density, or pressure, which does not depend on the size of the sample.

Intensive; intensive properties. Compare with extensive property. A property that does not change when the amount of sample changes. Examples are density, pressure, temperature, color.

Intensive properties : Properties which are independent of the amount of the substance.

Interference : Interfering. Compare with constructive interference and destructive interference. The amplitudes of waves moving into the same region of space add to produce a single resultant wave. The resultant wave can have higher or lower amplitude than the component waves. See constructive interference and destructive interference.

Intermediate : A *molecular entity* with a *lifetime* appreciably longer than a molecular vibration (corresponding to a local potential energy minimum of depth greater than RT) that is formed (directly or indirectly) from the reactants and reacts further to give (either directly or indirectly) the products of a chemical reaction; also the corresponding *chemical species*.

Reactive intermediate; reaction intermediate. A highly reactive substance that forms and then reacts further during the conversion of reactants to products in a chemical reaction. Intermediates never appear as products in the chemical equation for a net chemical reaction.

Intermediate Species : Species formed in a reaction consisting of more than one step. An intermediate is produced in one reaction and consumed in the following reaction.

Intermetallic compound : A compound, such as CuAl_2 , with a fixed composition that results from the combination of two or more metals.

Intermolecular : Descriptive of any process that involves a transfer (of atoms, *groups*, electrons, etc.) or interactions between two or more *molecular entities*.

Relating to a comparison between different molecular entities.

Intermolecular bonds : The weak bonds between molecules in a liquid or solid, such as the hydrogen bonds between water molecules.

Intermolecular force : An attraction or repulsion between molecules. Intermolecular forces are much weaker than chemical bonds. Hydrogen bonds, dipole-dipole interactions, and London forces are examples of intermolecular forces.

Internal energy (E) : The sum of the kinetic and potential energies of the particles in a system. The internal energy of the system is proportional to its temperature.

(U, E) Compare with enthalpy and energy. Internal energy (U) is defined so that changes in internal energy (ΔU) are equal to the heat absorbed or released by a process running at constant volume. While changes in internal energy can be measured using calorimetry, absolute values of internal energy usually cannot be determined. Changes in internal energy are equal to the heat transferred plus the work done for any process.

A property of a system that can be changed by a flow of work, heat or both; it is represented by the symbol E (ΔE represents the change in internal energy of a system) and is given in units of energy (Joules).

Interstitial solution : A solid solution formed when solute atoms are packed in the holes, or interstices, between solvent atoms.

Intramolecular : Descriptive of any process that involves a transfer (of atoms, *groups*, electrons, etc.) or interactions between different parts of the same *molecular entity*.

Relating to a comparison between atoms or groups within the same molecular entity.

Intramolecular bonds : The bonds that hold a molecule together, such as the covalent O-H bonds in water.

Intramolecular catalysis : The acceleration of a chemical transformation at one site of a *molecular entity* through the involvement of another *functional* ("catalytic") *group* in the same molecular entity, without that group appearing to have undergone change in the reaction product. The use of the term should be restricted to cases for which analogous *intermolecular catalysis* by *chemical species* bearing that catalytic group is observable. Intramolecular catalysis can be detected and expressed in quantitative form by a comparison of the reaction rate with that of a comparable model compound in which the catalytic group is absent, or by measurement of the *effective molarity* of the catalytic group.

Intrinsic barrier : The *Gibbs energy of activation* ($\Delta^\ddagger G$) in the limiting case where $\Delta G^\circ = 0$, i.e. when the effect of thermodynamic driving force is eliminated. According to the *Marcus equation*, the intrinsic barrier is related to the *reorganization energy*, λ , of the reaction by the equation $\Delta^\ddagger G = \lambda/4$

Inverted micelle : The reversible formation of association colloids from surfactants in non-polar solvents leads to aggregates termed inverted (or inverse, reverse or reversed) *micelles*. Such association is often of the type Monomer \rightleftharpoons Dimer \rightleftharpoons Trimer \rightleftharpoons ... *n*-mer and the phenomenon of *critical micelle concentration* (or an analogous effect) is consequently not observed. In an inverted micelle the polar *groups* of the surfactants are concentrated in the interior and the *lipophilic* groups extend towards and into the non-polar solvent.

Iodide : Any compound that contains either the I⁻ ion or iodine with an oxidation state of -1, such as KI.

Ion : An atom or molecule that carries an electrical charge, such as the Na⁺ or Cl⁻ ions.

An atom or molecule that has acquired a charge by either gaining or losing electrons. An atom or molecule with missing electrons has a net positive charge and is called a cation; one with extra electrons has a net negative charge and is called an anion.

An atom, or group of atoms, that has gained or lost one or more electrons and so developed an electrical charge. Ions behave differently from electrically neutral atoms and molecules. They can move in an electric field, and they can also bind strongly to solvent molecules such as water. Positively charged ions are called cations; negatively charged ions are called anions. Ions can carry an electrical current through solutions.

Ion exchange : Ion exchange resin; ion exchanger. Ion exchange is a method of separating ions from a solution by reversibly binding them onto a resin that has charged sites on its surface. Ion exchangers are used to remove metal ions from drinking water.

Ion pair : A pair of oppositely charged ions held together by Coulomb attraction without formation of a *covalent bond*. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behaviour, osmotic properties, etc. Following Bjerrum, oppositely charged ions with their centres closer together than a distance $q = 8.36 \times 10^6 \frac{Z^+ Z^-}{(\epsilon_r T)} \text{ pm}$ are considered to constitute an ion pair ("Bjerrum ion pair"). [Z^+ and Z^- are the charge numbers of the ions, and ϵ_r is the relative permittivity (or dielectric constant) of the medium.] An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule) is designated as a "tight ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of X^+ and Y^- is symbolically represented as X^+Y^- . By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a "loose ion pair", symbolically represented as $X^+||Y^-$. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g., by isotopic labelling) and thus afford an experimental distinction between tight and loose ion pairs. A further conceptual distinction has sometimes been made

between two types of loose ion pairs. In "solvent-shared ion pairs" the ionic constituents of the pair are separated by only a single solvent molecule, whereas in "solvent-separated ion pairs" more than one solvent molecule intervenes. However, the term "solvent-separated ion pair" must be used and interpreted with care since it has also widely been used as a less specific term for "loose" ion pair.

Ion pair return : The recombination of a pair of ions R^+ and Z^- formed from ionization of RZ . If the ions are paired as a tight *ion pair* and recombine without prior separation into a loose ion pair this is called "internal ion-pair return": R^+Z^- (tight ion pair) $\rightleftharpoons RZ$ (covalent molecule) It is a special case of "primary *geminate recombination*". If the ions are paired as a loose ion pair and form the covalent chemical species via a tight ion pair, this is called "external ion-pair return": $R^+||Z^-$ (loose ion pair) $\rightleftharpoons R^+Z^-$ (tight ion pair) $\rightleftharpoons RZ$ (covalent molecule) It is a special case of "secondary *geminate recombination*". When the covalent molecule RZ is reformed without direct evidence of prior partial racemization or without other direct evidence of prior formation of a tight ion pair, (e.g., without partial racemization if the group R is suitably chiral) the internal ion-pair return is sometimes called a "hidden return". External (unimolecular) ion-pair return is to be distinguished from "external (bimolecular) ion return", the (reversible) process whereby dissociated ions are converted into loose ion pairs: $R^+ + Z^- \rightleftharpoons R^+||Z^-$

Ion product (Q_{sp}) : The product of the concentrations of the ions in a solution at any moment in time.

Ionic bond : The bond between two ions that results from the force of attraction between particles of opposite charge.

The form of bonding that occurs between two ions when the ions have opposite charges. *Example:* sodium cations bond with chloride anions to form common salt ($NaCl$) when a salty solution is evaporated. Ionic bonds are strong bonds except in the presence of a solvent.

Ionic compound : A compound that consists of ions. *Example:* $NaCl$.

Ionic dissociation : When ionic substances dissolve, their ions are surrounded by solvent molecules and separated from each other. This phenomena is also called *ionization*.

Ionic equation. An ionic equation is a balanced chemical equation in which strong electrolytes are written as dissociated ions. For example, $\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{AgCl}(\text{s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ is an ionic equation; $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) = \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$ is not.

The radii of anions and cations in crystalline ionic compounds, as determined by consistently partitioning the center-to-center distance of ions in those compounds.

Ionic solid : A solid composed of ions, such as NaCl. Also called a salt.

Ionic strength, I (SI unit: mol dm^{-3}) : In a solution of fully dissociated electrolytes the ionic strength is defined as $I = 0.5 \sum_i c_i Z_i^2$, in which c_i is the concentration and Z_i the charge number of ionic species i . It is also defined as $I_m = 0.5 \sum_i m_i Z_i^2$, where m_i is the molality.

Ionization : A process in which an ion is created from a neutral atom or molecule by adding or subtracting one or more electrons.

The generation of one or more ions. It may occur, e.g. by loss of an electron from a neutral *molecular entity*, by the *unimolecular heterolysis* of such an entity into two or more ions, or by a heterolytic *substitution reaction* involving neutral molecules, such as $\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{CH}_3\text{CO}_2^-$ $\text{Ph}_3\text{CCl} + \text{AlCl}_3 \longrightarrow \text{Ph}_3\text{C}^+ + \text{AlCl}_4^-$ (electrophile-assisted) $\text{Ph}_3\text{CCl} \longrightarrow \text{Ph}_3\text{C}^+ \text{Cl}^-$ (ion pair, in benzene) The loss of an electron from a singly, doubly, etc. charged cation is called second, third, etc. ionization. This terminology is used especially in mass spectroscopy.

Ionization energy : (IE, IP) ionization potential. Compare with adiabatic ionization energy, vertical ionization energy, electronegativity, and electron affinity. The energy needed to remove an electron from a gaseous atom or ion.

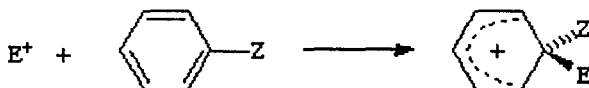
E_i (SI unit kJ mol^{-1} or J per molecule) : The minimum energy required to remove an electron from an isolated *molecular entity* (in its vibrational ground state) in the gaseous phase. If the resulting molecular entity is considered to be in its vibrational ground state, one refers to the energy as the "adiabatic ionization energy". If the molecular entity produced possesses the vibrational energy determined by the Franck-Condon principle (according to which the electron ejection takes place without an accompanying change in molecular geometry), the energy is called the "vertical ionization energy". The name ionization energy is preferred to the somewhat misleading earlier name "ionization potential".

Ionize : A process in which ions are created. HCl, for example, is a covalent compound that ionizes when it dissolves in water.

Ionizing power : A term to denote the tendency of a particular solvent to promote *ionization* of an uncharged or, less often, charged solute. The term has been used both in a kinetic and in a thermodynamic context.

Ionizing radiation : Radiation with enough energy to remove an electron from a neutral atom or molecule to produce free radicals.

Ipso-attack : The attachment of an entering group to a position in an aromatic compound already carrying a *substituent* group (other than hydrogen). The entering group may displace that substituent group but may also itself be expelled or migrate to a different position in a subsequent step. The term "ipso-substitution" is not used, since it is synonymous with substitution. For example :where E^+ is an *electrophile* and Z is a substituent (other than hydrogen).



Irreversible process : Any real process; when a system undergoes the changes State 1 \rightarrow State 2 \rightarrow State 1 by any real pathway, the universe is different that before the cyclic process took place in the system.

isobar. Compare with isotope. A contour line that corresponds to values measured at identical pressures. For example, curves on a plot of gas volumes measured at different temperatures in an open container are isobars.

Nuclides that have the same isotopic mass but different atomic number.

Isobaric : Having constant pressure.

Nuclides with the same mass number, such as ^{40}K and ^{40}Ca .

Isochore : A contour line that corresponds to values measured at identical volumes. For example, a curve on a plot of gas pressure measured at different temperatures in a rigid container is an isochore.

Isochoric : Having constant volume.

A reaction (actual or hypothetical) in which the types of bonds that are made in forming the products are the same as those which are broken in the reactants, e.g. $\text{PhCOOH} + p\text{-ClC}_6\text{H}_4\text{COO}^- \longrightarrow \text{PhCOO}^- + p\text{-ClC}_6\text{H}_4\text{COOH}$ $\text{ClCH=CH}_2 + \text{ClCH}_2\text{CH}_2\text{Cl} \longrightarrow \text{CH}_2=\text{CH}_2 + \text{Cl}_2\text{CHCH}_2\text{Cl}$ Such processes have advantages for theoretical treatment. The *Hammett equation* as applied to equilibria (cf. (a)) essentially deals with isodesmic processes. For the use of isodesmic processes in quantum chemistry,

Isoelectronic : Atoms or ions that have the same number of electrons and therefore the same electron configuration, such as C^{4+} , N^{3+} , O^{2+} , F^+ , and Ne .

Isoelectronic : 1. Refers to a group of atoms or ions having the same number of electrons. For example, F^- , Ne , and Na^+ are isoelectronic. $\text{CH}_2=\text{C}=\text{O}$ and $\text{CH}_2=\text{N}=\text{N}$ are isoelectronic. CH_3COCH_3 and $\text{CH}_3\text{N}=\text{NCH}_3$ have the same number of electrons, but have different structures, hence they are not described as isoelectronic. 2. Two or more *molecular entities* are described as isoelectronic if they have the same number of valence electrons and the same structure, i.e. number and *connectivity* of atoms, but differ in some of the elements involved. Thus CO , N_2 and NO^+ are isoelectronic

Isoentropic : A reaction series is said to be isoentropic if the individual reactions of the series have the same standard *entropy of activation*.

Isoequilibrium relationship : A relationship analogous to the *isokinetic relationship* but applied to equilibrium data. The equation defining the isoequilibrium temperature β is $\Delta_r H - \beta \Delta_r S = \text{constant}$ where ΔH and ΔS are enthalpy and entropy of reaction, respectively.

Isokinetic relationship : When a series of structurally related substrates undergo the same general reaction or when the reaction conditions for a single substrate are changed in a systematic way, the *enthalpies* and *entropies of activation* sometimes satisfy the relation $\Delta^\ddagger H - \beta \Delta^\ddagger S = \text{constant}$ where the parameter β is independent of temperature. This equation (or some equivalent form) is said to represent an "isokinetic relationship". The temperature $T = \beta$ (at which all members of a series obeying the isokinetic relationship react at the same rate) is termed the "isokinetic temperature". Supposed isokinetic relationships as established by direct correlation of $\Delta^\ddagger H$ with $\Delta^\ddagger S$ are often spurious and the calculated value of β is meaningless, because errors in $\Delta^\ddagger H$ lead to compensating errors in $\Delta^\ddagger S$. Satisfactory methods of establishing such relationships have been devised.

Isolated system : A system which can exchange neither mass nor energy with its surroundings.

Isoleucine : $[(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}]$ A naturally occurring amino acid with a nonpolar side chain.

Isolobal : The term is used to compare molecular fragments with each other and with familiar species from organic chemistry. Two fragments are isolobal if the number, symmetry properties, approximate energy, and shape of the *frontier orbitals* and the number of electrons in them are similar.

Isomer : One of several species (or *molecular entities*) that have the same atomic composition (molecular formula) but different line formulae or different stereochemical formulae and hence different physical and/or chemical properties.

Isomer : Structural isomer. Molecules with identical molecular formulas but different structural formulas.

Isomers : Compounds with the same chemical formulas, but different structures, and therefore different chemical or physical properties.

Isomerization : A chemical change that involves a rearrangement of atoms and bonds within a molecule, without changing the molecular formula.

A *chemical reaction*, the principal product of which is isomeric with the principal reactant. An *intramolecular* isomerization that involves the breaking or making of bonds is a special case of a *molecular rearrangement*. Isomerization does not necessarily imply *molecular rearrangement* (e.g. in the case of the interconversion of conformational isomers).

Isosbestic point : This term is usually employed with reference to a set of absorption spectra, plotted on the same chart for a set of solutions in which the sum of the concentrations of two principal absorbing components, A and B, is constant. The curves of absorbance against wavelength (or frequency) for such a set of mixtures often all intersect at one or more points, called isosbestic points. Isosbestic points are commonly met when electronic spectra are taken (a) on a solution in which a *chemical reaction* is in progress (in which case the two absorbing components concerned are a reactant and a product, A + B), or (b) on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions, e.g., an acid-base indicator equilibrium. $A \rightleftharpoons B + H^+_{aq}$ The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration. In all these examples, A (and/or B) may be either a single *chemical species* or a mixture of chemical species present in invariant proportion. If A and B are single chemical species, isosbestic points will appear at all wavelengths at which their molar absorption coefficients (formerly called extinction coefficients) are the same. (A more involved identity applies when A and B are mixtures of

constant proportion.) If absorption spectra of the types considered above intersect not at one or more isosbestic points but over progressively changing wavelength, this is *prima facie* evidence in case (a) for the formation of a *reaction intermediate* in substantial concentration ($A \longrightarrow C \longrightarrow B$), in case (b) for the involvement of a third absorbing species in the equilibrium, e.g. $A \rightleftharpoons B + H^+_{aq}$, $\rightleftharpoons C + 2 H^+_{aq}$ or in case (c) for some interaction of A and B, e.g., $A + B \rightleftharpoons C$

Isoselective relationship : A relationship analogous to the *isokinetic relationship*, but applied to *selectivity* data of reactions. At the isoselective temperature, the selectivities of the series of reactions following the relationship are identical.

Isosteric : Having identical valence electron configurations.

Isotactic : Used to describe polymers in which all the substituents are oriented on the same side of the polymer backbone.

Isothermal : Constant temperature.

A contour line that corresponds to values measured at identical temperatures. For example, curves on a plot of gas pressure measured at different volumes in a constant temperature bath are isotherms.

Having constant temperature.

Isotone : One of a group of atoms or ions with nuclei that contain the same number of neutrons but different numbers of protons.

Isotones : Nuclides with the same number of neutrons, such as ^{13}C , ^{14}N , and ^{15}O .

Isotonic : Refers to solutions that have equal osmotic pressure.

Atoms or ions of an element with different numbers of neutrons in their atomic nucleus. Isotopes have the same atomic number but different mass number. Isotopes have very similar chemical properties but sometimes differ greatly in nuclear stability.

One of two or more atoms of the same element that have the same number of protons in their nucleus (atomic number),

but which have a different number of neutrons (atomic mass). *Example*: carbon-12 and carbon-14.

Isotope effect : The effect on the rate or equilibrium constant of two reactions that differ only in the isotopic composition of one or more of their otherwise chemically identical components is referred to as a kinetic isotope effect or a thermodynamic (or equilibrium) isotope effect respectively.

Isotope effect, heavy atom : An *isotope effect* due to isotopes other than those of hydrogen.

Isotope effect, intramolecular : A kinetic *isotope effect* observed when a single substrate, in which the isotopic atoms occupy equivalent reactive positions, reacts to produce a non-statistical distribution of *isotopologue* products. In such a case the isotope effect will favor the pathway with lower force constants for displacement of the isotopic nuclei in the *transition state*.

Isotope effect, inverse : A kinetic *isotope effect* which $k^l/k^h < 1$, i.e. the heavier substrate reacts more rapidly than the lighter one, as opposed to the more usual "normal" isotope effect, in which $k^l/k^h > 1$. The isotope effect will normally be "normal" when the frequency differences between the isotopic *transition states* are smaller than in the reactants. Conversely, in inverse isotope effect can be taken as evidence for an increase in the corresponding force constants on passing from the reactant to the transition state.

Isotope effect, kinetic : The effect of isotopic substitution on a rate constant is referred to as a kinetic isotope effect. For example in the reaction $A + B \longrightarrow C$ the effect of isotopic substitution in reactant A is expressed as the ratio of rate constants k^l/k^h , where the superscripts l and h represent reactions in which the molecules A contain the light and heavy isotopes, respectively. Within the framework of *transition state* theory in which the reaction is rewritten as $A + B \rightleftharpoons [TS]^\ddagger \longrightarrow C$ and with neglect of isotopic mass on *tunnelling* and the transmission coefficient, k^l/k^h can be regarded as if it were the equilibrium constant for an isotope exchange reaction between the transition state $[TS]^\ddagger$ and the isotopically substituted reactant A, and calculated from their vibrational frequencies as in the case of a thermodynamic isotope effect. Isotope effects like the above, involving a direct or indirect

comparison of the rates of reaction of *isotopologues*, are called "intermolecular", in contrast to intramolecular isotope effects in which a single substrate reacts to produce a non-statistical distribution of isotopologue product molecules.

Isotope effect, primary : A kinetic isotope effect attributable to isotopic substitution of an atom to which a bond is made or broken in the *rate-controlling step* or in a *pre-equilibrium* step of a specified reaction is termed a primary isotope effect. The corresponding isotope effect on the equilibrium constant of a reaction in which one or more bonds to isotopic atoms are broken, is called a "primary equilibrium isotope effect".

Isotope effect, secondary : A kinetic isotope effect that is attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the *rate-controlling step* or in a *pre-equilibrium* step of a specified reaction, and is therefore not a primary isotope effect, is termed a secondary isotope effect. One speaks of α , (etc.) secondary isotope effects, where α , β (etc.) denote the position of isotopic substitution relative to the reaction centre. The corresponding isotope effect on the equilibrium constant of such a reaction is called a "secondary equilibrium isotope effect". Secondary isotope effects have been discussed in terms of the conventional electronic effects of physical organic chemistry, e.g. induction, *hyperconjugation*, *hybridization*, etc., since these properties are determined by the electron distribution, that depends on vibrationally averaged bond lengths and angles which vary slightly with isotopic substitution. While this usage is legitimate, the term "electronic isotope effect" should be avoided, because of the misleading implication that such an effect is electronic rather than vibrational in origin.

Isotope effect, solvent : A kinetic or equilibrium isotope effect resulting from change in the isotopic composition of the solvent.

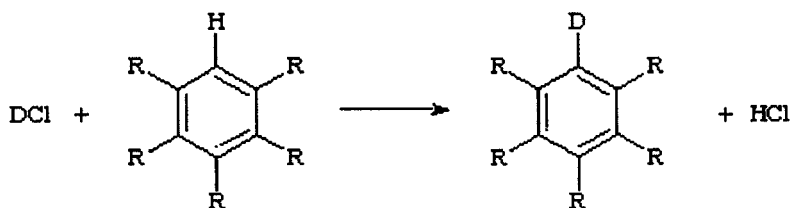
Isotope effect, steric : A secondary isotope effect attributed to the different vibrational amplitudes of *isotopologues*. For example, both the mean and mean-square amplitudes of vibrations associated with C-H bonds are greater than those of C-D bonds. The greater effective bulk of molecules containing the former may be manifested by a *steric effect* on a rate or equilibrium constant.

Isotope effect, thermodynamic : The effect of isotopic substitution on an equilibrium constant is referred to as a thermodynamic (or equilibrium) isotope effect. For example, the effect of isotopic substitution in reactant A that participates in the equilibrium: $A + B \rightleftharpoons C$ is the ratio K^l/K^h of the equilibrium constant for the reaction in which A contains the light isotope to that in which it contains the heavy isotope. The ratio can be expressed as the equilibrium constant for the isotopic exchange reaction: $A^l + C^h \rightleftharpoons A^h + C^l$ in which reactants such as B that are not isotopically substituted do not appear. The potential energy surfaces of isotopic molecules are identical to a high degree of approximation, so thermodynamic isotope effects can only arise from the effect of isotopic mass on the nuclear motions of the reactants and products, and can be expressed quantitatively in terms of partition function ratios for nuclear motion:

$$\frac{K^l}{K^h} = \frac{(\mathcal{Q}_{\text{nuc}}^l / \mathcal{Q}_{\text{nuc}}^h)_C}{(\mathcal{Q}_{\text{nuc}}^l / \mathcal{Q}_{\text{nuc}}^h)_A}$$

Although the nuclear partition function is a product of the translational, rotational and vibrational partition functions, the isotope effect is determined almost entirely by the last named, specifically by vibrational modes involving motion of isotopically different atoms. In the case of light atoms (i.e. protium vs. deuterium or tritium) at moderate temperatures, the isotope effect is dominated by zero-point energy differences.

Isotope exchange : A *chemical reaction* in which the reactant and product *chemical species* are chemically identical but have different isotopic composition. In such a reaction the isotope distribution tends towards equilibrium (as expressed by fractionation factors) as a result of transfers of isotopically different atoms or groups. For example,



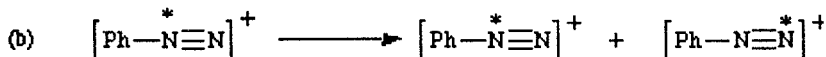
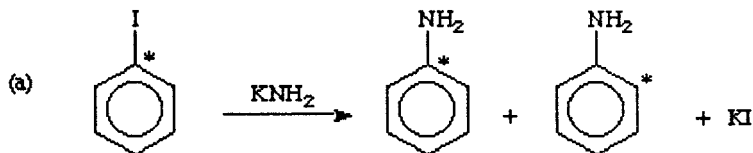
Isotopes : Nuclides with the same number of protons, such as ^{12}C , ^{13}C , and ^{14}C .

Isotopic abundance : Compare with natural abundance. The fraction of atoms of a given isotope in a sample of an element.

Isotopic mass : isotopic masses. The mass of a single atom of a given isotope, usually given in daltons.

Isotopic perturbation, method of : NMR shift difference measurement of the isotope effect on a fast (degenerate) equilibrium between two, except for isotopic substitution, species which are equivalent. This can be used to distinguish a rapidly equilibrating mixture with time-averaged symmetry from a single structure with higher symmetry.

Isotopic scrambling : The achievement, or the process of achieving, an equilibrium distribution of isotopes within a specified set of atoms in a *chemical species* or group of chemical species. For example,



(* denotes position of an isotopically different atom.)

Isotopologue : A *molecular entity* that differs only in isotopic composition (number of isotopic substitutions), e.g. CH_4 , CH_3D , CH_2D_2 ...

Isotopomer : Isomers having the same number of each isotopic atom but differing in their positions. The term is a contraction of "isotopic isomer". Isotopomers can be either constitutional isomers (e.g. $\text{CH}_2\text{DCH}=\text{O}$ and $\text{CH}_3\text{CD}=\text{O}$) or isotopic stereoisomers (e.g. (*R*)- and (*S*)- CH_3CHDOH or (*Z*)- and (*E*)- $\text{CH}_3\text{CH}=\text{CHD}$).

Isotropic : Literally the same in all directions. Used to describe the pressure of a gas.

IUPAC : International Union of Pure and Applied Chemistry, an organization which sets international standards for chemical nomenclature, atomic weights, and the names of newly discovered elements.

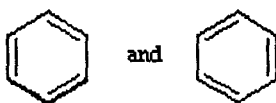


Joule : (J) The SI unit of energy, equal to the work required to move a 1 kg mass against an opposing force of 1 newton. $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = 4.184 \text{ calories}$.

K

Kamlet-Taft solvent parameters : Parameters of the Kamlet-Taft solvatochromic relationship which measure separately the hydrogen bond donor (α), hydrogen bond acceptor (β), and dipolarity/polarizability (π^*) properties of solvents as contributing to overall solvent *polarity*. KAMLET, ABBOUD and TAFT (1981).

Kekulé structure (for aromatic compounds) : A representation of an *aromatic molecular entity* (such as benzene), with fixed alternating single and double bonds, in which interactions between multiple bonds are assumed to be absent. For benzene, are the Kekulé structures.



Kelvin : (K) The SI base unit of temperature, defined by assigning 273.16 K to the temperature at which steam, ice, and water are at equilibrium (called the triple point of water). The freezing point of water is 273.15 K.

Ketone : 1. (R-CO-R') An organic compound that contains a carbonyl group. For example, methyl ethyl ketone is $\text{CH}_3\text{COCH}_2\text{CH}_3$ is used in some adhesives. 2. A compound in which a C=O (carbonyl) function group is bound to two carbon atoms, such as CH_3COCH_3 .

Kilo- : (k) Prefix used in the SI system meaning "one thousand of". For example 1 km means "one thousand meters"; 2.8 kg could also be written " 2.8×10^3 g" or "2800 g".

Kilogram : (kg) The kilogram (kg) is the base unit of mass in the SI system of units. The standard kilogram is a 1 kg corrosion resistant platinum/iridium cylinder, carefully preserved in the suburbs of Paris (with a backup copy kept in Gaithersburg, Maryland.) Efforts are underway to replace these artifacts by redefining the kilogram as the mass of a certain number of silicon atoms.

Kinetic ambiguity : Synonymous with *kinetic equivalence* .

Kinetic control (of product composition) : The term characterizes conditions (including reaction times) that lead to reaction products in a proportion governed by the relative rates of the parallel (forward) reactions in which the products are formed, rather than by the respective overall equilibrium constants.

Kinetic control : Describes a chemical reaction in which the products are determined by the rate of the reaction.

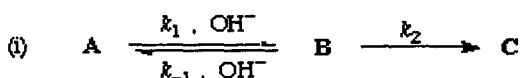
Kinetic electrolyte effect (kinetic ionic-strength effect) : The general effect of an added electrolyte (i.e. an effect other than, or in addition to, that due to its possible involvement as a reactant or catalyst) on the observed rate constant of a reaction in solution. At low concentrations (when only long-range coulombic forces need to be considered) the effect on a given reaction is determined only by the *ionic strength* of the solution and not by the chemical identity of the ions. For practical purposes, this concentration range is roughly the same as the region of validity of the Debye-Hückel limiting law for activity coefficients. At higher concentrations, the effect of an added electrolyte depends also on the chemical identity of the ions. Such specific action can usually be interpreted as the incursion of a *reaction path* involving an ion of the electrolyte as reactant or catalyst, in which case the action is not properly to be regarded just as a kinetic electrolyte effect. Kinetic electrolyte effects are usually (too restrictively and therefore incorrectly) referred to as "kinetic salt effects". A kinetic electrolyte effect ascribable solely to the influence of the ionic strength on activity coefficients of ionic reactants and transition states is called a "primary kinetic electrolyte effect". A

kinetic electrolyte effect arising from the influence of the ionic strength of the solution upon the *pre-equilibrium* concentration of an ionic species that is involved in a subsequent *rate-limiting step* of a reaction is called a "secondary kinetic electrolyte effect". A common case encountered in practice is the effect on the concentration of hydrogen ion (acting as catalyst) produced from the *ionization* of a weak acid in a buffer solution.

Kinetic energy : The energy associated with a moving object. The kinetic energy of the object is equal to one-half the product of its mass times its velocity squared ($KE = 1/2 mv^2$).

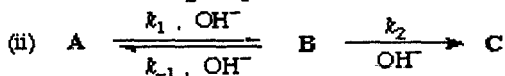
Compare with potential energy. The energy an object possesses by virtue of its motion. An object of mass m moving at velocity v has a kinetic energy of $\frac{1}{2}mv^2$.

Kinetic equivalence : Two reaction schemes are kinetically equivalent if they imply the same *rate law*. For example, consider the two schemes (i) and (ii) for the formation of C from A :



Providing that B does not accumulate as a reaction intermediate.

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][OH^-]}{k_2 + k_{-1}[OH^-]} \quad (1)$$



Providing that B does not accumulate as a reaction intermediate

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][OH^-]}{k_{-1} + k_2 [OH^-]} \quad (2)$$

Both equations for $d[C]/dt$ are of the form

$$\frac{d[C]}{dt} = \frac{r[A][OH^-]}{1 + s[OH^-]} \quad (3)$$

where r and s are constants (sometimes called "coefficients in the rate equation"). The equations are identical in their dependence on concentrations and do not distinguish whether OH^- catalyses the formation of B, and necessarily also its reversion to A, or is involved in its further transformation to C. The two schemes are therefore kinetically equivalent under conditions to which the stated provisos apply.

Kinetic molecular theory : The theory which assumes that heat is associated with the thermal motion of particles. In the kinetic theory, heat is not conserved an inexhaustible amount of heat can be created by doing work on a system.

Kinetic region : The portion of a plot of the concentration of a compound versus time in which the concentration changes. The portion of this plot between the initial conditions and the point at which the system reaches equilibrium.

Kipp's apparatus : a special piece of glassware consisting of three chambers, designed to provide a continuous and regulated production of gas by bringing the reactants into contact in a controlled way.

Koppel-Palm solvent parameters : Parameters to measure separately the ability of a solvent to enter into non-specific solvent-solute interactions (permittivity ϵ and refractive index n_D) and specific solvent-solute interaction (solvent basicity or nucleophilicity B and solvent acidity or electrophilicity E) as contributing to overall solvent polarity.

K_w , Kw. Symbol for the autoprotolysis constant for water, equal to 1.01×10^{-14} at $25^\circ C$.



L- : L-isomer. Compare with D-. Prefix used to designate a levorotatory enantiomer.

Labile : The term has loosely been used to describe a relatively *unstable* and *transient chemical species* or (less commonly) a relatively *stable* but reactive species. It must therefore not be used without explanation of the intended meaning.

Lambert's law : The intensity of radiation passing through a material decays exponentially with path length b .

Lanthanide contraction : An effect that causes sixth period elements with filled $4f$ subshells to be smaller than otherwise expected. The intervention of the lanthanides increases the effective nuclear charge, which offsets the size increase expected from filling the $n=6$ valence shell. As a consequence, sixth period transition metals are about the same size as their fifth period counterparts.

Lanthanide series or lanthanide metals : a series of 15 similar metallic elements between lanthanum and lutetium. They are transition metals and are also called rare earths.

Lanthanide. Compare with actinide and inner transition metals. Elements 57-70 are called lanthanides. Electrons added during the Aufbau construction of lanthanide atoms go into the $4f$ subshell.

Latent heat : Heat that is absorbed without causing a rise in temperature. For example, "latent heat of vaporization" refers to the amount of heat required to convert a liquid to vapor at a particular temperature.

Heat that cannot be detected. The heat that enters a system when ice melts to form water or when water boils to form

steam is latent heat, because there is no change in the temperature of the system. See sensible heat.

The amount of heat that is absorbed or released during the process of changing state between gas, liquid or solid. For example, heat is absorbed when a substance melts and it is released again when the substance solidifies.

Lattice : A regular arrangement of atoms, ions or molecules in a crystalline solid.

Lattice energy : The energy given off when oppositely charged ions in the gas phase come together to form a solid. For example, the energy given off in the following reaction: $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$.

Lattice point : A point about which an atom, ion, or molecule is free to vibrate in a crystal.

Law of combining volumes : Gay-Lussac's law. When gases react, they do so in a definite proportion by volume, if the volumes are measured at the same pressure and temperature. For example, in the reaction $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) = 2 \text{NH}_3(\text{g})$, 3 liters of hydrogen will react with 1 liter of nitrogen to give 2 liters of ammonia if all volumes are measured at the same temperature and pressure.

Law of conservation of mass : There is no change in total mass during a chemical change. The demonstration of conservation of mass by Antoine Lavoisier in the late 18th century was a milestone in the development of modern chemistry.

Law of conservation of matter : The notion that matter cannot be created or destroyed.

Law of constant composition : The notion that a compound always contains the same ratio by mass of its elements, regardless of its source.

Law of definite proportions : The notion that the ratio by mass of compounds consumed in a chemical reaction is always the same.

When two pure substances react to form a compound, they do so in a definite proportion by mass. For example, when water is formed from the reaction between hydrogen and oxygen, the 'definite proportion' is 1 g of H for every 8 g of O.

Law of multiple proportions : When one element can combine with another to form more than one compound, the mass ratios of the elements in the compounds are simple whole-number ratios of each other. For example, in CO and in CO₂, the oxygen-to-carbon ratios are 16:12 and 32:12, respectively. Note that the second ratio is exactly twice the first, because there are exactly twice as many oxygens in CO₂ per carbon as there are in CO.

Le Chatelier's principle : Le Chatelier's principle predicts that when a stress is applied to an equilibrium mixture, the equilibrium will shift to relieve the stress. Stresses include temperature changes, pressure changes, and changes in the concentrations of species in the mixture. For example, increasing the concentration of a reactant drives the reaction forward; increasing the concentration of a product drives it backward.

Leaching : the extraction of a substance by percolating a solvent through a material. *Example*: when water flows through an ore, some of the heavy metals in it may be leached out causing environmental pollution.

Lead storage battery : a battery (used in cars) in which the anode is lead, the cathode is lead coated with lead dioxide, and the electrolyte is a sulfuric acid solution.

Least nuclear motion : The hypothesis that, for given reactants, the reactions involving the smallest change in nuclear positions will have the lowest *energy of activation*. (It is also often simply referred to as principle of least motion.)

Leaving group : An atom or *group* (charged or uncharged) that becomes detached from an atom in what is considered to be the residual or main part of the *substrate* in a specified reaction. For example, in the heterolytic *solvolysis* of benzyl bromide in acetic acid $\text{PhCH}_2\text{Br} + \text{AcOH} \longrightarrow \text{PhCH}_2\text{OAc} + \text{HBr}$ the leaving group is Br^- ; in the reaction $\text{MeS}^- + \text{PhCH}_2\text{N}^+\text{Me}_3 \longrightarrow \text{MeSCH}_2\text{Ph} + \text{NMe}_3$ the leaving group is NMe_3 ; in the *electrophilic* nitration of benzene, it is H^+ . The term has meaning only in relation to a specified reaction. The leaving group is not, in general, the same as the *substituent* group present in the substrate (e.g. bromo and trimethylammonio in the substrates of the first two examples above.) A slightly different usage of the term prevails in the (non-

mechanistic) naming of transformations, where the actual substituent group present in the substrate (and also in the product) is referred to as the leaving group.

LeChatelier's principle : A principle that describes the effect of changes in the temperature, pressure, or concentration of one of the reactants or products of a reaction at equilibrium. It states that when a system at equilibrium is subjected to a stress, it will shift in the direction that minimizes the effect of this stress.

Left-to-right convention : Arrangement of the structural formulae of the reactants so that the bonds to be made or broken form a linear array in which the electrons move from left to right.

Leucine : $[(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}]$ A naturally occurring aliphatic amino acid with a nonpolar side chain.

Leveling effect : The tendency of water to limit the strength of the strongest acids and bases to the strength of the H_3O^+ and OH^- ions.

The tendency of a solvent to make all *Brønsted acids* whose acidity exceeds a certain value appear equally acidic. It is due to the complete transfer to a *protophilic* solvent of a hydron from a dissolved acid stronger than the *conjugate acid* of the solvent. The only acid present to any significant extent in all such solutions is the *lyonium ion*. For example, the solvent water has a levelling effect on the acidities of HClO_4 , HCl , and HI : aqueous solutions of these acids at the same (moderately low) concentrations have the same acidities. A corresponding levelling effect applies to strong bases in *protogenic* solvents.

Leverotatory (-): A chiral molecule which rotates plane-polarized light to the left.

Having the property of rotating plane-polarized light counterclockwise.

Describes compounds that rotate plane-polarized light to the left (counterclockwise) when viewed in the direction of the light source. See dextrorotatory.

Lewis acid : A *molecular entity* (and the corresponding *chemical species*) that is an electron-pair acceptor and therefore able to react with a *Lewis base* to form a *Lewis adduct* , by sharing the electron pair furnished by the Lewis base. For example: Me_3B (Lewis acid) + $:\text{NH}_3$ (Lewis base) \longrightarrow $\text{Me}_3\text{B}^-\text{N}^+\text{H}_3$ (Lewis adduct).

Lewis acid : An electron-pair acceptor. A substance that acts in the same way as the H^+ ion to accept a pair of electrons.

The thermodynamic tendency of a substrate to act as a *Lewis acid* . Comparative measures of this property are provided by the equilibrium constants for *Lewis adduct* formation of a series of Lewis acids with a common reference *Lewis base* .

Lewis adduct : The *adduct* formed between a *Lewis acid* and a *Lewis base* .

Lewis base : An electron-pair donor. A substance that acts in the same way as the OH^- ion to donate a pair of electrons.

A *molecular entity* (and the corresponding *chemical species*) able to provide a pair of electrons and thus capable of *coordination* to a *Lewis acid* , thereby producing a *Lewis adduct* .

Lewis basicity : The thermodynamic tendency of a substance to act as a *Lewis base* . Comparative measures of this property are provided by the equilibrium constants for *Lewis adduct* formation for a series of Lewis bases with a common reference *Lewis acid* . See also *donor number (DN)* , *nucleophilicity* .

Lewis formula (electron dot or Lewis structure) : Molecular structure in which the valency electrons are shown as dots so placed between the bonded atoms that one pair of dots represents two electrons or one (single) *covalent bond* , e.g.



A double bond is represented by two pairs of dots, etc. Dots representing non-bonded outer-shell electrons are placed adjacent to the atoms with which they are associated, but not

between the atoms. Formal charges (e.g. +, -, 2+, etc.) are attached to atoms to indicate the difference between the positive nuclear charge (atomic number) and the total number of electrons (including those in the inner shells), on the formal basis that bonding electrons are shared equally between atoms they join. (Bonding pairs of electrons are usually denoted by lines, representing covalent bonds, as in *line formulae* .)

Lewis structure : A symbolic description of the distribution of valence electrons in a molecule. Lewis structures use dots to represent individual electrons and lines to represent covalent bonds.

Electron dot structure; dot structure. A model pioneered by Gilbert N. Lewis and Irving Langmuir that represents the electronic structure of a molecule by writing the valence electrons of atoms as dots. Pairs of dots (or lines) wedged between atoms represent bonds; dots drawn elsewhere represent nonbonding electrons.

Liebig condenser : A piece of glassware consisting of a sloping water-cooled tube. The design allows a volatile material to be condensed and collected.

Lifetime (mean lifetime), τ : The lifetime of a *chemical species* which decays in a first-order process is the time needed for a concentration of this species to decrease to 1/e of its original value. Statistically, it represents the mean life expectancy of an excited species. In a reacting system in which the decrease in concentration of a particular chemical species is governed by a first-order *rate law* , it is equal to the reciprocal of the sum of the (pseudo)unimolecular rate constants of all processes which cause the decay. When the term is used for processes which are not first order, the lifetime depends on the initial concentration of the species, or of a quencher, and should be called apparent lifetime instead.

Ligand : In inorganic chemistry, a molecule or ion that binds to a metal cation to form a complex.

In biochemistry, a molecule that binds to a receptor, having a biological effect.

Ligand : A Lewis base that can coordinate to a metal atom.

Ligand : If it is possible to indicate a "central atom" in a polyatomic *molecular entity*, the atoms or *groups* bound to that atom are called ligands. The term is generally used in connection with metallic "central atoms". In biochemistry a part of a polyatomic molecular entity may be considered central, and atoms, groups or molecules bound to that part are considered ligands.

Ligand-field theory : A molecular orbital description of the bonding in transition-metal complexes.

Lime (quicklime) : Calcium oxide (CaO). A white, caustic solid, manufactured by heating limestone and used for making mortar, fertiliser or bleach.

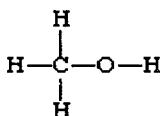
Limewater : an aqueous solution of calcium hydroxide, used especially to detect the presence of carbon dioxide.

Limit of quantitation : (LOD) quantitative detection limit; limit of determination. The smallest detectable concentration an analytical instrument can determine at a given confidence level. IUPAC defines the quantitative detection limit as $C_{ld} = ks/m$, where k is 10, s is the standard deviation of instrument readings taken on a "blank" (a solution with zero concentration of analyte), and m is the slope of a plot of instrument response vs. concentration, as calculated by linear regression.

Limiting reactant : limiting reagent. The reactant that limits the amount of product produced in a chemical reaction. For example, mixing one mole of $H_2(g)$ with one mole of O_2 produces one mole of steam ($H_2O(g)$), with half a mole of $O_2(g)$ remaining. The hydrogen gas limits the amount of steam produced in this case.

Limiting reagent : The reactant in a chemical reaction that limits the amount of product that can be formed. The reaction will stop when all the limiting reagent is consumed.

Line formula : A two-dimensional representation of *molecular entities* in which atoms are shown joined by lines representing single or multiple bonds, without any indication or implication concerning the spatial direction of bonds. For example, methanol is represented as



(The term should not be confused with the representation of chemical formulae by the "Wiswesser line notation", a method of string notation. Formulae in this notation are also known as "Wiswesser line formulae".)

Line notation : A system for representing electrochemical reactions.

Line spectrum : line spectra; line emission spectrum. Compare with band spectrum and continuous spectrum. A emission spectrum that contains very sharp peaks, corresponding to transitions between states in free atoms. For example, the line spectrum of hydrogen contains 4 sharp lines in the visible part of the spectrum.

Linear free-energy relation : A linear correlation between the logarithm of a rate constant or equilibrium constant for one series of reactions and the logarithm of the rate constant or equilibrium constant for a related series of reactions. Typical examples of such relations (also known as linear Gibbs energy relations) are the *Brønsted relation* , and the *Hammett equation* (see also σ -value). The name arises because the logarithm of an equilibrium constant (at constant temperature and pressure) is proportional to a standard free energy (Gibbs energy) change, and the logarithm of a rate constant is a linear function of the free energy (Gibbs energy) of activation. It has been suggested that this name should be replaced by *Linear Gibbs Energy Relation*, but at present there is little sign of acceptance of this change. The area of physical organic chemistry which deals with such relations is commonly referred to as "Linear Free-Energy Relationships".

Linear solvation energy relationships : Equations involving the application of *solvent parameters* in linear or multiple (linear) regression expressing the solvent effect on the rate or equilibrium constant of a reaction. See *Dimroth-Reichardt E_T parameter*, *Kamlet-Taft solvent parameter* , *Koppel-Palm solvent parameter* , *Z-value* .

Line-shape analysis : Determination of rate constants for a chemical exchange from the shapes of spectroscopic lines of dynamic processes. The method is most often used in nuclear magnetic resonance spectroscopy.

Lipid : Biologically important molecules that are soluble in nonpolar solvents. A diverse group of organic molecules that contain long hydrocarbon chains or rings and are hydrophobic. Examples are fats, oils, waxes, and steroids.

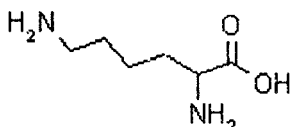
Lipophilic : Literally "fat-loving". Applied to *molecular entities* (or parts of molecular entities) having a tendency to dissolve in fat-like (e.g. hydrocarbon) solvents. Lipophilicity. Refers to a substance's solubility in fat. Lipophilicity can be measured by shaking the substance with a two-phase mixture of water and 1-octanol and observing the final concentrations of the substance in the two layers. Lipophilic substances will move into the 1-octanol layer, while hydrophilic substances stay in the water.

Liquefaction : The transformation of a gas into a liquid; to make something liquid.

Liquid : 1. A state of matter that has a high density and is incompressible compared to a gas. Liquids take the shape of their container but do not expand to fill the container as gases do. Liquids diffuse much more slowly than gases. 2. A substance that flows freely and therefore conforms to the shape of the walls of its container, but cannot expand to fill the container.

Liquid crystal : A substance that has some of the long-range order of a solid but the freedom of motion of a liquid.

Liquid/liquid phase : A form of matter that has a fixed volume but no fixed shape.



Liter : The fundamental unit of volume in the metric system. The volume of 1000 grams of water at 4°C.

Lithium : (Li) Li. Element 3, atomic weight 6.939. The lightest alkali metal, used in special-purpose metal alloys and other industrial applications.

Litmus : A mixture of pigments extracted from certain lichens that turns blue in basic solution and red in acidic solution.

Litmus : An indicator obtained from lichens. Used as a solution or impregnated into paper (litmus paper), which is dampened before use. Litmus turns red under acid conditions and purple in alkaline conditions. Litmus is a crude indicator when compared with Universal Indicator.

Litmus paper : Litmus test. Paper impregnated with litmus, usually cut in narrow strips. Dipping red litmus paper into a basic solution turns it blue; dipping blue litmus paper into an acidic solution turns it red.

Load (electronics) : An impedance or circuit that receives or develops the output of a cell or other power supply.

Lock and key model : lock-and-key. A model that explains the role of enzymes in chemical reactions by assuming that the reactants fit into the enzyme like a key fits into a lock.

London dispersion forces : The forces that exist in nonpolar molecules that involve an accidental dipole that induces a momentary dipole in a neighbor.

London force : Dispersion force. An intermolecular attractive force that arises from a cooperative oscillation of electron clouds on a collection of molecules at close range.

London forces : Attractive forces between apolar molecules, due to their mutual polarizability. They are also components of the forces between polar molecules. Also called "dispersion forces".

Lone (electron) pair : Two paired electrons localized in the valence shell on a single atom. Lone pairs should be designated with two dots. The term "nonbonding electron pair" is more appropriate, and is found in many modern text books.

Nonbonding pair; unshared pair. Electrons that are not involved in bonding.

Low-spin complex : A transition-metal complex in which the difference between the energies of the t_{2g} and e_g orbitals is larger than the energy it takes to pair electrons. As a result, the valence-shell d electrons on the metal are all placed in the lower-energy set of orbitals, the t_{2g} set for octahedral complexes and the e_g set for tetrahedral complexes. See high-spin complex.

Low-spin complex. Compare with high spin complex. A metal-ligand complex with fewer unpaired electrons than the uncomplexed metal ion. When a strong ligand complexes the metal ion, the crystal field splitting is large and some electrons pair rather than occupying the higher energy d orbitals.

Lustre : The shininess of a substance.

Lyate ion : The anion produced by *hydron* removal from a solvent molecule. For example, the hydroxide ion is the lyate ion of water.

Lyonium ion : The cation produced by hydronation of a solvent molecule. For example, CH_3OH_2^+ is the lyonium ion of methanol.

Lysine : Lys. A naturally occurring amino acid with an amine group on its side chain.



Macroscopic : Something that can be seen with the naked eye.

Macrostate : A time-average of many microstates; this is a state of the system that can actually be observed.

Magnetic equivalence : Nuclei having the same resonance frequency in nuclear magnetic resonance spectroscopy and also identical spin-spin interactions with the nuclei of a neighbouring group are magnetically equivalent. The spin-spin interaction between magnetically equivalent nuclei does not appear, and thus has no effect on the multiplicity of the respective NMR signals. Magnetically equivalent nuclei are necessarily also chemically equivalent, but the reverse is not necessarily true.

Magnetic quantum number (m) : The quantum number used to describe the orientation of an atomic orbital in space.

Magnetization transfer : NMR method for determining kinetics of chemical exchange by perturbing the magnetization of nuclei in a particular site or sites and following the rate at which magnetic equilibrium is restored. The most common perturbations are saturation and inversion, and the corresponding techniques are often called "saturation transfer" and "selective inversion-recovery". See also *saturation transfer*.

Main group elements : Elements of the s and p blocks. An element in one of the groups of the periodic table in which s and p orbitals are filled. Also known as the representative elements.

Mak : The German Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area. It is responsible for setting MAK values (Maximale Arbeitsplatz-Konzentration :

maximum workplace concentration - equivalent to an OEL) for chemicals.

Malleable : Something that can be hammered, pounded, or pressed into different shapes without breaking; Able to be pressed or hammered into shape.

Manometer : A device for measuring gas pressure. A simple manometer is made by partly filling a U-shaped rubber tube with water and connecting one end to the source of gas whose pressure is to be measured. The pressure is always relative to atmospheric pressure.

Compare with barometer. An instrument for measuring gas pressures. A mercury or oil manometer measures gas pressure as the height of a fluid column the gas sample is able to support. Open manometers measure gas pressure relative to atmospheric pressure.

Marcus equation : A general expression which correlates the *Gibbs energy of activation* ($\Delta^\ddagger G$) with the driving force ($\Delta_r G^\circ$) of the reaction: $\Delta^\ddagger G = (\lambda/4)(1 + \Delta_r G^\circ/\lambda)^2$ where λ is the *reorganization energy* and $\Delta_r G^\circ$ is the standard free energy of the reaction corrected for the electrostatic work required to bring the reactants together. $\lambda/4$ is the *intrinsic barrier* of the reaction. Originally developed for *outer-sphere electron transfer* reactions, the Marcus equation has later been applied also to atom and group transfer reactions.

Markownikoff rule : "In the addition of hydrogen halides to unsymmetrically constituted [unsaturated] hydrocarbons, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms." Originally formulated by Markownikoff (Markovnikov) to generalize the orientation in additions of hydrogen halides to simple alkenes, this rule has been extended to polar *addition reactions* as follows. " In the *heterolytic* addition of a polar molecule to an alkene or alkyne, the more electronegative (nucleophilic) atom (or part) of the polar molecule becomes attached to the carbon atom bearing the smaller number of hydrogen atoms." This is an indirect statement of the common mechanistic observation, that the more electropositive (electrophilic) atom (or part) of the polar molecule becomes attached to the end of the multiple bond that

would result in the more stable *carbenium ion* (whether or not a carbenium ion is actually formed as a *reaction intermediate* in the addition reaction). Addition in the opposite sense is commonly called "anti-Markovnikov addition".

Compare with weight. Mass is a measure of the tendency of an object to resist acceleration. It's harder to roll a tractor trailer than a roller skate; the tractor trailer has a far greater mass.

Mass : (m) A measure of the amount of matter in an object. The quantity of matter in an object.

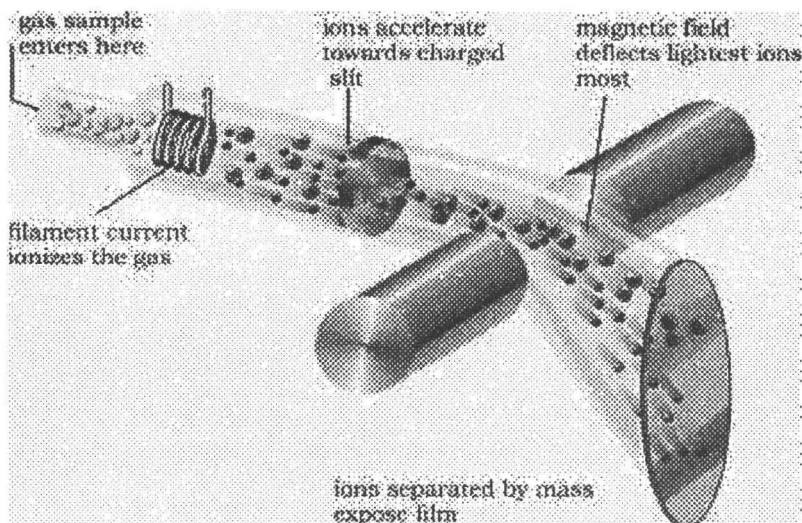
Mass defect : The difference between the mass of an atom and the sum of the masses of the protons and neutrons that form the nucleus of the atom.

Mass number (M) : An integer equal to the number of protons and neutrons in the nucleus of an atom.

(M,A) Compare with atomic number and atomic weight. The total number of protons and neutrons in an atom or ion. In nuclide symbols the mass number is given as a leading superscript. In isotope names (e. g. carbon-14, sodium-23) the mass number is the number following the element name.

Mass percentage : [(w/w)%] Mass percentages express the concentration of a component in a mixture or an element in a compound. For example, household bleach is 5.25% NaOCl by mass, meaning that every 100 g of bleach contains 5.25 g of NaOCl. Mass percentage can be calculated as 100% times the mass of a component divided by the mass of the mixture containing the component.

Mass spectrometer : An instrument that measures the masses and relative abundances of a sample that has been vaporized and ionized.



Mass spectrometry : Mass spectroscopy. (of elements) A method for experimentally determining isotopic masses and isotopic abundances. A sample of an element is converted into a stream of ions and passed through an electromagnetic field. Ions with different charge-to-mass ratios are deflected by different amounts, and strike different spots on a film plate or other detector. From the position of the spots, the mass of the ions can be determined; from the intensity of the spot, the relative number of ions (the isotopic abundance) can be determined.

Mass spectrum : Mass spectra. A plot showing the results of a mass spectrometry experiment, which shows the presence of particles with different masses as a series of sharp, separate peaks. The position of the peaks on the x-axis indicates the mass of the particles; the peak heights indicate the relative abundance of the particles.

Mass-law effect : At equilibrium, the product of the activities (or concentrations) of the reacting species is constant. Thus for the equilibrium $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$ $K = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$

Matrix isolation : A term which refers to the isolation of a reactive or unstable species by dilution in an inert matrix (argon,

nitrogen, etc.), usually condensed on a window or in an optical cell at low temperature, to preserve its structure for identification by spectroscopic or other means.

Matter : Anything that has mass and takes up space.

Matter is anything that has mass and occupies space. Air, water, coffee, fire, human beings, and stars are matter. Light, X-rays, photons, gravitons, information, and love aren't matter.

The material of the universe.

Measurement : Measurement is the collection of quantitative data. Measurement involves comparison of the quantity of interest with a standard called a unit. The comparison is never perfect. As a result, measurements always include error. You must consider the reliability of the measurement when using it to make decisions or estimate other quantities.

The process by which the amount or quantity of something is measured.

Mechanism : A detailed description of the process leading from the reactants to the products of a reaction, including a characterization as complete as possible of the composition, structure, energy and other properties of *reaction intermediates*, products, and *transition states*. An acceptable mechanism of a specified reaction (and there may be a number of such alternative mechanisms not excluded by the evidence) must be consistent with the reaction stoichiometry, the *rate law*, and with all other available experimental data, such as the stereochemical course of the reaction. Inferences concerning the electronic motions which dynamically interconvert successive species along the *reaction path* (as represented by curved arrows, for example) are often included in the description of a mechanism. It should be noted that for many reactions all this information is not available and the suggested mechanism is based on incomplete experimental data. It is not appropriate to use the term mechanism to describe a statement of the probable sequence in a set of stepwise reactions. That should be referred to as a reaction sequence, and not a mechanism.

The steps by which a chemical reaction converts the reactants into the products.

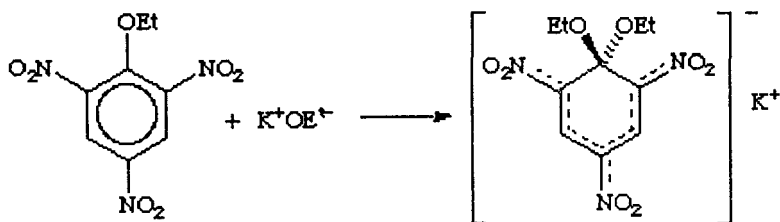
Mechanism-based inhibition : Irreversible *inhibition* of an enzyme due to its catalysis of the reaction of an artificial substrate. Also called "suicide inhibition".

Medicinal chemistry : A branch of chemistry concerned with the discovery, design, synthesis, and investigation of biologically active compounds and reactions that these compounds undergo in living things.

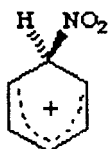
Medium : The phase (and composition of the phase) in which *chemical species* and their reactions are studied in a particular investigation.

Mega : (M) mega. SI prefix meaning "multiply by 10^6 ". For example, 3.2 MJ is 3200000 J.

Meisenheimer adduct : A cyclohexadienyl derivative formed as *Lewis adduct* from a *nucleophile* (*Lewis base*) and an *aromatic* or *heteroaromatic* compound, also called Jackson-Meisenheimer adduct. In earlier usage the term "Meisenheimer complex" was restricted to the typical Meisenheimer alkoxide *adducts* of nitro-substituted aromatic ethers, e.g.,



Analogous cationic adducts, such as considered to be *reaction intermediates* in *electrophilic aromatic substitution reactions*, are called "Wheland intermediates", and sometimes, inappropriately, σ -complexes.



Melting point : The temperature at which a substance changes state from a solid phase to a liquid phase. It is the same as freezing point.

The temperature at which the solid and liquid phases of a substance are in equilibrium at atmospheric pressure.

The term originally signified that a correction was made (not made) for the emergent stem of the thermometer. In current usage it often means that the accuracy of the thermometer was (was not) verified. This current usage is inappropriate and should be abandoned.

Membrane : A thin, flexible sheet. A semipermeable membrane has microscopic holes of a size that will selectively allow some ions and molecules to pass through but hold others back. It thus acts as a kind of filter. *Example*: a membrane used for osmosis.

Meniscus : Meniscuses; menisci. A phase boundary that is curved because of surface tension.

The curved surface of a liquid in a narrow-diameter glass tube.

The curved surface of a liquid that forms in a small bore or capillary tube. The meniscus is convex (bulges upwards) for mercury and is concave (sags downwards) for water.

Mercury : Mercury is a naturally occurring element which is present in various ores. The major source in Europe is in Spain (Almadén). Mercury has been used for 100 years in electrolytic chlorine production.

Meso compound : A compound that has two or more chiral centers but does **not** rotate plane-polarized light because it has an internal plane of symmetry. These compounds are identical to their mirror images.

Mesolytic cleavage : Cleavage of a bond in a *radical ion* whereby a *radical* and an ion are formed. The term reflects the mechanistic duality of the process, which can be viewed as homolytic or heterolytic depending on how the electrons are attributed to the fragments.

Mesomeric effect : The effect (on reaction rates, ionization equilibria, etc.) attributed to a substituent due to overlap of its p or pi orbitals with the p or pi orbitals of the rest of the *molecular entity*. *Delocalization* is thereby introduced or extended, and electronic charge may flow to or from the substituent. The effect is symbolized by M. Strictly understood, the mesomeric effect operates in the ground electronic state of the molecule. When the molecule undergoes electronic excitation or its energy is increased on the way to the *transition state* of a *chemical reaction*, the mesomeric effect may be enhanced by the *electromeric effect*, but this term is not much used, and the mesomeric and electromeric effects tend to be subsumed in the term *resonance effect* of a *substituent*.

Mesomerism : Essentially synonymous with *resonance*. The term is particularly associated with the picture of pi electrons as less localized in an actual molecule than in a *Lewis formula*. The term is intended to imply that the correct representation of a structure is intermediate between two or more Lewis formulae. See also *aromatic* (2), *delocalization*.

Mesophase : The phase of a liquid crystalline compound between the crystalline and the isotropic liquid phase.

Metabolism : metabolic; metabolic reaction. A sequence of biochemical reactions that converts fuel molecules into energy used to drive other biological processes. Also refers to the sequence of transformations foreign compounds undergo inside a living cell.

Metabolite : A compound produced by metabolic reactions.

Metal : A class of elements that is a good conductor of electricity and heat, has a metallic lustre, is malleable and ductile, forms cations and has oxides that are bases. Metals are formed as cations held together by a sea of electrons. A metal may also be an alloy of these elements. *Example*: sodium, calcium, gold.

An element that is solid, has a metallic luster, is malleable and ductile, and conducts both heat and electricity.

Metallic. Compare with nonmetal and metalloid. A metal is a substance that conducts heat and electricity, is shiny and reflects many colors of light, and can be hammered into sheets or drawn into wire. Metals lose electrons easily to

form cations. About 80% of the known chemical elements are metals.

Metallic bonding : Cations reside in a 'sea' of mobile electrons. It allows metals to be good conductors and means that they are not brittle.

Metallic compounds : Compounds that contain at least one metallic element.

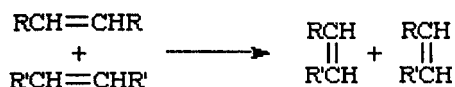
Metallic radius : Half the distance between the nuclei of adjacent atoms in a metal.

Metallic solid : A solid that has the properties of a metal.

Metalloid : A class of elements intermediate in properties between metals and non-metals. Metalloids are also called semi-metals or semiconductors. *Example*: silicon, germanium, antimony.

Metastable system : A system that should undergo a spontaneous change, but does not.

Metathesis : A *bimolecular* process formally involving the exchange of a bond (or bonds) between similar interacting *chemical species* so that the bonding affiliations in the products are identical (or closely similar) to those in the reactants. For example:



(The term has its origin in inorganic chemistry with a different meaning, but this older usage is not applicable in physical organic chemistry.)

Metathesis reaction : A reaction in which atoms or groups of atoms are interchanged, but none of the atoms undergo a change in oxidation number.

Meter : (m) metre. The meter is the basic unit of length in the SI system of units, defined as the distance light travels through a vacuum in exactly 1/299792458 seconds. 1 m = 39.37 inches. Meters are abbreviated as "m" in measurements.

Methionine. Met; α -amino- γ -methylthiobutyric acid. A naturally occurring amino acid and building block of proteins with a sulfur-containing side chain.

Methyl : ($-\text{CH}_3$) A group $-\text{CH}_3$, derived from methane. For example, CH_3Cl is "methyl chloride" (systematic name: chloromethane); CH_3OH is "methyl alcohol" (systematic name: methanol).

Methylene Chloride : Methylene chloride (dichloromethane), a versatile chlorinated solvent, is produced by chlorination of either methane or methyl chloride. It is used in a broad spectrum of applications: paint stripping, adhesives, aerosols, process solvent and tablet-coating agent in the pharmaceutical industry, solvent in polycarbonate production, blowing agent for polyurethanes, food extraction, cold degreasing of metals, printing, gauze coating, fabric coating, etc. See other information and comments under "Chlorinated Solvents".

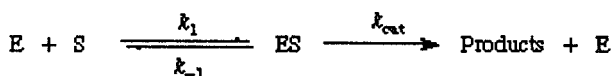
Metric system : A system of units introduced in 1790 based on three fundamental quantities: the gram (mass), liter (volume), and meter (length).

Micellar catalysis : The acceleration of a *chemical reaction* in solution by the addition of a surfactant at a concentration higher than its *critical micelle concentration* so that the reaction can proceed in the environment of surfactant aggregates (*micelles*). (Rate enhancements may be due, for example, to higher concentration of the reactants in that environment, more favourable orientation and solvation of the species, or enhanced rate constants in the micellar pseudophase of the surfactant aggregate.) Micelle formation can also lead to a decreased reaction rate.

Micelle : Surfactants in solution are often association colloids, that is, they tend to form aggregates of colloidal dimensions, which exist in equilibrium with the molecules or ions from which they are formed. Such aggregates are termed micelles.

Michaelis-Menten kinetics : The dependence of an initial *rate of reaction* upon the concentration of a *substrate* S that is present in large excess over the concentration of an enzyme or other *catalyst* (or reagent) E with the appearance of saturation behaviour following

the Michaelis-Menten equation, $v = V[S]/(K_m + [S])$, where v is the observed initial rate, V is its limiting value at substrate saturation (i.e., $[S] \gg K_m$), and K_m the substrate concentration when $v = V/2$. The definition is experimental, i.e., it applies to any reaction that follows an equation of this general form. The symbols V_{ma} or v_{ma} are sometimes used for V . The parameters V and K_m (the "Michaelis constant") of the equation can be evaluated from the slope and intercept of a linear plot of v^{-1} against $[S]^{-1}$ (a "Lineweaver-Burk plot") or from slope and intercept of a linear plot of v against $h/[S]$ ("Eadie-Hofstee plot"). A Michaelis-Menten equation is also applicable to the condition where E is present in large excess, in which case the concentration $[E]$ appears in the equation instead of $[S]$. The term has sometimes been used to describe reactions that proceed according to the scheme in which case $K_m = (k_{-1} + k_{cat})/k_1$ (Briggs-Haldane conditions). It has more usually been applied only to the special case in which $k_{-1} \gg k_{cat}$ and $K_m = k_{-1}/k_1 = K_s$; in this case K_m is a true dissociation constant (Michaelis-Menten conditions). See also *rate-determining step*.



Micro- : (μ) micro. Prefix used in the SI system meaning "one millionth of". For example 1 μm means "one millionth of a meter"; 3.1 μL means " 3.1×10^{-6} L".

Micron : (μm) micrometer. A unit of length, equivalent to 10^{-6} meters.

Micronutrient : An element that the body requires in small amounts. Another term is trace element.

Microscopic diffusion control (encounter control) : The observable consequence of the limitation that the rate of a bimolecular *chemical reaction* in a homogeneous medium cannot exceed the rate of encounter of the reacting *molecular entities*. If (hypothetically) a *bimolecular* reaction in a homogeneous medium occurred instantaneously when two reactant molecular entities made an encounter, the *rate of reaction* would be an *encounter-controlled rate*, determined solely by rates of diffusion of reactants. Such a hypothetical "fully diffusion controlled rate" is also said to correspond to "total microscopic diffusion control", and represents

the asymptotic limit of the rate of reaction as the rate constant for the chemical conversion of the encounter pair into product (or products) becomes large relative to the rate constant for separation (or dissociation) of the encounter pair. "Partial microscopic diffusion control" is said to operate in a homogeneous reaction when the rates of chemical conversion and of separation are comparable. (The degree of microscopic diffusion control cannot usually be determined with any precision.)

Microscopic reversibility, principle of : In a reversible reaction, the mechanism in one direction is exactly the reverse of the mechanism in the other direction. This does not apply to reactions that begin with a photochemical excitation.

Microstate : Each arrangement of the ensemble; every possible arrangement of the atoms or molecules in the system.

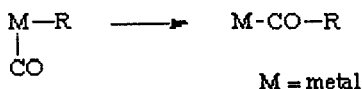
Microwave : Microwave radiation. Electromagnetic radiation with wavelength between 3 mm and 30 cm.

Migration : The (usually *intramolecular*) transfer of an atom or group during the course of a *molecular rearrangement*.

The movement of a *bond* to a new position, within the same *molecular entity*, is known as "bond migration". Allylic rearrangements, e.g., $\text{RCH=CHCH}_2\text{X} \longrightarrow \text{RCH(X)CH=CH}_2$ exemplify both types of migration.

Migratory aptitude : The term is applied to characterize the relative tendency of a group to participate in a rearrangement. In nucleophilic rearrangements (*migration* to an electron-deficient centre), the migratory aptitude of a group is loosely related to its capacity to stabilize a partial positive charge, but exceptions are known, and the position of hydrogen in the series is often unpredictable.

Migratory insertion : A combination of *migration* and *insertion*. The term is mainly used in organometallic chemistry.



Milli- : (m) Prefix used in the SI system meaning "one thousandth of". For example 1 mL means "one thousandth of a liter"; 1 mg means "one thousandth of a gram".

Mineral : A solid substance made of just one element or compound. *Example:* calcite is a mineral because it consists only of calcium carbonate; halite is a mineral because it contains only sodium chloride.

Mineral acid : An acid that does not contain carbon and which attacks minerals. Hydrochloric, sulphuric and nitric acids are the main mineral acids.

Mirix : A chemical that was used as a pesticide to control fire ants, and as a flame retardant in plastics, rubber, paint, paper, and electrical goods. It is based on perchloropentacyclodecane and classified as a POP.

Miscible : Miscibility; liquid miscibility. Capable of being mixed. Compare with immiscible and partial miscibility. Two liquids are considered "miscible" or mixable if shaking them together results in a single liquid phase, with no meniscus visible between layers of liquid.

Mixed glyceride : Compare with glyceride. A diglyceride or triglyceride that contains more than one type of fatty acid connected to glycerol via an ester linkage. Natural oils and fats usually contain several different mixed glycerides.

Mixing combustion : The form of combustion that occurs when two gases thoroughly mix before they ignite and so produce almost complete combustion. *Example:* when a Bunsen flame is blue.

Mixing control : The experimental limitation of the *rate of reaction* in solution by the rate of mixing of solutions of the two reactants. It can occur even when the reaction rate constant is several powers of 10 less than that for an *encounter-controlled* rate. Analogous (and even more important) effects of the limitation of reaction rates by the speed of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas) systems.

Mixture : A material of variable composition that contains two or more substances.

A material that can be separated into two or more substances using physical means. *Example:* a mixture of copper(ii) sulphate and cadmium sulphide .can be separated by filtration.

A substance that contains two or more elements or compounds that retain their chemical identity and can be separated into the individual components by a physical process. For example, the mixture of O_2 and N_2 in the atmosphere.

Möbius aromaticity : A monocyclic array of orbitals in which there is a single out-of-phase overlap (or, more generally, an odd number of out-of-phase overlaps) reveals the opposite pattern of *aromatic* character to Hückel systems; with $4n$ electrons it is stabilized (aromatic), whereas with $4n + 2$ it is destabilized (antiaromatic). In the excited state $4n + 2$ Möbius pi-electron systems are stabilized, and $4n$ systems are destabilized. No examples of ground-state Möbius pi systems are known, but the concept has been applied to *transition states of pericyclic reactions* [see *aromatic* (3)]. The name is derived from the topological analogy of such an arrangement of orbitals to a Möbius strip.

Moiety : In physical organic chemistry moiety is generally used to signify part of a molecule, e.g. in an ester R^1COOR^2 the alcohol moiety is R^2O . The term should not be used for a small fragment of a molecule.

Molality (m) : The number of moles of solute in a solution divided by the number of kilograms of solvent.

Compare with molarity. Concentration measured as moles of solute per kilogram of solvent. For example, a 1 *m* NaCl solution contains 1 mole of NaCl per kilogram of water. Molalities are preferred over molarities in experiments that involve temperature changes of solutions, e. g. calorimetry and freezing point depression experiments.

Molar : Of or pertaining to moles.

A synonym for molarity; for example, a "six molar solution of hydrochloric acid" contains 6 moles of HCl per liter of solution.

Molar absorptivity : (ϵ) molar extinction coefficient; molar absorption cross section. Compare with absorptivity and absorbance. The absorbance per centimeter of path length when the concentration of absorbing material is 1 M; $\epsilon = A/(bc)$ where a , A , b , and c are the molar absorptivity, absorbance, path length in cm, and concentration in mol/L, respectively. Molar absorptivities are sometimes written as absorption cross sections by expressing the concentration in units of mol/cm³, so that the molar absorptivity takes on units of cm²/mol.

Molar heat capacity (C) : The number of joules of heat required to raise the temperature of a mole of a substance by 1 K.

Atomic heat capacity. Compare with molar heat capacity and specific heat. The heat required to raise the temperature of one mole of a substance by 1°C is called the molar heat capacity of the substance. Molar heat capacity is an intensive property with SI system units of J mol⁻¹ K⁻¹. The molar heat capacity of elements is sometimes called the "atomic heat capacity".

The amount of energy required to raise the temperature of one mole of a substance by one degree Celsius (or Kelvin).

Molar mass : Literally, the mass of a mole. Often used by chemists who are not comfortable using the term molecular weight to describe measurements of mass.

The mass of one mole of a material. For example, the molar mass of H₂O is 18.015 g (obtained by adding twice the molar mass of hydrogen to the molar mass of oxygen). 3. The mass per mole of atoms of an element. It has the same value and uses the same units as atomic weight. *Example*: molar mass of chlorine is 35.45 g/mol.

Molar volume : The volume occupied by one mole of a material. For example, the molar volume of an ideal gas at STP is 22.4 L/mol.

Molarity : (M) Molar concentration. Concentration of a solution measured as the number of moles of solute per liter of solution. For example, a 6 M HCl solution contains 6 moles of HCl per liter of solution.

The number of moles of a solute in a solution divided by the volume of the solution in liters.

Mole : (mol) SI unit for amount of substance, defined as the number of atoms in exactly 12 g of carbon-12. One mole of a molecular compound contains Avogadro's number molecules and has a mass equal to the substance's molecular weight, in grams.

1 mole is the amount of a substance which contains Avogadro's number (6×10^{23}) of particles. *Example:* 1 mole of carbon-12 weighs exactly 12 g.

Literally, a small mass. The amount of any substance that contains the same number of atoms, ions, or molecules as there are ^{12}C atoms in exactly 12 grams of the ^{12}C isotope.

Mole fraction : Literally, the fraction of the total number of moles in a mixture due to one component of the mixture. The mole fraction of a solute, for example, is the number of moles of solute divided by the total number of moles of solute plus solvent.

Concentration of a substance in a mixture measured as moles of the substance per mole of mixture. For example, the mole fraction of oxygen in air is about 0.21, which means that 1 mol of air contains about 0.21 mol O_2 .

Mole ratio : The ratio of the moles of one reactant or product to the moles of another reactant or product in the balanced equation for a chemical reaction.

Molecular entity : Any constitutionally or isotopically distinct atom, *molecule*, ion, *ion pair*, *radical*, *radical ion*, *complex*, conformer etc., identifiable as a separately distinguishable entity. Molecular entity is used in this glossary as a general term for singular entities, irrespective of their nature, while *chemical species* stands for sets or ensembles of molecular entities. Note that the name of a compound may refer to the respective molecular entity or to the chemical species, e.g. methane, may mean a single molecule of CH_4 (molecular entity) or a molar amount, specified or not (chemical species), participating in a reaction. The degree of precision necessary to describe a molecular entity depends on the context. For example "hydrogen molecule" is an adequate definition of a certain molecular entity for some purposes, whereas for others it is

necessary to distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the hydrogen molecule.

Molecular equation : A molecular equation is a balanced chemical equation in which ionic compounds are written as neutral formulas rather than as ions. For example, $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) = \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$ is a molecular equation; $\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{AgCl}(\text{s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ is not.

Molecular formula : Formula; chemical formula. Compare with empirical formula. A notation that indicates the type and number of atoms in a molecule. The molecular formula of glucose is $\text{C}_6\text{H}_{12}\text{O}_6$, which indicates that a molecule of glucose contains 6 atoms of carbon, 12 atoms of hydrogen, and 6 atoms of oxygen.

Molecular geometry : The three-dimensional shape of a molecule. For example, methane (CH_4) has a tetrahedral molecular geometry.

The study of molecular shapes.

The shape, or geometry, of a molecule as defined by the positions of its nuclei.

Molecular mechanics calculation : An empirical calculational method intended to give estimates of structures and energies for conformations of molecules. The method is based on the assumption of "natural" bond lengths and angles, deviation from which leads to strain, and the existence of torsional interactions and attractive and/or repulsive *van der Waals* and dipolar forces between non-bonded atoms. The method is also called "(empirical) force-field calculations".

Molecular metal : A non-metallic material whose properties resemble those of metals, usually following oxidative doping; e.g. polyacetylene following oxidative doping with iodine.

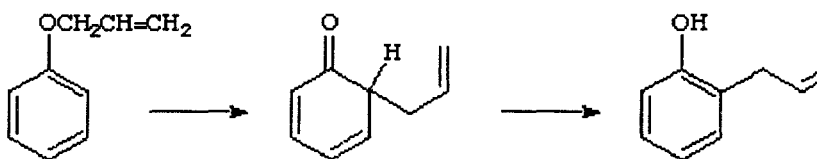
Molecular model : Stick model; ball and stick model; spacefilling model. A representation of a molecule. The model can be purely computational or it can be an actual physical object. Stick models show bonds, ball-and-stick models show bonds and atoms, and spacefilling models show relative atomic sizes.

Molecular orbital : A one-electron wavefunction describing an electron moving in the effective field provided by the nuclei and all other electrons of a *molecular entity* of more than one atom. Such molecular orbitals can be transformed in prescribed ways into component functions to give "localized molecular orbitals". Molecular orbitals can also be described, in terms of the number of nuclei (or "centres") encompassed, as two-centre, multi-centre, etc. molecular orbitals, and are often expressed as a linear combination of *atomic orbitals*. An orbital is usually depicted by sketching contours on which the wavefunction has a constant value (contour map) or by indicating schematically the envelope of the region of space in which there is an arbitrarily fixed high (say 96%) probability of finding the electron occupying the orbital, giving also the algebraic sign (+ or -) of the wavefunction in each part of that region.

A region in space within a molecule where electrons can be found. Molecular orbitals are formed by the overlap, or mixing, of atomic orbitals.

Compare with atomic orbital and orbital. A wavefunction that describes the behavior of an electron in a molecule. Molecular orbitals are usually spread across many atoms in the molecule, and they are often described as a combination of atomic orbitals on those atoms.

Molecular rearrangement : The term is traditionally applied to any reaction that involves a change of connectivity (sometimes including hydrogen), and violates the so-called "principle of minimum structural change". According to this oversimplified principle, *chemical species* do not isomerize in the course of a *transformation*, e.g. *substitution*, or the change of a functional *group* of a chemical species into a different functional group is not expected to involve the making or breaking of more than the minimum number of bonds required to effect that transformation. For example, any new substituents are expected to enter the precise positions previously occupied by displaced groups. The simplest type of rearrangement is an *intramolecular* reaction in which the product is isomeric with the reactant (one type of "intramolecular isomerization"). An example is the first step of the Claisen rearrangement :



The definition of molecular rearrangement includes changes in which there is a *migration* of an atom or bond (unexpected on the basis of the principle of minimum structural change), as in the reaction $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{AgOAc} \longrightarrow (\text{CH}_3)_2\text{CHOAc} + \text{AgBr}$ where the *rearrangement stage* can formally be represented as the "1,2-shift" of hydride between adjacent carbon atoms in the carbocation $\text{CH}_3\text{CH}_2\text{CH}_2^+ \longrightarrow (\text{CH}_3)_2\text{CH}^+$. Such migrations occur also in radicals, e.g.:



The definition also includes reactions in which an *entering group* takes up a different position from the *leaving group*, with accompanying bond migration. An example of the latter type is the "allylic rearrangement": $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Br} + \text{OH}^- \longrightarrow (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2 + \text{Br}^-$. A distinction is made between "intramolecular rearrangements" (or "true molecular rearrangements") and "intermolecular rearrangements" (or "apparent rearrangements"). In the former case the atoms and groups that are common to a reactant and a product never separate into independent fragments during the rearrangement stage (i.e. the change is intramolecular), whereas in an "intermolecular rearrangement" a migrating group is completely free from the parent molecule and is re-attached to a different position in a subsequent step, as in the Orton reaction: $\text{PhN}(\text{Cl})\text{COCH}_3 + \text{HCl} \longrightarrow \text{PhNHCOCH}_3 + \text{Cl}_2 \longrightarrow o\text{- and } p\text{-ClC}_6\text{H}_4\text{NHCOCCH}_3 + \text{HCl}$ MAYO (1980).

Molecular sieve : A material that contains many small cavities interconnected with pores of precisely uniform size. Zeolites are an example. Molecular sieves adsorb molecules that are small enough to pass through their pore systems- especially water. They are often used as drying agents, and to separate large molecules from smaller ones in preparatory work and in exclusion chromatography.

Molecular solid : A substance that consists of individual molecules held together in the solid by relatively weak intermolecular bonds.

Molecular weight : Molecular mass. Compare with formula weight and molecular formula.

The weight of the molecular formula, calculated from a table of atomic weights. The weighted average of the masses of the individual molecules in the substance. Because of the presence of different isotopes, the molecular weight differs from the precise mass of a single molecule.

Molecularity : Number of molecules consumed in a step of a chemical reaction. See bimolecular and unimolecular.

The number of reactant *molecular entities* that are involved in the "microscopic chemical event" constituting an *elementary reaction*. (For reactions in solution this number is always taken to exclude molecular entities that form part of the *medium* and which are involved solely by virtue of their solvation of solutes.) A reaction with a molecularity of one is called "unimolecular", one with a molecularity of two "bimolecular" and of three "termolecular".

Molecularity of a reaction : the number of species forming the transition state

Molecule : A group of two or more atoms held together by chemical bonds. *Example*: O₂.

An electrically neutral entity consisting of more than one atom ($n > 1$). Rigorously, a molecule, in which $n > 1$ must correspond to a depression on the potential energy surface that is deep enough to confine at least one vibrational state. See also *molecular entity*.

Compare with atom and ion. The smallest particle of an element or compound that retains the chemical properties of the element or compound. A molecule is a collection of chemically bound atoms with characteristic composition and structure. Making or breaking bonds in a molecule changes it into a new molecule. Ionic compounds are not composed of molecules, because there is no distinct collection of ions that are chemically bound in the crystal.

The smallest particle that has any of the chemical or physical properties of an element or compound.

Momentum : (p) Momentum is a property that measures the tendency of a moving object to keep moving in the same direction. Increasing the speed of an object increases its momentum, and a heavy object will have more momentum than a lighter one moving at the same speed. For a particle with mass m and velocity v , the momentum of the particle is mv .

The product of the mass times the velocity of an object in motion.

Monitoring : Area-wide analytical monitoring of chemical contamination.

Monochromatic : Radiation that has a single wavelength.

Monoclinic system : A grouping of crystals that look like double-ended chisel blades.

Monodentate : A ligand that has only one atom that coordinates directly to the central atom in a complex. For example, ammonia and chloride ion are monodentate ligands of copper in the complexes $[\text{Cu}(\text{NH}_3)_6]^{2+}$ and $[\text{CuCl}_6]^{2+}$.

Literally, "one toothed." Used to describe ligands, such as water or ammonia, that can only coordinate to a transition metal once.

Monomer : A small molecule and building block for larger chain molecules or polymers ('mono' means one, 'mer' means part).
Examples: tetrafluoroethene for teflon, ethene for polyethene

A small molecule that is linked with large numbers of other small molecules to form a chain or a network (polymer).

One of the relatively small molecules from which polymers are formed.

Monoprotic acid (HA) : An acid, such as HCl or HCN, that can lose only one H^+ ion or proton.

Monosaccharides : The simplest carbohydrates. A carbohydrate that cannot be decomposed into simpler carbohydrates by hydrolysis. Capable of being hammered into sheets. Metals are typically malleable materials.

A carbohydrate that cannot be hydrolyzed to a simpler carbohydrate. See disaccharide and polysaccharide.

More O'Ferrall-Jencks diagram : Visualization of the potential energy surfaces for a reacting system, as a function of two chosen coordinates. It is particularly useful to discuss structural effects on the *transition state* geometry for processes occurring either by stepwise or concerted routes. The use of such diagrams, first suggested for elimination reaction, was later extended to acid-base catalysis and to certain other reaction.

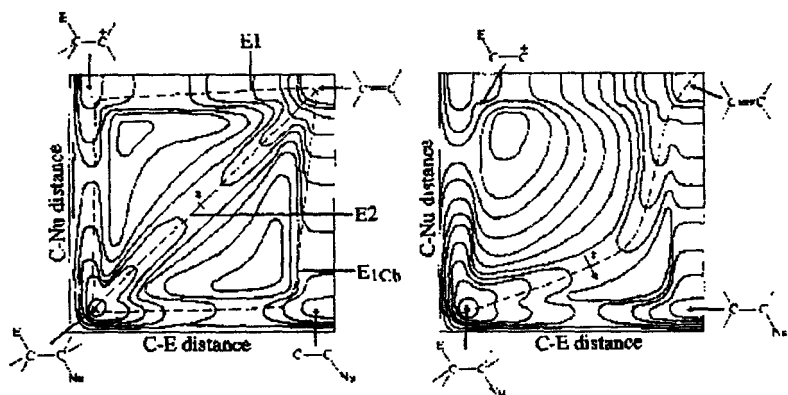


Figure. More O'Ferrall-Jencks diagrams of energy contours for β -elimination reactions as a function of lengths of the two bonds broken. Reaction coordinates follow the dotted lines.

Left : E_2 mechanism with "central" character, simultaneous fission of C^α -Nu and C^β -H bonds.

Right : The result of stabilization of the carbanion, Nu-C-C^- ; a continuation of this trend would result in a switch to the *Elcb* mechanism (Reproduced from N. S. ISAACS, "Physical Organic Chemistry", Longman Scientific, Essex, UK, (1987), with permission of Longman Scientific). Structural changes influencing vibrational modes of the transition states cause changes in transition state geometry. Changes in the direction of the reaction coordinate (reactant or product stabilizing- or destabilizing factors) cause changes according to the *Hammond principle*. Structural changes perpendicular to the reaction coordinate (anti-Hammond effects, perpendicular effects) cause changes opposite to the Hammond behaviour, i.e., the easier the process related to the structural change, the more advanced it will be at the transition state.

Mother liquor : The solution in recrystallization.

m-RNA : Messenger RNA. The polynucleotide that codes for the synthesis of a protein. m-RNA is assembled during transcription of a chain of DNA.

MSDS : material safety data sheet. Safety information sheet for a particular substance that lists physical properties, hazards, cleanup and disposal procedures, fire and explosion data, and protective equipment required.

MSG : monosodium glutamate. MSG is monosodium glutamate, used as a flavor enhancer in many foods.

μ : Notation for a ligand (prefix) that bridges two or more metal centres. The symbol μ is used for dipole moments.

Multi-centre bond : Representation of some *molecular entities* solely by localized two-electron two-centre *bonds* appears to be unsatisfactory. Instead, multi-centre bonds have to be considered in which electron pairs occupy orbitals encompassing three or more atomic centres. Examples include the three-centre bonds in diborane, the delocalized pi bonding of benzene, and *bridged carbocations*.

Multi-centre reaction : A synonym for *pericyclic reaction*. The number of "centres" is the number of atoms not bonded initially, between which single bonds are breaking or new bonds are formed in

the *transition state*. This number does not necessarily correspond to the ring size of the transition state for the pericyclic reaction. Thus, a Diels-Alder reaction is a "four-centre reaction". This terminology has largely been superseded by the more detailed one developed for the various pericyclic reactions.

Multident : See *ambident*.

Multiple bond : Sharing of more than one electron pair between bonded atoms. A double bond consists of two shared pairs of electrons; a triple bond consists of three shared pairs.

Mutarotation : Name given to the phenomenon that occurs when glucose is dissolved in water. There is an equilibrium that is formed between the open-chain form and the alpha and beta pyranose forms. The beta is the most stable conformation because it puts the -OH in an equatorial position and thus most of the glucose in the aqueous solution is in the beta form.



n- σ delocalization (or n- σ no bond resonance) :
Delocalization of a free electron pair (n) into an antibonding σ -orbital (s).

Nano- : (n) Prefix used in the SI system meaning "multiply by 10^{-9} ". For example 1 nm means "0.000000001 m"; 2.8 ng could also be written " 2.8×10^{-9} g".

Nanometer : (nm) A unit of length, equal to 10^{-9} meters, and equal to 10 Å (Angstroms).

Narcissistic reaction : A *chemical reaction* that can be described as the conversion of a reactant into its mirror image, without rotation or translation of the product, so that the product enantiomer actually coincides with the mirror image of the reactant molecule. Examples of such reactions are cited under the entries *fluxional* and *degenerate rearrangement*. SALEM (1971).

Native : Naturally occurring forms of precious metals, for example, native copper, native gold, and native silver. Native metals are often very impure.

Native element : An element that occurs in an uncombined state. *Examples:* sulphur, gold.

Native metal : A pure form of a metal, not combined as a compound. Native metal is more common in poorly reactive elements than in those that are very reactive. *Examples:* copper, gold.

Natural abundance : Compare with isotopic abundance. The average fraction of atoms of a given isotope of an element on Earth.

Natural gas : A mixture of methane and other gases, found trapped over petroleum deposits under the earth.

Natural radioactivity : The radioactive decay that occurs naturally, as opposed to induced radioactivity. Also known as spontaneous fission.

Needle valve : A valve which allows fine control over the rate of gas or liquid flowing through it. The valve contains a thin needle with a point that fits into a conical cup. When the valve is closed, the needle blocks an orifice in the bottom of the cup.

Negative electrode : The electrode in an electrochemical cell that carries a negative charge. In an electrolytic cell, it is the cathode. In a voltaic cell, it is the anode.

Neighbouring group participation : The direct interaction of the reaction centre (usually, but not necessarily, an incipient *carbenium centre*) with a lone pair of electrons of an atom or with the electrons of a sigma or pi bond contained within the parent molecule but not conjugated with the reaction centre. A distinction is sometimes made between n, sigma, and pi participation. A rate increase due to neighbouring group participation is known as "anchimeric assistance". "Synartetic acceleration" is the special case of anchimeric assistance ascribed to participation by electrons binding a substituent to a carbon atom in a β -position relative to the leaving group attached to the α -carbon atom. According to the underlying model, these electrons then provide a three-centre bond (or "bridge") "fastening together" (as the word "synartetic" is intended to suggest) the α - and β -carbon atoms between which the charge is divided in the intermediate *bridged ion* formed (and in the *transition state* preceding its formation). The term synartetic acceleration is not widely used.

Nernst equation : Describes the relationship between the potential of an electrochemical cell at any moment in time and the standard-state cell potential. Used to understand what happens to the potential of a voltaic cell as it comes to equilibrium.

Net chemical reaction : Net reaction A reaction that actually occurs as several elementary steps. Equations for net reactions often omit intermediates and catalysts.

Net ionic equation : Compare with net ionic equation and molecular equation. A net ionic equation is an ionic equation with all **DEFINE** [spectator ions">spectator ions eliminated. For example, $\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{AgCl}(\text{s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ is an ionic equation; the net ionic equation would be $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{AgCl}(\text{s})$ because the sodium and nitrate ions are spectators (they appear on both sides of the ionic equation).

Net ionic reaction : The overall, or net, change that occurs in a reaction, seen in terms of ions.

Network covalent solid : Network covalent substance. A substance which consists of an array of atoms held together by an array of covalent bonds. A crystal of a network covalent solid is actually a single, gigantic molecule. Diamond and quartz are examples.

Neurotransmitter : Neurotransmitters are molecules that are used to carry signals from one neuron to another. One neuron releases the neurotransmitter near another neuron's receptors. The neurotransmitter diffuses across the gap between the neurons and locks into a receptor site on the surface of the downstream neuron. This induces a change in the downstream neuron.

Neutron-poor nuclide : A nuclide with fewer neutrons than the lightest stable isotope of the element. A nuclide that decays by either electron capture, positron emission, or the emission of an alpha particle.

Neutral : Having no net electrical charge. Atoms are electrically neutral; ions are not.

A solution containing equal concentrations of H^+ and OH^- .

Neutralisation : The reaction of acids and bases to produce a salt and water. The reaction causes hydrogen from the acid and hydroxide from the base to be changed to water. *Example:* hydrochloric acid reacts with, and neutralises, sodium hydroxide to form the salt sodium chloride (common salt) and water. The term is more generally used for any reaction in which the pH changes toward 7.0, which is the pH of a neutral solution.

Neutralization reaction : Neutralization; acid-base reaction. A chemical change in which one compound acquires H^+ from another.

The compound that receives the hydrogen ion is the base; the compound that surrenders it is an acid.

Neutrino : A particle with no charge and little or no mass that is ejected from the nucleus at the same time as an electron or positron.

An elementary particle produced by certain nuclear decay processes. Neutrinos have no charge and extremely small masses compared to other subatomic particles.

(n, ^1_0n) Compare with proton and electron. An elementary particle found in the atomic nucleus of all stable atoms except the hydrogen-1 atom. Neutrons have no charge and have a mass of 1.008665 daltons.

Neutron : A particle inside the nucleus of an atom that is neutral and has no charge.

A subatomic particle with a mass of about 1 amu and no charge.

Neutron activation analysis : Activation analysis. An extremely sensitive technique for analyzing trace amounts of elements in a sample. The sample is bombarded with neutrons in a nuclear reactor, making it radioactive. Different elements produce different 'signatures' in the induced radiation which makes determination of their concentration in the sample possible.

Neutron-rich nuclide : A nuclide with more neutrons than the heaviest stable isotope of the element. A nuclide that decays by the emission of an electron.

Newton (N) : The unit of force required to give one kilogram an acceleration of one metre per second every second (1 ms^{-2}).

Newtonian fluid : Compare with non-Newtonian fluid. A fluid whose viscosity doesn't depend on gradients in flow speed. Gases and low-molecular weight liquids are usually Newtonian fluids.

NIH shift : The *intramolecular* hydrogen *migration* which can be observed in enzymatic and chemical hydroxylations of aromatic rings. It is evidenced by appropriate deuterium labelling, i.e.



In enzymatic reactions the NIH shift is generally thought to derive from the rearrangement of arene oxide intermediates, but other pathways have been suggested. (NIH stands for National Institutes of Health where the shift was discovered).

Nitrate : (NO_3^-) The NO_3^- ion, formed by reaction of nitric acid with a base.

A compound containing the NO_3^- ion, for example ammonium nitrate, NH_4NO_3 .

A compound that includes nitrogen and oxygen and contains more oxygen than a nitrite. Nitrate ions have the chemical formula NO_3^- . *Examples*: sodium nitrate NaNO_3 and lead nitrate $\text{Pb}(\text{NO}_3)_2$.

Nitrene : Generic name for HN : and substitution derivatives thereof, containing an electrically neutral univalent nitrogen atom with four non-bonding electrons. Two of these are paired; the other two may have parallel spins (triplet state) or antiparallel spins (singlet state). The name is the strict analogue of *carbene* and, as a generic name, it is preferred to a number of alternatives proposed ("imene", "imine radical", "azene", "azylene", "azacarbene", "imin", "imidogen").

Nitrenium ion : The cation H_2N^+ and its *N*-hydrocarbyl derivatives R_2N^+ , in which the nitrogen has a positive charge, and two unshared electrons. A synonymous term is aminylium ion.

Nitric acid : (HNO_3) aqua fortis. A corrosive liquid with a sharp odor that acts as a strong acid when dissolved in water. Nitric acid is used to synthesize ammonium nitrate for fertilizers, and is also used in the manufacture of explosives, dyes, and pharmaceuticals. Salts of nitric acid are called nitrates.

Nitride : Any compound that contains either the N^{3-} ion or nitrogen with an oxidation state of -3, such as Li_3N or NH_3 .

Nitrite : (NO_2^-) The NO_2^- ion, formed by reaction of nitrous acid with a base.

A compound containing the NO_2^- ion.

Nitrite : A compound that includes nitrogen and oxygen and contains less oxygen than a nitrate. Nitrite ions have the chemical formula NO_2^- . *Example*: sodium nitrite NaNO_2 .

Nitrogen : (N) Element number 7, a colorless, odorless, tasteless gas that makes up about 80% of the earth's atmosphere.

Noble gas core : [(X), where X is the symbol of an inert gas element] core configuration. Compare with valence shell. All completely filled shells underneath the valence shell.

Noble gases : The members of Group 8 of the Periodic Table: helium, neon, argon, krypton, xenon, radon. These gases are almost entirely unreactive.

Noble metals : Silver, gold, platinum and mercury. These are the least reactive metals.

Node : A point, region, or surface where the amplitude of a standing wave is zero. The probability of finding an electron at an orbital node is zero.

Nomenclature : A system for naming things. For example, "organic nomenclature" is the system used to name organic compounds.

A systematic way of naming chemical compounds.

Nonbonding electrons : Electrons in the valence shell of an atom that are not used to form covalent bonds.

Nonbonding molecular orbital : A molecular orbital whose energy is more or less equal to the energy of the atomic orbitals from which it is formed.

Nonclassical carbocation : A *carbocation* the ground state of which has delocalized (bridged) bonding pi- or sigma-electrons. (N.B.: Allylic and benzylic carbocations are not considered nonclassical).

Non-combustible : A substance that will not combust or burn.

Example: carbon dioxide.

Nonelectrolyte : A nonelectrolyte is a substance which does not ionize in solution.

Nonionizing radiation : Radiation that carries enough energy to excite an atom or molecule, but not enough energy to remove an electron from the atom or molecule.

Nonmetal : (metal,metalloid) non-metal. A nonmetal is a substance that conducts heat and electricity poorly, is brittle or waxy or gaseous, and cannot be hammered into sheets or drawn into wire. Nonmetals gain electrons easily to form anions. About 20% of the known chemical elements are nonmetals.

A brittle substance that does not conduct electricity.

Examples: sulphur, phosphorus, all gases.

An element that lacks the properties generally associated with metals.

Non-Newtonian fluid : Compare with Newtonian fluid. A fluid whose viscosity changes when the gradient in flow speed changes. Colloidal suspensions and polymer solutions like ketchup and starch/water paste are non-Newtonian fluids.

Nonparticulate : Not composed of distinct particles.

Nonpolar : Having a relatively even or symmetrical distribution of charge.

Used to describe compounds that do not carry a dipole moment.

Nonpolar molecule : A molecule in which the center of positive charge and the center of negative charge coincide. Examples are CCl_4 and CO_2 ; counterexamples are CHCl_3 and H_2O .

Normal kinetic isotope effect : See *isotope effect*.

Normal salt : Salts that do not contain a hydroxide (OH^-) ion, which would make them basic salts, or a hydrogen ion, which would make them acid salts. *Example:* sodium chloride (NaCl).

Normality : (N) normal. A measure of solution concentration, defined as the number of equivalents of solute per liter of solution.

Nuclear binding energy : Energy needed to break an atomic nucleus into separate protons and neutrons.

Nuclear fission : Fission. Splitting of a nucleus into two smaller nuclei and neutrons. The smaller nuclei have higher binding energy than the original nucleus, and fission results in the release of energy.

Nuclear fusion : Fusion. Combination of two smaller nuclei to form a larger nucleus. The larger nucleus has higher binding energy per nucleon than the original nuclei, and fusion results in the release of energy.

Nucleation : The process of providing sites for new bubbles to form in a liquid that is boiling or supersaturated with gas;

New droplets to condense from a supersaturated vapor, or

New crystals to form in a supersaturated solution. Nucleation sites can be scratches in a surface, dust particles, seed crystals, and so on.

Nucleic acid : A molecule of very high molecular weight used to store and process the genetic information in cells.

A polymer made of repeating nucleotides. Examples are DNA and RNA.

Nucleofuge : A *leaving group* that carries away the bonding electron pair. For example, in the *hydrolysis* of an alkyl chloride, Cl^- is the nucleofuge. The tendency of atoms or groups to depart with the bonding electron pair is called nucleofugality. The adjective is nucleofugal.

Nucleon : A proton or neutron.

Nucleophile : A species that **loves** a nucleus. Since nuclei are positively charged, nucleophiles are negatively charged or bear a partial negative charge. Examples are lone pairs or a hydroxide ion.

Literally, something that loves nuclei. All nucleophiles are Lewis bases.

A nucleophile (or nucleophilic reagent) is a reagent that forms a bond to its reaction partner (the *electrophile*) by donating both bonding electrons. A "nucleophilic substitution reaction" is a *heterolytic* reaction in which the reagent supplying the entering group acts as a nucleophile. For example MeO^- (nucleophile) + $\text{Et-Cl} \longrightarrow \text{MeOEt} + \text{Cl}^-$ (nucleofuge). The term "nucleophilic" is also used to designate the apparent polar character of certain *radicals*, as inferred from their higher relative reactivity with reaction sites of lower electron density. Nucleophilic reagents are *Lewis bases*.

Nucleophilic catalysis : *Catalysis* by a *Lewis base*, involving formation of a *Lewis adduct* as a *reaction intermediate*. For example, the hydrolysis of acetic anhydride in aqueous solution catalysed by pyridine: $\text{C}_5\text{H}_5\text{N} + (\text{CH}_3\text{CO})_2\text{O} \longrightarrow [\text{C}_5\text{H}_5\text{NCOCH}_3]^+ + \text{CH}_3\text{CO}_2^-$
 $[\text{C}_5\text{H}_5\text{NCOCH}_3]^+ + \text{H}_2\text{O} \longrightarrow \text{C}_5\text{H}_5\text{N} + \text{CH}_3\text{CO}_2\text{H} + \text{H}^+_{\text{aq}}$

Nucleophilic substitution reaction : A reaction in which one nucleophile is substituted for another in a molecule.

Nucleophilicity : The property of being *nucleophilic*.

The relative reactivity of a *nucleophilic* reagent. (It is also sometimes referred to as "nucleophilic power".) Qualitatively, the concept is related to Lewis basicity. However, whereas Lewis basicity is measured by relative

equilibrium constants, $\text{B:} + \text{A} \xrightleftharpoons{K} \text{B}^+-\text{A}^-$ (equilibrium constant K) nucleophilicity of a Lewis base is measured by relative *rate constants* of different nucleophilic reagents towards a common *substrate*, most commonly involving formation of a bond to carbon, $\text{B:} + \text{A-Z} \xrightarrow{k} \text{B}^+-\text{A}^- + \text{Z:}^-$ (rate constant k).

Nucleoside : A nucleotide base bound to a five-carbon sugar.

Nucleotide : The smallest repeating unit out of which nucleic acids are built.

Compare with nucleoside. A molecule which is a basic building block of nucleic acids and which plays a key role in energy transfer in biochemical reactions. Nucleotides consist

of a five-carbon sugar, a heterocyclic nitrogen-containing organic base, and a phosphate group.

Nucleotide base : A heterocyclic nitrogen-containing base that is a constituent of nucleotides. Examples are adenine, guanine, thymine, uracil, and cytosine.

Nucleus : Literally, "little nut." It consists of neutrons and protons, occupies an infinitesimally small fraction of the total volume of an atom, and contains almost all of the mass of an atom. 2. The small, positively charged particle at the centre of an atom. The nucleus is responsible for most of the mass of an atom.

Nuclide : An atom with a particular combination of protons and neutrons, such as the ^{14}C nuclide.

Compare with atomic nucleus and nuclide symbol. An atom or ion with a specified mass number and atomic number. For example, uranium-235 and carbon-14 are nuclides.

Nuclide symbol : Compare with atomic nucleus, nuclide and element symbol. A symbol for an nuclide that contains the mass number as a leading superscript and the atomic number as a leading subscript. For ions, the ionic charge is given as a trailing superscript. For example, the nuclide symbol for the most common form of the chloride ion is $^{35}_{17}\text{Cl}^-$, where 35 is the mass number, 17 is the atomic number, and the charge on the ion is -1. The atomic number is sometimes omitted from nuclide symbols.



Onium ion : A cation (with its counterion) derived by addition of a hydron to a mononuclear parent hydride of the nitrogen, chalcogen and halogen family, e.g. H_4N^+ ammonium ion.

Derivatives formed by substitution of the above parent ions by univalent groups, e.g. $(\text{CH}_3)_2\text{S}^+\text{H}$ dimethylsulfonium, $(\text{CH}_3\text{CH}_2)_4\text{N}^+$ tetraethylammonium.

Derivatives formed by substitution of the above parent ions by groups having two or three free valencies on the same atom. Such derivatives are, whenever possible, designated by a specific class name. E.g. $\text{R}_2\text{C}=\text{NH}_2^+$ iminium ion.

Opaque : A substance that will not transmit light so that it is impossible to see through it. Most solids are opaque.

Open system : A system which can exchange both matter and energy with its surroundings.

Optical isomers : stereoisomers that exist because of the presence of chiral centers.

Optical yield : In a *chemical reaction* involving chiral reactants and products, the ratio of the optical purity of the product to that of the precursor, reactant or catalyst. This should not be confused with "enantiomeric excess". The optical yield is in no way related to the chemical yield of the reaction.

Optically active : A material which can rotate plane-polarized light.

Orbital steering : A concept expressing that the stereochemistry of approach of two reacting species is governed by the most favourable overlap of their appropriate *orbitals*.

Orbital symmetry : The behaviour of an atomic or localized *molecular orbital* under molecular symmetry operations characterizes its orbital symmetry. For example, under a reflection in an appropriate symmetry plane, the phase of the orbital may be unchanged (symmetric), or it may change sign (antisymmetric), i.e. the positive and negative lobes are interchanged. A principal context for the use of orbital symmetry is the discussion of chemical changes that involve "conservation of orbital symmetry". If a certain symmetry element (e.g. the reflection plane) is retained along a reaction pathway, that pathway is "allowed" by orbital symmetry conservation if each of the occupied orbitals of the reactant(s) is of the same symmetry type as a similarly (e.g. singly or doubly) occupied orbital of the product(s). This principle permits the qualitative construction of correlation diagrams to show how molecular orbitals transform (and how their energies change) during idealized chemical changes (e.g. *cycloadditions*). An idealized single bond is a sigma bond, i.e., it has cylindrical symmetry, whereas a p-orbital or pi-bond orbital has pi symmetry, i.e. it is antisymmetric with respect to reflection in a plane passing through the atomic centres with which it is associated. In ethene, the pi-bonding orbital is symmetric with respect to reflection in a plane perpendicular to and bisecting the C-C bond, whereas the pi-antibonding orbital is antisymmetric with respect to this operation. Considerations of orbital symmetry are frequently grossly simplified in that, for example, the pi orbitals of a carbonyl group would be treated as having the same symmetry as those of ethene, and the fact that the carbonyl group in, for example, camphor, unlike that in formaldehyde, has no mirror planes would be ignored. These simplified considerations nevertheless afford the basis of one approach to the understanding of the rules which indicate whether *pericyclic reactions* are likely to occur under thermal or photochemical conditions.

Order of reaction, n (SI unit: 1) : If the macroscopic (observed, empirical or phenomenological) *rate of reaction* (v) for any reaction can be expressed by an empirical differential rate equation (or *rate*

law) which contains a factor of the form $k [A]^\alpha [B]^\beta \dots$ (expressing in full the dependence of the rate of reaction on the concentrations $[A]$, $[B]$...) where α , β are constant exponents (independent of concentration and time) and k is independent of $[A]$ and $[B]$ etc. (rate constant, rate coefficient), then the reaction is said to be of order α with respect to A, of order β with respect to B,..., and of (total or overall) order $\nu = \alpha + \beta + \dots$. The exponents α , β , ... can be positive or negative integral or rational nonintegral numbers. They are the reaction orders with respect to A, B,... and are sometimes called "partial orders of reaction". Orders of reaction deduced from the dependence of initial rates of reaction on concentration are called "orders of reaction with respect to concentration"; orders of reaction deduced from the dependence of the rate of reaction on time of reaction are called "orders of reaction with respect to time". The concept of order of reaction is also applicable to chemical rate processes occurring in systems for which concentration changes (and hence the rate of reaction) are not themselves measurable, provided it is possible to measure a *chemical flux*. For example, if there is a dynamic equilibrium according to the equation $aA \rightleftharpoons pP$ and if a chemical flux is experimentally found, (e.g. by NMR *line shape analysis*) to be related to concentrations by the equation $\phi_{-A/a} = k[A]^\alpha [L]^\lambda$, then the corresponding reaction is of order α with respect to A... and of total (or overall) order $\nu (= \alpha + \lambda + \dots)$. The proportionality factor k above is called the (ν th order) "rate coefficient". Rate coefficients referring to (or believed to refer to) *elementary reactions* are called "rate constants" or, more appropriately "microscopic" (hypothetical, mechanistic) rate constants. The (overall) order of a reaction cannot be deduced from measurements of a "rate of appearance" or "rate of disappearance" at a single value of the concentration of a species whose concentration is constant (or effectively constant) during the course of the reaction. If the overall rate of reaction is, for example, given by $\nu = k[A]^\alpha [B]^\beta$ but $[B]$ stays constant, then the order of the reaction (with respect to time), as observed from the concentration change of A with time, will be α , and the rate of disappearance of A can be

expressed in the form $v_A = k_{\text{obs}}[A]^\alpha$. The proportionality factor k_{obs} deduced from such an experiment is called the "observed rate coefficient" and it is related to the $(\alpha + \beta)$ th order rate coefficient k by the equation $k_{\text{obs}} = k[B]^\beta$. For the common case when $\alpha = 1$, k_{obs} is often referred to as a "pseudo-first order rate coefficient" (k_Ψ). For a simple (*elementary*) reactions a partial order of reaction is the same as the stoichiometric number of the reactant concerned and must therefore be a positive integer (see *rate of reaction*). The overall order is then the same as the *molecularity*. For *stepwise reactions* there is no general connection between stoichiometric numbers and partial orders. Such reactions may have more complex rate laws, so that an apparent order of reaction may vary with the concentrations of the *chemical species* involved and with the progress of the reaction: in such cases it is not useful to speak of orders of reaction, although apparent orders of reaction may be deducible from initial rates. In a *stepwise reaction*, orders of reaction may in principle always be assigned to the elementary steps.

Ore : A rock containing enough of a useful substance to make mining it worthwhile. *Example*: bauxite, aluminium ore.

Organic acid : An acid containing carbon and hydrogen. *Example*: methanoic (formic) acid (HCOOH).

Organic Acids : THE CARBOXYLIC ACID GROUP $\text{R}-\text{C}(=\text{O})\text{OH}$ -oic acid | O-H COMMON ACIDS Methanoic acid (formic acid)-- bee stings. Ethanoic acid (acetic acid)-- vinegar. Butanoic acid (yuk)- essence of barf. SALICYLIC ACID Phenol with an acid group attached. Part of aspirin.

Organic chemistry : The study of organic compounds.

Organic compound (organic substance; organic material) : a compound (or substance) that contains carbon and usually hydrogen. (The carbonates are usually excluded.) *Examples*: methane (CH_4), chloromethane (CH_3Cl), ethene (C_2H_4), ethanol ($\text{C}_2\text{H}_5\text{OH}$), ethanoic acid ($\text{C}_2\text{H}_3\text{OOH}$), etc.

Organic solvent : An organic substance that will dissolve other substances. *Example*: carbon tetrachloride (CCl_4).

Osmosis : A process whereby molecules of a liquid solvent move through a semipermeable membrane from a region of low concentration of a solute to a region with a high concentration of a solute.

Outer-sphere (electron transfer) : An outer-sphere electron transfer is a reaction in which the electron transfer takes place with no or very weak ($4 - 16 \text{ kJ mol}^{-1}$) electronic interaction between the reactants in the transition state. If instead the donor and the acceptor exhibit a strong electronic coupling, the reaction is described as inner-sphere electron transfer. The two terms derive from studies concerning metal complexes and it has been suggested that for organic reactions the term "nonbonded" and "bonded" electron transfer should be used.

Oxidation : The complete, net removal of one or more electrons from a *molecular entity* (also called "de-electronation").

An increase in the *oxidation number* of any atom within any *substrate*.

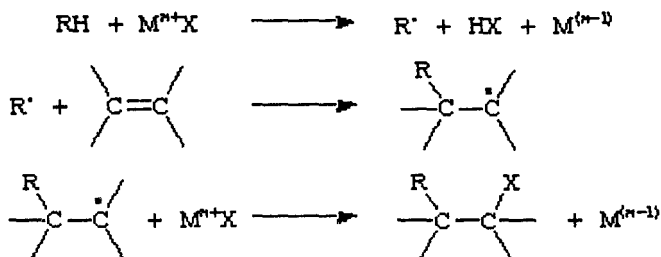
Gain of oxygen and/or loss of hydrogen of an organic *substrate*. All oxidations meet criteria (1) and (2), and many meet criterion (3), but this is not always easy to demonstrate. Alternatively, an oxidation can be described as a *transformation* of an organic substrate that can be rationally dissected into steps or *primitive changes*. The latter consist in removal of one or several electrons from the substrate followed or preceded by gain or loss of water and/or *hydrons* or hydroxide ions, or by *nucleophilic* substitution by water or its reverse and/or by an *intramolecular molecular rearrangement*. This formal definition allows the original idea of oxidation (combination with oxygen), together with its extension to removal of hydrogen, as well as processes closely akin to this type of

transformation (and generally regarded in current usage of the term in organic chemistry to be oxidations and to be effected by "oxidizing agents") to be descriptively related to definition (1). For example the oxidation of methane to chloromethane may be considered as follows: $\text{CH}_4 - 2\text{e}^- - \text{H}^+ + \text{OH}^- = \text{CH}_3\text{OH}$ (oxidation) $\longrightarrow \text{CH}_3\text{Cl}$ (reversal of hydrolysis)

Oxidation number (oxidation state) : The effective charge on an atom in a compound. An increase in oxidation number corresponds to oxidation, and a decrease to reduction. Shown in Roman numerals. *Example:* manganate(IV).

Oxidation-reduction reaction (redox reaction) : Reaction in which oxidation and reduction occurs; a reaction in which electrons are transferred. *Example:* copper and oxygen react to produce copper(II) oxide. The copper is oxidised, and oxygen is reduced.

Oxidative addition : The *insertion* of a metal of a metal complex into a covalent bond involving formally an overall two-electron loss on one metal or a one-electron loss on each of two metals, i.e., $\text{L}_n\text{M}^m + \text{XY} \longrightarrow \text{L}_n\text{M}^{m+2}(\text{X})(\text{Y})$, or $2 \text{L}_n\text{M}^m + \text{XY} \longrightarrow \text{L}_n\text{M}^{m+1}(\text{X}) + \text{L}_n\text{M}^{m+1}(\text{Y})$. In free-radical chemistry, the term is used to indicate a free radical addition to a carbon-carbon double bond, under oxidative conditions. For example:



Oxidative coupling : The coupling of two *molecular entities* through an oxidative process, usually catalysed by a transition metal compound and involving dioxygen as the oxidant; e.g., $2 \text{CO} + 2 \text{MeOH} + 1/2 \text{O}_2$ (+ catalyst) $\longrightarrow \text{MeOOC-COOMe} + \text{H}_2\text{O}$

Oxide : A compound that includes oxygen and one other element. *Example:* copper oxide (CuO).

Oxidise : To combine with or gain oxygen or to react such that an atom, ion or molecule loses electrons to an oxidising agent.

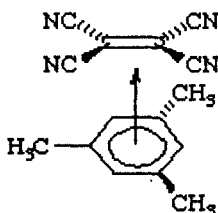
Oxidising agent : A substance that removes electrons from another substance being oxidised (and therefore is itself reduced) in a redox reaction. *Example:* chlorine (Cl_2).

A reactant that accepts electrons from another reactant. The oxidizing agent is the species getting reduced.

Ozone : A form of oxygen whose molecules contain three atoms of oxygen. Ozone is regarded as a beneficial gas when high in the atmosphere because it blocks ultraviolet rays. It is a harmful gas when breathed in, so low level ozone which is produced as part of city smog is regarded as a form of pollution. The ozone layer is the uppermost part of the stratosphere.

P

π -adduct (pi-adduct) : An *adduct* formed by electron-pair donation from a pi orbital into a sigma orbital, or from a sigma orbital into a pi orbital, or from a pi orbital into a pi orbital. For example :



Such an adduct has commonly been known as a "pi complex", but, as the bonding is not necessarily weak, it is better to avoid the term *complex*.

π -electron acceptor, π -electron donor group :—A *substituent* capable of a +R (e.g. NO_2) or -R (e.g. OCH_3) effect, respectively. See *electronic effect, polar effect, σ -constant*.

Paraffin. paraffin wax. A waxy substance that is a mixture of alkanes with chains containing 18 to 36 carbon atoms.

An alkane.

Paramagnetic : A compound that is attracted to a magnetic field. A compound that contains one or more unpaired electrons.

Substances having a magnetic susceptibility greater than 0 are paramagnetic. They are drawn into a magnetic field.

Paramagnetism : Paramagnetic. Compare with diamagnetism and ferromagnetism. Paramagnetic materials are attracted to a

magnetic field due to the presence of least one unpaired spin in their atoms or molecules.

Partial miscibility : Partially miscible. Compare with miscible and immiscible. Two liquids are considered partially miscible if shaking equal volumes of the liquids together results in a meniscus visible between two layers of liquid, but the volumes of the layers are not identical to the volumes of the liquids originally added.

Partial pressure : The fraction of the total pressure of a mixture of gases that is due to one component of the mixture.

The pressure a gas in a mixture would exert if it alone occupied a flask. *Example:* oxygen makes up about a fifth of the atmosphere. Its partial pressure is therefore about a fifth of normal atmospheric pressure.

The independent pressure exerted by different gases in a mixture.

Partial rate factor : The rate of substitution at one specific site in an *aromatic* compound relative to the rate of substitution at one position in benzene. For example, the partial rate factor f_P^Z for para-substitution in a monosubstituted benzene C_6H_5Z is related to the rate constants $k(C_6H_5Z)$ and $k(C_6H_6)$ for the total reaction (i.e. at all positions) of C_6H_5Z and benzene, respectively, and- para (the percentage para-substitution in the total product formed from C_6H_5Z) by the relation

$$f_P^Z = \frac{6k(C_6H_5Z)}{k(C_6H_6)} \frac{\%para}{100}$$

$$f_m^Z = \frac{6k(C_6H_5Z)}{2k(C_6H_6)} \frac{\%meta}{100}$$

Similarly for meta-substitution :

(The symbols p_i^Z , m_i^Z , o_i^Z are also in use.) The term applies equally to the *ipso* position, and it can be extended to other substituted *substrates* undergoing parallel reactions at different sites with the same reagent according to the same *rate law*.

Partial vacuum : A volume that contains traces of gas at very low pressure.

Particle : Any object that has mass and therefore occupies space.

Particulate : Composed of distinct particles. Smoke is particulate; pure gases are not.

Parts per million : (ppm) Concentration expressed as parts of solute per million parts of solution. Usually refers to parts per million by mass. For example, a 10 ppm NaCl solution can be written as: 10 mg NaCl/kg solution, 10 μ g NaCl/g solution, 10 ng NaCl/mg solution. In very dilute aqueous solutions, ppm is approximately equal to mg solute per liter of solution.

Pascal : (Pa) The SI unit of pressure, equal to a force of one newton per square meter. 101325 pascals = 1 atmosphere; 10^5 pascals = 1 bar.

The SI unit of pressure; equal to newtons per meter squared.

Pascal : The unit of pressure, equal to one newton per square metre of surface.

Path function : A property that is dependent on the path taken.

Path length : (b) In absorption spectroscopy, the length of a path taken by radiation through a sample.

Patina : A surface coating that develops on metals and protects them from further corrosion. *Example*: the green coating of copper carbonate that forms on copper statues.

A thin layer of corrosion products with a distinctive coloration that forms on a metal surface exposed to air and water. Patina usually refers to the greenish coating that forms on copper alloys over time.

Pattern recognition : A computational technique used to find patterns and develop classification schemes for data in very large data sets.

Pauli principle : Exclusion principle; Pauli exclusion; Pauli exclusion principle. No two electrons in an atom can have the same set of 4 quantum numbers. Because the n , ℓ , and m_ℓ quantum numbers address a particular orbital, and because the m_s quantum number has only two possible values, the Pauli principle says that a

maximum of two electrons can occupy an atomic orbital- and these electrons must have opposite spins.

Penetration : Electrons in penetrating orbitals can reach the nucleus. The n and ℓ quantum numbers determine how well an orbital penetrates. Lower n and lower ℓ values mean better penetration. A low n value means the orbital is small. A low ℓ value means the orbital has fewer nuclear nodes (planes that pass through the nucleus where the probability of locating the electron is zero). In order of decreasing penetration, the subshells are $s > p > d > f$. A $1s$ orbital penetrates better than a $2s$ orbital.

Peptide : A relatively small polymer of amino acids. Peptides are usually too small to have extensive secondary or tertiary structures.

A short polymer made by linking together amino acid molecules.

Peptide bond : The bond between amino acids in a peptide or protein.

Percent error : Percentage error. The relative error times 100%.

Percent yield : Compare with theoretical yield and actual yield. Percent yield equals experimental yield divided by theoretical yield times 100%.

Percolate : To move slowly through the pores of a rock.

Perfect crystal : A crystal with no defects or impurities, made of completely identical repeating subunits. Further, a perfect crystal has only one possible arrangement of subunits, with every subunit making exactly the same contribution to the total energy of the crystal.

Pericyclic reaction : A *chemical reaction* in which *concerted* reorganization of bonding takes place throughout a cyclic array of continuously bonded atoms. It may be viewed as a reaction proceeding through a fully *conjugated* cyclic transition state. The number of atoms in the cyclic array is usually six, but other numbers are also possible. The term embraces a variety of processes, including *cycloadditions*, *cheletropic reactions*, *electrocyclic*

reactions and sigmatropic rearrangements, etc. (provided they are concerted).

Period : A horizontal row in the periodic table, such as the second period which contains the elements Li, Be, B, C, N, O, F, and Ne.

A row in the Periodic Table.

Period : Rows in the periodic table are called periods. For example, all of the elements in the second row are referred to as 'second period elements'. All elements currently known fall in the first seven periods.

Periodic law : The periodic law states that physical and chemical properties of the elements recur in a regular way when the elements are arranged in order of increasing atomic number.

Periodic Table : A chart organising elements by atomic number and chemical properties into groups and periods.

A matrix in which the elements are arranged across rows in order of increasing atomic number so that elements with similar chemical properties fall in the same vertical column.

An arrangement of the elements according to increasing atomic number that shows relationships between element properties.

A regular variation in element properties with increasing atomic number that is ultimately due to regular variations in atomic structure.

Periselectivity : The differentiation between two symmetry-allowed processes, for example the [2+4] vs. [4+6] *cycloaddition* of cyclopentadiene to tropone.

Permanent hardness : permanent water hardness. Compare with temporary hardness and water hardness. Water hardness that remains after boiling the water, mainly due to dissolved calcium sulfate. Chlorides also contribute to permanent hardness.

Permanganate : (MnO_4^-) permanganate ion. Permanganate ion (MnO_4^-) is a powerful oxidizing agent used in chemical analysis and water treatment. The ion has an intense purple color.

Peroxide : Literally, a compound that is rich in oxygen. Used to describe compounds that formally contain the O_2^{2-} ion.

Persistent : The term persistent is used to characterize *radicals* which have lifetimes of several minutes or greater in dilute solution in inert solvents. Persistence is a kinetic or reactivity property. In contrast, radical stability, which is a thermodynamic property, is expressed in terms of the C-H bond strength of the appropriate hydrocarbon. The lifetime of a radical is profoundly influenced by steric shielding of the radical centre by bulky substituents.

Pestle and mortar : A pestle is a ceramic rod with a rounded end, a mortar is a ceramic dish. Pestle and mortar are used together to pound or grind solids into fine powders.

Petri dish : A shallow glass or plastic dish with a lid.

Petroleum : A natural mixture of a range of gases, liquids and solids derived from the decomposed remains of plants and animals.

Petroleum Processing : SEPARATION OF CRUDE OIL INTO ITS FRACTIONS: FRACTIONAL DISTILLATION Each compound has its own boiling point and can be separated by distillation. Groups of compounds are called boiling fractions. BOILING FRACTIONS: Because these are ranges, there is an overlap of the number of carbons. Bottle gases CH_4 to C_4H_{10} Methane, Ethane, Propane, Butane. Petroleum Ethers C_5H_{12} to C_6H_{14} Highly volatile liquids for solvents. Gasoline C_7 to C_{12} Kerosene and Jet Fuel C_{12} to C_{16} Lubricating Oils C_{16} to C_{20} Greases C_{20} to C_{30} Paraffin Wax C_{30} to C_{40} Asphalt C_{60} and up CRACKING. Breaking up large oil sized molecules into smaller gasoline molecules in order to increase the amount of gasoline produced. $C_{16} \rightarrow 2C_8$ this is done by A) Thermal Pyrolysis (heating sans oxygen so it won't burn) B) Catalytic action The "Cat Cracker" POLYMERIZATION Building large molecules from smaller ones (changing butane into gasoline to increase the yield of the latter). $cat\ 2C_4 \rightarrow C_8$ REFORMING Rearranging molecules to increase "octane rating". Branched and ring chains burn more slowly to increase engine performance. CATALYTIC & ISOMERIZATION Branching the chain: $C-C-C-C-C-C-C \rightarrow C-C-C-C-C | C$ Octane \rightarrow 2,2,4-trimethyl pentane (100 octane gasoline) OCTANE RATING. The comparison of fuel performance in a standard test engine. The octane

rating scale calls Heptane "0 octane" and 2,2,4 - trimethyl pentane "100 octane".

pH : A measure of acidity. The negative of the logarithm of the H_3O^+ ion concentration: $\text{pH} = -\log [\text{H}_3\text{O}^+]$

A measure of the hydrogen ion concentration in a liquid. Neutral is pH 7.0; numbers greater than this are alkaline; smaller numbers are acidic.

pH is a measure of effective concentration of hydrogen ions in a solution. It is approximately related to the molarity of H^+ by $\text{pH} = -\log [\text{H}^+]$

pH meter : A device that accurately measures the pH of a solution. A pH meter is a voltmeter that measures the electric potential difference between two electrodes (which are attached to the meter through a probe) when they are submerged in a solution. The readings are shown on a dial or digital display.

Pharmacognosy : Identification, isolation, and characterization of biologically active substances in living things.

Pharmacology : The study of drugs, which includes determination of biological activity, biological effects, breakdown and synthesis, and delivery.

Phase : A particular state of matter. A substance may exist as a solid, liquid or gas and may change between these phases with addition or removal of energy. *Examples*: ice, liquid and vapour are the three phases of water. Ice undergoes a phase change to water when heat energy is added.

In phase; out of phase; wave phase.

A phase is a part of a sample of matter that is in contact with other parts but is separate from them. Properties within a phase are homogeneous (uniform). For example, oil and vinegar salad dressing contains two phases: an oil-rich liquid, and a vinegar-rich liquid. Shaking the bottle breaks the phases up into tiny droplets, but there are still two distinct phases.

In wave motion, **phase** is the fraction of a complete cycle that has passed a fixed point since the current cycle began. The phase is often expressed as an angle, since a full cycle is 360° ; (2π). Two waves are "in phase" if the peaks of one wave align with the peaks of the other; they are "out of phase" if the peaks of one wave align with the troughs of the other.

Phase boundary : A phase boundary is a surface where two samples of matter with different properties are in contact. The surface of a gas bubble in water or the surface of a crystal are examples of phase boundaries.

Phase change : Phase transition. A change in the state of a sample of matter; for example, solid to liquid or liquid to gas. Phase changes are considered physical rather than chemical changes.

Phase diagram : A two-dimensional graph that shows the state, or phase, of a substance at any combination of temperature and pressure.

Phase map. A map that shows which phases of a sample are most stable for a given set of conditions. Phases are depicted as regions on the map; the borderlines between regions correspond to conditions where the phases can coexist in equilibrium.

Phase-transfer catalysis : The phenomenon of rate enhancement of a reaction between *chemical species* located in different phases (immiscible liquids or solid and liquid) by addition of a small quantity of an agent (called the "phase-transfer *catalyst*") that extracts one of the reactants, most commonly an anion, across the interface into the other phase so that reaction can proceed. These catalysts are salts of "*onium ions*" (e.g. tetraalkylammonium salts) or agents that complex inorganic cations (e.g. *crown ethers*). The catalyst cation is not consumed in the reaction although an anion exchange does occur.

Phenol : A group or molecule containing a benzene ring that has a hydroxyl group substituted for a ring hydrogen.

Phenolphthalein : An organic compound used as an acid-base indicator. The compound is colorless in acidic solution and pink in

basic solution (with the transition occurring around pH 8.3). Phenolphthalein was used for many years as a laxative in very low concentrations- high concentrations are toxic!

Phenolphthalein : A common misspelling of phenolphthalein.

Phenyl : (ϕ) A molecular group or fragment formed by abstracting or substituting one of the hydrogen atoms attached to a benzene ring. -amino- β -3b-phenylpropionic-20acid]">**phenylalanine**. Phe; α -amino- β -phenylpropionic acid].

Phlogiston : An imaginary element once thought to be given off when objects burned.

Phosphate : (PO_4^{-3}) The PO_4^{-3} ion.

A compound containing the PO_4^{-3} ion.

Phosphide : Any compound that contains either the P^{3-} ion or phosphorus with an oxidation state of -3, such as Ca_3P_2 or PH_3 .

Phospholipid : A triester of glycerol with two fatty acids and one phosphate ion. Polar lipids found in biological membranes.

Phospholipid : An ester of glycerol with two fatty acids and phosphoric acid (H_3PO_4) or a derivative of phosphoric acid group (like $\text{H}_2\text{PO}_4\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_3$). Phospholipids have a hydrophilic head (the phosphate group) and a lipophilic tail (the fatty acids).

Phospholipid bilayer : Bilayer; phospholipid membrane. In an aqueous environment phospholipids can form a two-layered "sandwich" with the hydrophobic lipid tails on the inside and the hydrophilic phosphate heads facing outward. These bilayers are the essential structure for building cell membranes.

Phosphor : Any material that glows when energised by ultraviolet or electron beams, such as in fluorescent tubes and cathode ray tubes. Phosphors, such as phosphorus, emit light after the source of excitation is cut off. This is why they glow in the dark. By contrast, fluorescers, such as fluorite, only emit light while they are being excited by ultraviolet light or an electron beam.

Photochemical smog : Photochemical reactions are caused by the energy of sunlight. Photochemical smog is a mixture of tiny particles and a brown haze caused by the reaction of colourless nitric

oxide from vehicle exhausts and oxygen of the air to form brown nitrogen dioxide.

Photochemistry : The study of chemical changes caused by light. For example, many of the key reactions that generate smog are photochemical.

Photoelectric effect : Ejection of electrons from an atom or molecule that has absorbed a photon of sufficient energy. The photoelectric effect is the operating principle behind "electric eyes"; it is experimental evidence for particle-like behavior of electromagnetic radiation.

Photoelectron : An electron ejected from an atom or molecule that has absorbed a photon.

Photolysis : The cleavage of one or more covalent *bonds* in a *molecular entity* resulting from absorption of light, or a photochemical process in which such cleavage is an essential part. For example : $\text{Cl}_2 \longrightarrow 2 \text{Cl}^\cdot$ The term is used incorrectly to describe irradiation of a sample, although in the combination flash photolysis this usage is accepted.

Photon : ($h\nu$) quantum; quanta. A discrete packet of energy associated with electromagnetic radiation. Each photon carries energy E proportional to the frequency ν of the radiation: $E = h\nu$, where h is Planck's constant.

A parcel of light energy.

The smallest unit of electromagnetic energy.

Photosynthesis : A complex process used by many plants and bacteria to build carbohydrates from carbon dioxide and water, using energy derived from light.

The process by which plants use the energy of the Sun to make the compounds they need for life. In six molecules of carbon dioxide from the air combine with six molecules of water, forming one molecule of glucose (sugar) and releasing six molecules of oxygen back into the atmosphere.

pH-rate profile : A plot of observed rate coefficient, or more usually its decadic logarithm, against pH of solution, other variables being kept constant.

Physical change : A change which does not transform one substance into another. For example, freezing water is a physical change because both water and ice are H_2O . However, electrolysis of water would not be a physical change because passing a strong electric current through water can decompose it into H_2 and O_2 .

Physical chemistry : Chemical physics. A branch of chemistry that studies chemical phenomena from a physical and mathematical perspective. Physical chemistry includes chemical thermodynamics, kinetics, spectroscopy, quantum chemistry, and statistical mechanics.

Physical property : Physical properties. Measurement of a physical property may change the arrangement but not the structure of the molecules of a material. Examples of physical properties are density, color, boiling point, volume, temperature, and mass.

Phytochemistry : Phytochemical. The study of substances found in plants. "Phytochemicals" are materials extracted from plant tissue.

Pi bond : A bond formed by the edge-on overlap of p atomic orbitals.

A bond formed from the overlap of two parallel p-orbitals.

(π bond) In the valence bond theory, a pi bond is a valence bond formed by side-by-side overlap of p orbitals on two bonded atoms. In most multiple bonds, the first bond is a sigma bond and all of the others are pi bonds.

Pico- : (p) Prefix used in the SI system meaning "multiply by 10^{-12} ". For example, 3 pm means 3×10^{-12} meters.

Picogram : pg. One picogram is 10^{-12} grams.

Picoliter : pL. One picoliter is 10^{-12} liters.

Picometer : pm. One picometer is 10^{-12} meters.

Pipe-clay triangle : A device made from three small pieces of ceramic tube which are wired together in the shape of a triangle. Pipe-clay triangles are used to support round-bottomed dishes when they are heated in a Bunsen flame.

Pipette : A log, slender, glass tube used, in conjunction with a pipette filler, to draw up and then transfer accurately measured amounts of liquid.

pK_a : (pK_a) The pK_a of an acid is minus the base-10 log of its acid dissociation constant, $pK_a = -\log K_a$. For example, a pK_a of 5 is equivalent to an acid dissociation constant of 10^{-5} .

pK_b : (pK_b) The pK_b of a base is minus the base-10 log of its base hydrolysis constant, $pK_b = -\log K_b$. For example, a pK_b of 5 is equivalent to an base hydrolysis constant of 10^{-5} .

Planck's constant : (h) A proportionality constant that relates the energy carried by a photon to its frequency. Planck's constant has a value of 6.6262×10^{-34} J s.

Plane-polarized light : Light which is passed through a filter which blocks out all the light except that which oscillates in one plane.

Plasma : In biology, the fluid in which blood cells or lymph cells are suspended.

A gaslike state of matter consisting of positively charged ions, free electrons, and neutral particles. Plasma is found in stars, the sun, the solar wind, lightning, and fire.

Plastic (material) : A carbon-based substance consisting of long chains (polymers) of simple molecules. The word plastic is commonly restricted to synthetic polymers. *Examples*: polyvinyl chloride, nylon.

Plastic (property) : A material is plastic if it can be made to change shape easily. Plastic materials will remain in the new shape.

Plastic : Literally, a material that can flow. Used to describe polymers that can be shaped, molded, or milled.

Pneumatic trough : A shallow water-filled glass dish used to house a beehive shelf and a gas jar as part of the apparatus for collecting a gas over water.

pOH : The negative of the logarithm of the OH⁻ ion concentration: $pOH = -\log [OH^-]$

Poise : (P) A cgs unit of resistance to fluid flow (viscosity). If a force of 1 dyne is needed to force two fluid layers with 1 cm^2 area that are 1 cm apart past each other at a speed of 1 cm/s, the liquid has a viscosity of 1 poise.

Poise : The unit of measurement for viscosity.

Polar : Used to describe compounds that have a dipole moment because they consist of molecules that have negative and positive poles.

Polar bond : A bond involving electrons that are unequally shared. Polar bonds can be thought of as intermediate between the extremes represented by covalent bonds and ionic bonds.

Polar covalent bond : A bond in a molecule, such as H_2O , that is neither strictly covalent nor strictly ionic.

Polar effect : For a reactant molecule RY, the polar effect of the group R comprises all the processes whereby a substituent may modify the electrostatic forces operating at the reaction centre Y, relative to the standard R°Y . These forces may be governed by charge separations arising from differences in the *electronegativity* of atoms (leading to the presence of dipoles), the presence of unipoles, or electron *delocalization*. It is synonymous with *electronic effect* or "electrical effect" of a substituent as distinguished from other substituent effects, e.g. *steric effects*. Sometimes, however, the term "polar effect" is taken to refer to the influence, other than steric, that non-conjugated substituents exert on reaction rates, i.e. effects connected with electron delocalization between a substituent and the molecular framework to which it is attached are excluded. Polar effect is then not synonymous with electronic effect.

Polar molecule : Polar, ionic compound and polar bond. An asymmetric molecule containing polar bonds. H_2O , NH_3 , and HCl are examples of polar molecules. Non-examples are CO_2 , CCl_4 , and BCl_3 which contain polar bonds but are nonpolar because they have symmetric shapes. Alkanes⁺ are usually asymmetric but are nonpolar because they contain no polar bonds. Polar molecules are electric dipoles⁺ and they attract each other via dipole-dipole forces.

Polar solvent : a solvent in which the atoms have partial electric charges. *Example:* water.

Polarity : A property associated with molecules when the center of positive charge and the center of negative charge don't coincide.

The tendency of a molecule to have positive and negative poles because of the unequal sharing of a pair of electrons.

When applied to solvents, this rather ill-defined term covers their overall solvation capability (solvation power) for solutes (i.e. in chemical equilibria: reactants and products; in reaction rates: reactants and *activated complex*; in light absorptions: ions or molecules in the ground and excited state), which in turn depends on the action of all possible, nonspecific and specific, intermolecular interactions between solute ions or molecules and solvent molecules, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute. Occasionally, the term solvent polarity is restricted to nonspecific solute/solvent interactions only (i.e. to *van der Waals forces*).

Polarizability : Of orbitals means that the electron cloud can be shifted towards a positive charge or away from a negative charge due to electrostatic attraction and repulsion.

Polarizability : The ease of distortion of the electron cloud of a *molecular entity* by an electric field (such as that due to the proximity of a charged reagent). It is experimentally measured as the ratio of induced dipole moment (μ_{ind}) to the field E which induces it: $\alpha = \mu_{ind}/E$. The units of α are $C^2 m^2 V^{-1}$. In ordinary usage the term refers to the "mean polarizability", i.e., the average over three rectilinear axes of the molecule. Polarizabilities in different directions (e.g. along the bond in Cl_2 , called "longitudinal polarizability", and in the direction perpendicular to the bond, called "transverse polarizability") can be distinguished, at least in principle. Polarizability along the bond joining a substituent to the rest of the molecule is seen in certain modern theoretical approaches as a factor influencing chemical *reactivity*, etc., and parametrization thereof has been proposed.

Polarizing power : Means that a charged species such as a proton can attract negatively charged electrons which causes a shift

in the orbital. The higher the positive charge and the smaller the size, the greater the polarizing power of the species.

Polyamide : A polymer, such as nylon or a protein, held together by -CO-NH- bonds.

Polyatomic ion : An ion that contains more than one atom.

Compare with molecule, ion and polyatomic molecule. A polyatomic ion is a charged particle that contains more than two covalently bound atoms.

Polyatomic molecule : A polyatomic molecule is an uncharged particle that contains more than two atoms.

Polycrystalline solid : A solid composed of many individual crystals or grains arranged in a more or less random order.

Polydentate : polydentate ligand. A ligand that has more than one atom that coordinates directly to the central atom in a complex. Polydentate ligands are called chelating agents when two or more coordinating atoms are attached to the same metal ion in a complex. For example, EDTA^{*} or ethylenediaminetetracetic acid is a hexadentate ligand of calcium ion.

Polyester : A polymer held together by ester linkages between the monomers.

Polymer : A compound that is made of long chains by combining molecules (called monomers) as repeating units. ('Poly' means many, 'mer' means part.) *Examples*: polytetrafluoroethene or Teflon from tetrafluoroethene, Terylene from terephthalic acid and ethane-1,2-diol (ethylene glycol).

. A large molecule made by linking smaller molecules ("monomers") together.

A molecule with a large molecular weight formed by the linking of 30 to 100,000 (or more) repeating units.

Polymerisation : A chemical reaction in which large numbers of similar molecules arrange themselves into large molecules, usually long chains. This process usually happens when there is a suitable catalyst present. *Example*: ethene gas reacts to form polyethene in the presence of certain catalysts.

A process that links smaller molecules together to form a larger molecule.

Polymerize : To link smaller molecules together to form a larger molecule.

Polymorph : Polymorphism; polymorphic. Compare with isotope and allotrope. Solid substances that occur in several distinct forms. Polymorphs have different chemical and physical properties. Allotropes are polymorphs of elements.

Polymorphism : (meaning many shapes) The tendency of some materials to have more than one solid form. *Example*: carbon as diamond, graphite and buckminsterfullerene.

Polynucleotide : A condensation polymer formed by the linking of nucleotides.

Polyprotic acid : An acid, such as H_2SO_4 or H_3PO_4 , that can lose more than one H^+ ion, or proton.

Polyprotic base : A base, such as the PO_4^{3-} ion, that can accept more than one H^+ ion, or proton.

Polysaccharide : A carbohydrate made by polymerizing many monosaccharide units.

Polysaccharide : Compare with oligosaccharide and monosaccharide. A carbohydrate consisting of a large number of linked monosaccharide units. Examples of polysaccharides are cellulose and starch.

Long chains of monosaccharides.

Porous : A material containing many small holes or cracks. Quite often the pores are connected, and liquids, such as water or oil, can move through them.

Porous disk : A disk in a tube connecting two different solutions in a voltaic cell that allows ion flow without extensive mixing of the solutions; similar to a salt bridge.

Position of equilibrium : When a reaction's equilibrium "lies to the right", the concentrations of products will be greater than the concentrations of reactants when equilibrium is established.

Conversely, an equilibrium that lies to the left will have a relatively small fraction of products.

Positional probability : A type of probability that depends on the number of arrangements in space that yield a particular state.

Positive electrode : The electrode in an electrochemical cell that carries a positive charge. In an electrolytic cell, it is the anode. In a voltaic cell, it is the cathode.

Positron : The antimatter analog of an electron (β^+). Positrons have the same mass as electrons but the opposite charge.

Positron emission : A nuclear reaction in which a positron is emitted. Positron emission leads to a decrease by one in the atomic number and no change in the mass number of the nuclide.

Potential : A measure of the driving force behind an electrochemical reaction that is reported in units of volts.

Potential difference : A measure of the work that must be done to move an electric charge from one point to the other in a circuit. Potential difference is measured in volts (V).

Electrical potential difference. Work that must be done to move an electric charge between specified points. Electric potential differences are measured in volts.

Potential energy : Compare with kinetic energy. energy an object possesses by virtue of its position. For example, lifting a mass m by h meters increases its potential energy by mgh , where g is the acceleration due to gravity.

Energy due to position; it is stored energy which can be used to do work.

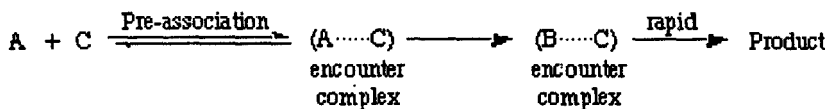
Potential-energy (reaction) surface : A geometric hypersurface on which the potential energy of a set of reactants is plotted as a function of the coordinates representing the molecular geometries of the system. For simple systems two such coordinates (characterizing two variables that change during the progress from reactants to products) can be selected, and the potential energy plotted as a contour map. For simple *elementary reactions*, e.g. $A-B + C \longrightarrow A + B-C$, the surface can show the potential energy for all

values of the A, B, C geometry, providing that the ABC angle is fixed. For more complicated reactions a different choice of two coordinates is sometimes preferred, e.g. the *bond orders* of two different *bonds*. Such a diagram is often arranged so that reactants are located at the bottom left corner and products at the top right. If the trace of the representative point characterizing the route from reactants to products follows two adjacent edges of the diagram, the changes represented by the two coordinates take place in distinct succession; if the trace leaves the edges and crosses the interior of the diagram, the two changes are *concerted*. In many qualitative applications it is convenient (although not strictly equivalent) for the third coordinate to represent the standard Gibbs energy rather than potential energy. Using bond orders is, however, an oversimplification, since these are not well-defined, even for the transition state. (Some reservations concerning the diagrammatic use of Gibbs energies are noted under *Gibbs energy diagram*.) The energetically easiest route from reactants to products on the potential-energy contour map defines the *potential-energy profile*.

Potential-energy profile : A curve describing the variation of the potential energy of the system of atoms that make up the reactants and products of a reaction as a function of one geometric coordinate, and corresponding to the "energetically easiest passage" from reactants to products (i.e. along the line produced by joining the paths of steepest descent from the *transition state* to the reactants and to the products). For an *elementary reaction* the relevant geometric coordinate is the *reaction coordinate*; for a *stepwise reaction* it is the succession of reaction coordinates for the successive individual reaction steps. (The reaction coordinate is sometimes approximated by a quasi-chemical index of reaction progress, such as "degree of atom transfer" or *bond order* of some specified bond).

Power : The rate at which energy is supplied. Power has define [SI] units of J/s, sometimes called "Watts" (W).

Pre-association : A step on the *reaction path* of some *stepwise reactions* in which the *molecular entity* C is already present in an encounter pair or *encounter complex* with A during the formation of B from A, e.g.



In this mechanism the *chemical species* C may but does not necessarily assist the formation of B from A, which may itself be a *bimolecular* reaction with some other reagent. Pre-association is important when B is too short-lived to permit B and C to come together by diffusion.

Precious metal : Silver, gold, platinum, iridium and palladium. Each is prized for its rarity.

Precipitate : (↓) ppt. An insoluble substance that has been formed from substances dissolved in a solution. For example, mixing silver nitrate and sodium chloride solutions produces a precipitate, insoluble silver chloride (along with soluble sodium nitrate).

A solid substance formed as a result of a chemical reaction between two liquids or gases. *Example*: iron(iii) hydroxide is precipitated when sodium hydroxide solution is added to iron(iii) chloride.

Precipitation : A process in which positive and negative ions combine to form a salt that precipitates out of the solution as a solid.

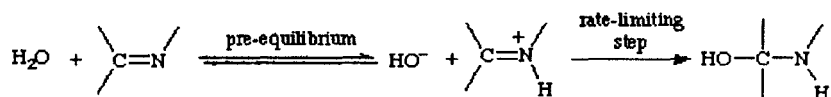
Precipitation is the conversion of a dissolved substance into insoluble form by chemical or physical means.

Precipitation hardening : A process by which an alloy becomes harder when an intermetallic compound, such as CuAl_2 , is allowed to precipitate from a supersaturated solution of two metals.

Precision : Reproducibility. Compare with accuracy. Precision is reproducibility. Saying "These measurements are precise" is the same as saying, "The same measurement was repeated several times, and the measurements were all very close to one another". Don't confuse precision with accuracy.

A measure of the extent to which individual measurements of the same quantity agree.

Pre-equilibrium (or prior equilibrium) : A rapidly reversible step preceding the *rate-limiting step* in a *stepwise reaction*. For example



Preservative : a substance that prevents the natural organic decay processes from occurring. Many substances can be used safely for this purpose, including sulphites and nitrogen gas.

Pressure : (P) Force per unit area. The SI unit of pressure is the pascal, defined as one newton per square meter. Other common pressure units are the atmosphere, the bar, and the Torr.

The force exerted on a surface divided by the area of the surface.

Pressure : The force per unit area measured in pascals.

Primary battery : A battery that cannot be charged. See secondary battery.

Primary standard : A stable, high-purity material used in titrations and other chemical analyses to prepare solutions of precisely known concentration, or to determine the concentrations of substances which react with the primary standard material. For example, NaCl is a primary standard that can be used to determine the concentration of AgNO₃ in a solution by titration: NaCl(aq) + AgNO₃(aq) = AgCl(s) + NaNO₃(aq).

Primary structure : The sequence of amino acids in a protein.

Primary valence : The number of negative ions needed to satisfy the charge on a metal ion. In the [Co(NH₃)₆] Cl₃ complex, for example, it is three.

Primitive change : One of the conceptually simpler molecular changes into which an *elementary reaction* can be notionally dissected. Such changes include *bond* rupture, bond formation, internal rotation, change of bond length or bond angle, bond *migration*, redistribution of charge, etc. The concept of primitive changes is helpful in the detailed verbal description of elementary reactions, but a primitive change does not represent a process that is

by itself necessarily observable as a component of an elementary reaction.

Principal quantum number (n) : The quantum number that describes the size, and therefore the relative energy, of an orbital.

(n) The quantum number that determines the size and (in hydrogen atoms) the energy of an orbital. n is used to label electron shells. n may take on integer values from 1 to infinity.

Process : A change from one state to another.

Product : A substance formed in a chemical reaction.

A substance produced by a chemical reaction. *Example:* when the reactants copper and oxygen react, they produce the product, copper oxide.

A substance that is produced during a chemical change.

Product development control : The term is used for reactions under *kinetic control* where the *selectivity* parallels the relative (thermodynamic) stabilities of the products. Product development control is usually associated with a *transition state* occurring late on the *reaction coordinate*. See also *steric-approach control*, *thermodynamic control*.

Product-determining step : The step of a *stepwise reaction*, in which the product distribution is determined. The product-determining step may be identical to, or occur later than, the *rate-controlling step* on the reaction coordinate.

Proline : Pro. A naturally occurring amino acid with a heterocyclic ring that is classified as nonessential in the diet.

Propane : (C₃H₈) Compare with alkane and hydrocarbon. A colorless, odorless, flammable gas, found in petroleum and natural gas. It is used as a fuel and as a raw material for building more complex organic molecules. Propane is the third member of the alkane series.

Propellant : A mixture of fuel and oxidizing agent that reacts to produce a high-energy stream of product gases that can produce thrust. For examples, see What makes a good rocket fuel?

A compressed gas used to push a material through a nozzle, forming an aerosol or a foam. For example, nitrogen or propane are used as propellants for shaving cream; nitrous oxide is used as a propellant for whipped cream.

Property : Any measurable aspect of the system.

Protein : A complex polymer made by linking together amino acid molecules. Proteins sometimes contain non-amino acid components such as metal ions or porphyrin rings embedded within.

A relatively large polymer of amino acids. A polypeptide that is large enough to have an extensive secondary and tertiary structure.

Protogenic (solvent) : Capable of acting as a proton (hydron) donor strongly or weakly acidic (as a *Brønsted acid*). The term is preferred to the synonym "protic" or the more ambiguous expression "acidic" by itself. Also called HBD (hydrogen bond donor) solvent.

Protolysis : This term has been used synonymously with proton (hydron)-transfer reaction. Because of its misleading similarity to *hydrolysis*, *photolysis*, etc., its use is discouraged. See also *autoprotolysis*.

Proton : (p^+) Compare with electron and neutron. An elementary particle found in the atomic nucleus with a positive charge equal and opposite that of the electron. Protons have a mass of 1.007276 daltons.

A positively charged particle in the nucleus of an atom that balances out the charge of the surrounding electrons. 3. A subatomic particle that has a charge of +1 and a mass of about 1 amu.

Proton acceptor : An ion or molecule that can gain an H^+ ion, or proton. A Brønsted base.

Proton affinity : The negative of the enthalpy change in the gas phase reaction (real or hypothetical) between a proton (more appropriately *hydron*) and the *chemical species* concerned, usually an electrically neutral species to give the *conjugate acid* of that species.

Proton donor : Acid. Compare with base. Because a free H^+ ion is technically a bare proton, acids are sometimes referred to as "proton donors" because they release hydrogen ions in solution. The term "proton donor" is misleading, since in aqueous solution, the hydrogen ion is never a bare proton- it's covalently bound to a water molecule as an H_3O^+ ion. Further, acids don't "donate" protons; they yield them to bases with a stronger affinity for them.

An ion or molecule that can lose an H^+ ion, or proton. A Brønsted acid.

Proton number : This is the modern expression for atomic number.

Proton transfer reaction : A *chemical reaction*, the main feature of which is the *intermolecular* or *intramolecular* transfer of a proton (*hydron*) from one *binding site* to another. For example, $\text{CH}_3\text{CO}_2\text{H} + (\text{CH}_3)_2\text{C}=\text{O} \longrightarrow \text{CH}_3\text{CO}_2^- + (\text{CH}_3)_2\text{C}=\text{O}^+\text{H}$ In the detailed description of proton transfer reactions, especially of rapid proton transfers between electronegative atoms, it should always be specified whether the term is used to refer to the overall process (including the more-or-less *encounter-controlled* formation of a hydrogen bonded complex and the separation of the products; see *microscopic diffusion control*) or just to the proton transfer event (including solvent rearrangement) by itself.

Protophilic (solvent) : Capable of acting as proton acceptor, strongly or weakly basic (as a *Brønsted base*). Also called HBA (hydrogen bond acceptor) solvent.

Pseudo-catalysis : If an acid or base is present in nearly constant concentration throughout a reaction in solution (owing to buffering or the use of a large excess), it may be found to increase the rate of that reaction and also to be consumed during the process. The acid or base is then not a *catalyst* and the phenomenon cannot be called *catalysis* according to the well-established meaning of these terms in chemical kinetics, although the *mechanism* of such a process is often intimately related to that of a catalysed reaction. It is recommended that the term pseudo-catalysis be used in these and analogous cases (not necessarily involving acids or bases). For example, if a *Brønsted acid* accelerates the hydrolysis of an ester to a carboxylic acid and an alcohol, this is properly called acid catalysis,

whereas the acceleration, by the same acid, of hydrolysis of an amide should be described as pseudo-catalysis by the acid: the "acid pseudo-catalyst" is consumed during the reaction through formation of an ammonium ion. The terms "general acid pseudo-catalysis" and "general base pseudo-catalysis" may be used as the analogues of *general acid catalysis* and *general base catalysis*. The term "base-promoted", "base-accelerated, or "base-induced" is sometimes used for reactions that are pseudo-catalysed by bases. However, the term "promotion" also has a different meaning in other chemical contexts.

Pseudocore : Electrons in *d* or *f* subshells which are outside the noble gas core.

Pseudo-first-order reaction : A reaction that is formally first-order in two reactants, but appears first-order in only one of these reactants because it is run in the presence of a large excess of the other reactant.

Pseudomolecular rearrangement : The use of this awkwardly formed term is discouraged. It is synonymous with "intermolecular rearrangement".

Pseudopericyclic : A *concerted transformation* is pseudopericyclic if the primary changes in bonding occur within a cyclic array of atoms at one (or more) of which nonbonding and bonding atomic orbitals interchange roles. A formal example is the enol



Because the pi and sigma atomic orbitals that interchange roles are orthogonal, such a reaction does not proceed through a fully *conjugated transition state* and is thus not a pericyclic reaction and therefore not governed by the rules that express *orbital symmetry* restrictions applicable to pericyclic reactions.

Pseudo-unimolecular : A term sometimes used as synonymous with pseudo-first order, but is inherently meaningless.

Pure substance : Substance. A sample of matter that cannot be separated into simpler components without chemical change.

Physical changes can alter the state of matter but not the chemical identity of a pure substance. Pure substances have fixed, characteristic elemental compositions and properties.

Purify : To remove all impurities from a mixture, perhaps by precipitation, or filtration.

Purine : A heterocyclic aromatic compound containing nitrogen found in nucleic acids. See pyrimidine.

Pyranose ring : A six-membered cyclic hemiacetal or ketal.

Pyrimidine : A heterocyclic aromatic compound containing nitrogen found in nucleic acids.

Pyrolysis : Chemical decomposition brought about by heat.
Example: decomposition of lead nitrate.

Thermolysis, usually associated with exposure to a high temperature.

Pyrometallurgy : Refining a metal from its ore using heat. A blast furnace or smelter is the main equipment used.

Pyrophoric : Pyrophoric solid. Catches fire spontaneously when exposed to air at normal room temperature. For example, powdered potassium metal is pyrophoric.

Used to describe compounds that burst into flame in the presence of air.



Quadratic formula : A formula for solving quadratic equations.

Qualitative analysis : A chemical analysis that detects the presence of a substance in a sample.

Quantitative : measurement of the amounts of constituents of a substance, for example by mass or volume.

Quantitative analysis : A chemical analysis that determines the concentration of a substance in a sample.

Quantitative structure-activity relationships (QSAR) : A mathematical connection between chemical structure and biological activity, established by statistical analysis or pattern recognition techniques.

The building of structure-biological activity models by using regression analysis with physicochemical constants, indicator variables or theoretical calculations. The term has been extended by some authors to include chemical reactivity, i.e. activity is regarded as synonymous with reactivity. This extension is, however, discouraged.

Quantized : Literally, countable. Oranges are quantized; orange juice is not.

Quantum : Quanta. A discrete packet of energy.

Quantum mechanics : Quantum theory. A branch of physics that describes the behavior of objects of atomic and subatomic size.

Quantum number : An integer that describes the size, shape, and orientation in space of an atomic orbital.

Indices that label quantized energy states. Quantum numbers are used to describe the state of a confined electron, e. g. an electron in an atom.

Quantum yield : The number of defined events which occur per photon absorbed by the system.

The integral quantum yield is $\phi = \frac{\text{number of events}}{\text{number of photons absorbed}}$

For a photochemical reaction,

$$\phi = \frac{\text{moles of reactant consumed or product formed}}{\text{moles of photons absorbed}}$$

The differential quantum yield is $\phi = \frac{d[X]/dt}{n}$ where $d[X]/dt$ is the rate of change of the amount of (substance) concentration of a measurable quantity, and n the amount of photons (mol or its equivalent *einsteins*) absorbed per unit time. ϕ can be used for photophysical processes or photochemical reactions.

Quaternary structure : The ionic or hydrophobic interactions between individual chains of amino acids in some proteins.



Racemic : Racemic mixture. A mixture of equal parts of the levorotatory and dextrorotatory isomers of the the same substance. Racemic mixtures are not optically active.

Racemic mixture : A 50:50 mixture of two enantiomers (such a mixture does **not** rotate plane-polarized light).

Rad : A unit in which the dose of radiation absorbed by an object is reported: $1 \text{ rad} = 10^{-5} \text{ J/g}$.

Radian : (rad) An angle with vertex at the center of a circle of radius r that encompasses an arc of length r .

Radiant intensity : (P,I) radiant power; intensity; radiation intensity. Energy of radiation striking a unit area per unit time. The SI unit of radiant power is $\text{J m}^{-2} \text{ s}^{-1}$.

Radiation : The exchange of energy with the surroundings through the transmission of waves or particles of energy. Radiation is a form of energy transfer that can happen through space; no intervening medium is required (as would be the case for conduction and convection).

Radical : an atom, molecule, or ion with at least one unpaired electron. *Example*: nitrogen monoxide (NO).

Radical centre(s) : The atom (or group of atoms) in a polyatomic radical on which an unpaired electron is largely localized. Attachment of a monovalent atom to a radical centre gives a molecule for which it is possible to write a *Lewis formula* in which the normal stable valencies are assigned to all atoms.

Radical ion : A radical that carries an electric charge. A positively charged radical is called a "radical cation" (e.g., the

benzene radical cation $\text{C}_6\text{H}_6^{\cdot+}$); a negatively charged radical is called a "radical anion" (e.g., the benzene radical anion $\text{C}_6\text{H}_6^{\cdot-}$ or the benzophenone radical anion $\text{Ph}_2\text{C-O}^{\cdot-}$). Commonly, but not necessarily, the odd electron and the charge are associated with the same atom. Unless the positions of unpaired spin and charge can be associated with specific atoms, superscript dot and charge designations should be placed in the order \cdot^+ or $^{\cdot-}$ suggested by the name "radical ion", (e.g. $\text{C}_3\text{H}_6^{\cdot+}$).

Radical pair (or geminate pair) : The term is used to identify two *radicals* in close proximity in solution, within a solvent *cage*. They may be formed simultaneously by some *unimolecular* process, e.g., peroxide decomposition, or they may have come together by diffusion. While the radicals are together, correlation of the unpaired electron spins of the two species cannot be ignored: this correlation is responsible for the *CIDNP* phenomenon. See also *geminate recombination*.

Radioactive : Emitting radiation or particles from the nucleus of its atoms.

Radioactive decay : A change in a radioactive element due to loss of mass through radiation. For example, uranium decays (changes) to lead.

Radioactivity : Radiation; radioactive. Spontaneous emission of particles or high-energy electromagnetic radiation from the nuclei of unstable atoms. "Radiation" refers to the emissions, and "radioactive source" refers to the source of the radiation.

The spontaneous disintegration of an unstable nuclide by a first-order rate law.

Radioisotope : Compare with isotope. A radioactive isotope. For example, tritium is a radioisotope of hydrogen.

Radiolysis : The cleavage of one or several bonds resulting from exposure to high-energy radiation. The term is also often used loosely to specify the method of irradiation ("pulse radiolysis") used in any radiochemical reaction, not necessarily one involving bond cleavage.

Radius ratio : The radius of the positive ion divided by the radius of the negative ion in a salt.

Random error : A source of error that limits the precision of a measurement. An error that is equally likely to give results that are too large or too small.

Indeterminate error. Compare with systematic error, gross error and mistake. Random errors are errors that affect the precision of a set of measurements. Random error scatters measurements above and below the mean, with small random errors being more likely than large ones.

Raoult's law : A law that describes the relationship between the vapor pressure of a solution, the mole fraction of the solute, and the vapor pressure of the solute.

The vapor pressure of a solvent in an ideal solution equals the mole fraction of the solvent times the vapor pressure of the pure solvent.

Rare earth : An oxide of a rare earth element.

Rare earth element : Rare earth metal. A metallic element that belongs to Group 3B or to the lanthanide series.

Rare gases : A group of elements (He, Ne, Ar, Kr, Xe, Rn) that was once erroneously known as the inert gases. Also known as the noble gases.

Rate constant : (k) A rate constant is a proportionality constant that appears in a rate law. For example, k is the rate constant in the rate law $d[A]/dt = k[A]$. Rate constants are independent of concentration but depend on other factors, most notably temperature.

The proportionality constant in the equation that describes the relationship between the rate of a step in a chemical reaction and the product of the concentrations of the reactants consumed in that step. k (SI unit: $s^{-1} (dm^3 mol^{-1})^{n-1}$).

Rate law (or empirical differential rate equation) : An expression for the *rate of reaction* of a particular reaction in terms of concentrations of *chemical species* and constant parameters (normally *rate coefficients* and *partial orders of reaction*) only. For

examples of rate laws see equations (1) to (3) under *kinetic equivalence*, and (1) under *steady state*.

A rate law or rate equation relates reaction rate with the concentrations of reactants, catalysts, and inhibitors. For example, the rate law for the one-step reaction $A + B \rightarrow C$ is $d[C]/dt = k[A][B]$.

An equation that describes how the rate of a chemical reaction depends on the concentrations of the reactants consumed in that reaction.

Rate of reaction : 1. For the general *chemical reaction* $aA + bB \rightarrow pP + qQ$... occurring under constant-volume conditions, without an appreciable build-up of reaction *intermediates*, the rate of reaction v is defined as

$$v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{p} \frac{d[P]}{dt} = +\frac{1}{q} \frac{d[Q]}{dt}$$

where symbols placed inside square brackets denote amount (or amount of substance) concentrations (conventionally expressed in units of mol dm^{-3}). The symbols R and r are also commonly used in place of v . It is recommended that the unit of time should always be the second. In such a case the rate of reaction differs from the rate of increase of concentration of a product P by a constant factor (the reciprocal of its coefficient in the stoichiometric equation, p) and from the rate of decrease of concentration of the reactant A by $1/a$. [It should be noted that all coefficients in the stoichiometric equation are positive; those for products ($p, q...$) will therefore differ in sign from the stoichiometric numbers defined in] The quantity $\dot{\xi} = \frac{d\xi}{dt}$ defined by the equation

$$\dot{\xi} = -\frac{1}{a} \frac{dn_A}{dt} = -\frac{1}{b} \frac{dn_B}{dt} = +\frac{1}{p} \frac{dn_P}{dt} = +\frac{1}{q} \frac{dn_Q}{dt}$$

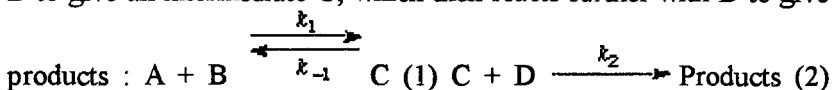
(where nA designates the amount of substance A , conventionally expressed in units of mole) may be called the "rate of conversion" and is appropriate when the use of concentrations is inconvenient, e.g. under conditions of varying volume. In a system of constant volume, the rate of

reaction is equal to the rate of conversion per unit volume throughout the reaction. For a *stepwise reaction* this definition of "rate of reaction" (and "extent of reaction", π) will apply only if there is no accumulation of intermediate or formation of side products. It is therefore recommended that the term "rate of reaction" be used only in cases where it is experimentally established that these conditions apply. More generally, it is recommended that, instead, the terms "rate of disappearance" or "rate of consumption" of A (i.e. $-d[A]/dt$, the rate of decrease of concentration of A) or "rate of appearance" of P_i (i.e. $d[P_i]/dt$, the rate of increase of concentration of product P) be used, depending on the concentration change of the particular *chemical species* that is actually observed. In some cases reference to the *chemical flux* observed may be more appropriate. The symbol ν (without lettered subscript) should be used only for rate of reaction; ν with a lettered subscript (e.g. ν_A) refers to a rate of appearance or rate of disappearance (e.g. of the chemical species A).

The change in the concentration of a compound divided by the amount of time necessary for this change to occur: rate = $d(X)/dt$.

Rate-controlling step : A rate-controlling (rate-determining or rate-limiting) step in a reaction occurring by a composite reaction sequence is an *elementary reaction* the rate constant for which exerts a strong effect - stronger than that of any other rate constant - on the overall rate. It is recommended that the expressions rate-controlling, rate-determining and rate-limiting be regarded as synonymous, but some special meanings sometimes given to the last two expressions are considered under a separate heading. A rate-controlling step can be formally defined on the basis of a control function (or control factor) CF, identified for an elementary reaction having a rate constant k_i by $CF = (\partial \ln \nu / \partial \ln k_i)_{K_j, k_j}$ where ν is the overall rate of reaction. In performing the partial differentiation all equilibrium constants K_j and all rate constants except k_i are held constant. The elementary reaction having the largest control factor exerts the strongest influence on the rate ν , and a step having a CF much larger than any other step may be said to be rate-controlling. A rate-

controlling step defined in the way recommended here has the advantage that it is directly related to the interpretation of *kinetic isotope effects*. As formulated this implies that all rate constants are of the same dimensionality. Consider however the reaction of A and B to give an intermediate C, which then reacts further with D to give



Assuming that C reaches a *steady state*, then the observed rate is

given by
$$v = \frac{k_1 k_2 [A][B][D]}{k_{-1} + k_2 [D]}$$
 Considering $k_2 [D]$ a pseudo-first order rate constant, then $k_2 [D] \gg k_{-1}$, and the observed rate $v = k_1 [A][B]$ and $k_{\text{obs}} = k_1$ Step (1) is said to be the rate-controlling step.

$$v = \frac{k_1 k_2}{k_{-1}} [A][B][D]$$

If $k_2 [D] \ll k_{-1}$, then the observed rate $= K k_2 [A][B][D]$

where K is the equilibrium constant for the pre-equilibrium (1) and is equal to k_1/k_{-1} , and $k_{\text{obs}} = K k_2$. Step (2) is said to be the rate-controlling step.

Rate-determining step, rate-limiting step : These terms are best regarded as synonymous with *rate-controlling step*. However, other meanings that have been given to them should be mentioned, as it is necessary to be aware of them in order to avoid confusion: Sometimes the term rate-determining is used as a special case of rate-controlling, being assigned only to an initial slow step which is followed by rapid steps. Such a step imposes an upper limit on the rate, and has also been called rate-limiting. In view of the considerable danger of confusion when special meanings are applied to rate-determining and rate-limiting, it is recommended that they be regarded as synonymous, with the meaning explained under the entry *rate-controlling step*.

Rate-limiting step : The slowest step in a chemical reaction. RBE Radiation biological effectiveness. Used to correct for differences in the effect of equivalent doses of different forms of radiation.

Reactant : A starting material that takes part in, and undergoes, change during a chemical reaction. *Example:* hydrochloric acid and

calcium carbonate are reactants; the reaction produces the products calcium chloride, carbon dioxide and water. 2. Compare with product. A substance that is consumed during a chemical change.

One of the starting materials in a chemical reaction.

Reacting bond rules : For an internal motion of a *molecular entity* corresponding to progress over a *transition state* (energy maximum), any change that makes the motion more difficult will lead to a new molecular geometry at the energy maximum, in which the motion has proceeded further. Changes that make the motion less difficult will have the opposite effect. (This rule corresponds to the *Hammond principle*).

For an internal motion of a *molecular entity* that corresponds to a vibration, any change that tends to modify the equilibrium point of the vibration in a particular direction will actually shift the equilibrium in that direction.

Effects on reacting bonds (bonds made or broken in the reaction) are the most significant. The bonds nearest the site of structural change are those most strongly affected.

Reaction : The recombination of two substances using parts of each substance to produce new substances. *Example:* the reactants sodium chloride and sulphuric acid react and recombine to form the products sodium sulphate, chlorine and water.

Reaction coordinate : A geometric parameter that changes during the conversion of one (or more) reactant *molecular entities* into one (or more) product molecular entities and whose value can be taken for a measure of the progress of an *elementary reaction* (for example, a bond length or bond angle or a combination of bond lengths and/or bond angles; it is sometimes approximated by a non-geometric parameter, such as the *bond order* of some specified bond). In the formalism of "*transition-state theory*", the reaction coordinate is that coordinate in a set of curvilinear coordinates obtained from the conventional ones for the reactants which, for each reaction step, leads smoothly from the configuration of the reactants through that of the transition state to the configuration of the products. The reaction coordinate is typically chosen to follow the path along the gradient (path of shallowest ascent/deepest descent) of

potential energy from reactants to products. The term has also been used interchangeably with the term transition coordinate, applicable to the coordinate in the immediate vicinity of the potential energy maximum. Being more specific, the name transition coordinate is to be preferred in that context. See also *potential-energy profile*, *potential-energy reaction surface*.

The sequence of infinitesimally small steps that must be taken to convert the reactants into the products of a reaction.

Reaction mechanism : Mechanism. A list of all elementary reactions that occur in the course of an overall chemical reaction.

Reaction path : A synonym for *mechanism*.

A trajectory on the *potential-energy surface*.

A sequence of synthetic steps.

Reaction quotient (Q_c or Q_p) : The quotient obtained when the concentrations (or partial pressures) of the products of a reaction are multiplied and the result is divided by the product of the concentrations (or partial pressures) of the reactants. The reaction quotient can have any value between zero and infinity. When the reaction is at equilibrium, the reaction quotient is equal to the equilibrium constant for the reaction. (Q) Compare with equilibrium constant.

A constant represented by the symbol Q which is defined as the product of the concentrations of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the concentrations of reactants, each raised to the power that corresponds to its coefficient in the balanced equation (see the equation in the equations page). At equilibrium conditions $Q=K$, the equilibrium constant.

Reaction rate : A reaction rate is the speed at which reactants are converted into products in a chemical reaction. The reaction rate is given as the instantaneous rate of change for any reactant or product, and is usually written as a derivative (e. g. $d[A]/dt$) with units of concentration per unit time (e. g. $\text{mol L}^{-1} \text{s}^{-1}$).

Reaction stage : A set of one or more (possibly experimentally inseparable) *reaction steps* leading to and/or from a detectable or presumed reaction *intermediate*.

Reaction step : An *elementary reaction*, constituting one of the stages of a *stepwise reaction* in which a reaction *intermediate* (or, for the first step, the reactants) is converted into the next reaction intermediate (or, for the last step, the products) in the sequence of intermediates between reactants and products.

Reactive, reactivity : As applied to a *chemical species*, the term expresses a kinetic property. A species is said to be more reactive or to have a higher reactivity in some given context than some other (reference) species if it has a larger rate constant for a specified *elementary reaction*. The term has meaning only by reference to some explicitly stated or implicitly assumed set of conditions. It is not to be used for reactions or reaction patterns of compounds in general. The term is also more loosely used as a phenomenological description not restricted to elementary reactions. When applied in this sense the property under consideration may reflect not only rate, but also equilibrium, constants. See also *stable, unreactive, unstable*.

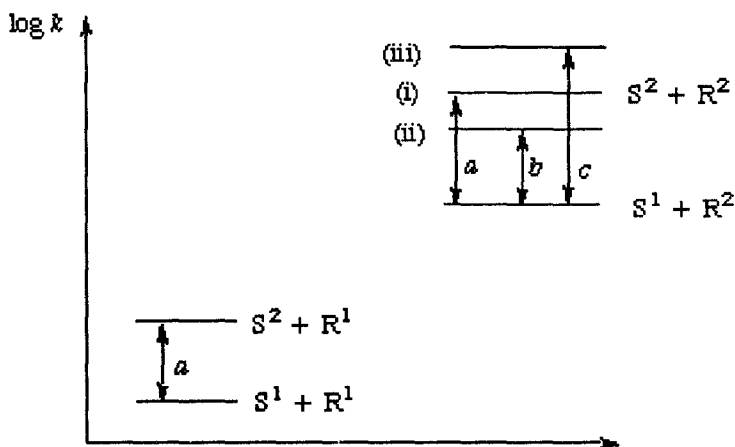
The tendency of a substance to react with other substances. The term is most widely used in comparing the reactivity of metals. Metals are arranged in a reactivity series.

Reactivity index : Any numerical index derived from quantum mechanical model calculations that permits the prediction of relative reactivities of different molecular sites. Many indices are in use, based on a variety of theories and relating to various types of reaction. The more successful applications have been to the *substitution reactions* of *conjugated systems* where relative reactivities are determined largely by changes of pi-electron energy.

Reactivity series : the series of metals organised in order of their reactivity, with the most reactive metals, such as sodium, at the top and the least react metals, such as gold, at the bottom. Hydrogen is usually included in the series for comparative purposes.

Reactivity-selectivity principle (RSP) : This idea may be expressed loosely as: the more *reactive* a reagent is, the less selective

it is. Consider two substrates S^1 and S^2 undergoing the same type of reaction with two reagents R^1 and R^2 , S^2 being more reactive than S^1 , and R^2 more reactive than R^1 in the given type of reaction. The relative reactivities (in log units, see *selectivity*) for the four possible reactions may notionally be represented as follows :



With the positions of $(S^1 + R^1)$, $(S^2 + R^1)$, and $(S^1 + R^2)$ fixed, there are three types of positions for $(S^2 + R^2)$: In position (i) the selectivity of R^2 for the two substrates, measured by a is the same as the selectivity of R^1 for the two substrates, also a . In position (ii) the selectivity of R^2 for the two substrates, measured by b , is less than the selectivity of R^1 for the two substrates, i.e. $b < a$. It is this situation which is in accord with the RSP. In position (iii) the selectivity of R^2 for the two substrates, measured by c , is greater than the selectivity of R^1 for the two substrates, i.e. $c > a$. This situation may be described as anti-RSP. There are many examples in which the RSP is followed, but there are also many examples corresponding to situations (i) and (iii). The RSP is in accord with intuitive feeling and certainly holds in the limiting case when reactivity is controlled by diffusion. However, the validity of the RSP is a matter of great controversy "...and diverse opinions have been expressed, from declaring the reactivity-selectivity principle as a universal law up to 'virtually useless in practice as a general rule'."

Reagent : A commonly available substance (reactant) used to create a reaction. Reagents are the chemicals normally kept on

chemistry laboratory benches. Many substances called reagents are most commonly used for test purposes.

A substance or mixture that is useful in chemical analysis or synthesis.

Rearrangement reaction : Isomerization; isomerize. A reaction in which a reactant and product are isomers of each other. Chemical bonds within the reactant are broken and reformed to produce the product.

Rearrangement stage : The *elementary reaction* or *reaction stage* (of a *molecular rearrangement*) in which there is both making and breaking of bonds between atoms common to a reactant and a reaction product or a reaction *intermediate*. If the rearrangement stage consists of a single elementary reaction, this is a "rearrangement step".

Receptor : Receptor site. A molecule or surface in a cell that recognizes and binds to a specific messenger molecule, leading to a biological response.

Recrystallization : A technique for purifying solids that removes impurities when the solid is dissolved in an appropriate solvent and then allowed to recrystallize.

Redox : An abbreviation for oxidation-reduction.

Redox indicator : Oxidation-reduction indicator. An organic molecule that has reduced and oxidized forms with different colors; interconversion of the reduced and oxidized forms of the indicator must be reversible. Ferroin is an example.

Redox reaction (oxidation-reduction reaction) : A reaction that involves oxidation and reduction; a reactions in which electrons are transferred.

A reaction in which one or more electrons are transferred.

Electrochemical reaction; oxidation-reduction reaction; redox. A reaction that involves transfer of electrons from one substance to another. Redox reactions always involve a change in oxidation number for at least two elements in the reactants.

Redox titration : Oxidation-reduction titration. A titration based on a redox reaction. For example, iron in water can be determined by converting dissolved iron to Fe^{2+} and titrating the solution with potassium permanganate (KMnO_4), a powerful oxidizing agent.

Reducing agent : A reactant that donates electrons to another substance to reduce the oxidation state of one of its atoms. The reducing agent is the species that is getting oxidized.

A substance that gives electrons to another substance being reduced (and therefore itself being oxidised) in a redox reaction. *Example*: hydrogen sulphide (H_2S).

An atom, ion, or molecule that loses electrons in a chemical reaction, thereby reducing the substance with which it reacts.

Reductant. Compare with oxidizing agent. A reducing agent is a substance that reduce another substance by supplying electrons to it. Reducing agents cause other substances to be reduced in chemical reactions while they themselves are oxidized. For example, tin(II) is a reducing agent in the following reaction : $\text{Sn}^{2+}(\text{aq}) + 2 \text{Fe}^{3+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2 \text{Fe}^{2+}(\text{aq})$

Reduction : A gain of electrons. The oxidation number decreases, becomes more negative.

Any process that leads to a decrease in the oxidation number of an atom.

Reduce; reduced; reducing. Compare with oxidation. Reduction is gain of one or more electrons by an atom, molecule, or ion. Reduction is accompanied by a decrease in oxidation number.

The complete transfer of one or more electrons to a *molecular entity* (also called "electronation"), and, more generally, the reverse of the processes described under *oxidation* (2), (3).

The removal of oxygen from, or the addition of hydrogen to, a compound. Also a reaction in which an atom, ion or

molecule gains electrons from an reducing agent. (The opposite of reduction is oxidation.)

Reduction half reaction : reduction half-reaction. Compare with oxidation half reaction. That part of a redox reaction that involves gain of electrons. In the oxidation half reaction, the oxidation number of one or more atoms within the reactants is reduced.

Reduction potential : The tendency of a substance to be reduced; this value is measured relative to the standard hydrogen electrode which is defined as zero. The more positive the number the stronger the tendency for the species to be reduced. Sometimes oxidation potentials are used. They simply are the reverse of the reduction potential and refer to the oxidation reaction.

Reduction tube : A boiling tube with a small hole near the closed end. The tube is mounted horizontally, a sample is placed in the tube and a reducing gas, such as carbon monoxide, is passed through the tube. The oxidised gas escapes through the small hole.

Reductive elimination : The reverse of *oxidative addition*.

Refining : Separating a mixture into the simpler substances of which it is made.

Reflux distillation system : A form of distillation using a Liebig condenser placed vertically, so that all the vapours created during boiling are condensed back into the liquid, rather than escaping. In this way, the concentration of all the reactants remains constant.

Regioselectivity, regioselective : A regioselective reaction is one in which one direction of bond making or breaking occurs preferentially over all other possible directions. Reactions are termed completely (100%) regioselective if the discrimination is complete, or partially ($x\%$), if the product of reaction at one site predominates over the product of reaction at other sites. The discrimination may also semi-quantitatively be referred to as high or low regioselectivity. (Originally the term was restricted to *addition reactions* of unsymmetrical reagents to unsymmetrical alkenes.) In the past, the term "regiospecificity" was proposed for 100%

regioselectivity. This terminology is not recommended owing to inconsistency with the terms *stereoselectivity* and *stereospecificity*.

Relative atomic mass : In the past a measure of the mass of an atom on a scale relative to the mass of an atom of hydrogen, where hydrogen is 1. Nowadays a measure of the mass of an atom relative to the mass of one twelfth of an atom of carbon-12. If the relative atomic mass is given as a rounded figure, it is called an approximate relative atomic mass. *Examples*: chlorine 35, calcium 40, gold 197.

Relative error : Relative uncertainty. Compare with absolute error. The uncertainty in a measurement compared to the size of the measurement. For example, if three replicate weights for an object are 2.00 g, 2.05 g, and 1.95 g, the absolute error can be expressed as ± 0.05 g and the relative error is $\pm 0.05 \text{ g} / 2.00 \text{ g} = 0.025 = 2.5\%$.

Relative standard deviation : (RSD) Compare with standard deviation.

Relaxation : Passage of an excited or otherwise perturbed system towards or into thermal equilibrium with its environment.

Rem : A unit of radiation absorbed dose equal to the product of the rads of absorbed radiation times the RBE.

Reorganization energy : In a one-electron transfer reaction $A + D \rightleftharpoons A^{\cdot-} + D^+$ the reorganization energy λ is the energy required for all structural adjustments (in the reactants and in the surrounding solvent molecules) which are needed in order that A and D assume the configuration required for the transfer of the electron.

Replication : The process by which copies of DNA are made to be passed down to future generations of cells.

Residue : The substances left after an evaporation or distillation.

A recognizable molecular fragment embedded in a larger molecule; for example, amino acid "residues" within a protein.

An averaging or mixing process that occurs when more than one Lewis structure can be written for a molecule.

Description of the ground state of a molecule with delocalized electrons as an average of several Lewis structures. The actual ground state doesn't switch rapidly between the separate structures: it is an average.

In the context of chemistry, the term refers to the representation of the electronic structure of a *molecular entity* in terms of *contributing structures*. Resonance among contributing structures means that the wavefunction is represented by "mixing" the wavefunctions of the contributing structures. The concept is the basis of the quantum mechanical valence bond methods. The resulting stabilization is linked to the quantum mechanical concept of "resonance energy". The term resonance is also used to refer to the delocalization phenomenon itself.

Resonance effect : Mesomeric effect. If electron density at a particular point in a molecule is higher or lower than what you'd expect from a single Lewis structure, and various canonical structures can be drawn to show how electron delocalization will explain the discrepancy, the difference in electron density is called a "resonance effect" or "mesomeric effect".

This is the term most commonly used to describe the influence (on reactivity, spectra, etc.) of a *substituent* through electron *delocalization* into or from the substituent. The use of the term obviates the need to attempt to distinguish between the operation of the *mesomeric effect* and the *electromeric effect*. (An alternative term with essentially the same meaning is "conjugative effect". At one time "tautomeric effect" was also used, but was abandoned because *tautomerism* implies reorganization of the atomic nuclei.) The effect is symbolized by R.

Resonance energy : The difference in potential energy between the actual *molecular entity* and the *contributing structure* of lowest potential energy. The resonance energy cannot be measured, but only estimated, since contributing structures are not observable *molecular entities*.

Resonance hybrid : A mixture, or average, of two or more Lewis structures.

Reverse osmosis : Solvent molecules flow spontaneously from a dilute solution through a semipermeable membrane to a more concentrated solution (osmosis). In reverse osmosis, pressure is applied to the more concentrated solution to force the flow of solvent to go from more concentrated to more dilute solution. Reverse osmosis is used to produce fresh water from sea water.

Reversible process : (A process or reaction that can be reversed by an infinitesimally small change in conditions. For example, ice and water coexist at 1 atm and 0°C; a very slight temperature increase causes the ice to melt; a tiny temperature decrease causes the water to freeze. Melting or freezing under these conditions can be considered reversible. Reversible processes are infinitesimally close to equilibrium.) reversible process; reversible reaction. Compare with irreversible and irreversible process.

A cyclic process carried out by a hypothetical pathway, which leaves the universe exactly the same as it was before the process; no real process is reversible. For chemical systems we consider a process at equilibrium to be reversible. Examples are phase transitions that occur at the melting point or boiling point temperatures at 1 atm pressure.

Reversible reaction : A reaction in which the products can be transformed back into their original chemical form. *Example:* heated iron reacts with steam to produce iron oxide and hydrogen. If the hydrogen is passed over this heated oxide, it forms iron and steam.

$$3\text{Fe} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{H}_2$$

Ritchie equation : The *linear free energy relation* $\log k_N = \log k_0 + N_+$ applied to the reactions between nucleophiles and certain large and relatively stable organic cations, e.g. arenediazonium, triarylmethyl, and aryltropylium cations in various solvents. k_N is the rate constant for reaction of a given cation with a given nucleophilic system (i.e. given nucleophile in a given solvent). k_0 is the rate constant for the same cation with water in water, and N_+ is a parameter which is characteristic of the nucleophilic system and independent of the cation. A surprising feature of the equation is the absence of a coefficient of N_+ , characteristic of the substrate (cf. the s in the *Swain-Scott equation*), even though values of N_+ vary over 13

log units. The equation thus involves a gigantic breakdown of the *reactivity-selectivity principle*. The equation has been extended both in form and in range of application.

RNA : Ribonucleic acid, the nucleic acid involved in transcribing the genetic information for the synthesis of proteins stored in DNA and then translating this information into the sequence of amino acids in the protein.

Ribonucleic acid. Compare with nucleic acid and nucleotide. A nucleic acid with D-ribose as the sugar component in its nucleotides.

Roast : Heating a substance for a long time at a high temperature, as in a furnace.

Roasting : A process in which a metal ore (such as PbS or ZnS) is transformed into the corresponding oxide (PbO or ZnO) and SO₂.

R-process : The process by which nuclides are built up by the rapid capture of neutrons. The R-process produces heavy nuclides such as ²³⁸U. It requires a large neutron flux, which occurs when a star becomes a supernova. See S-process.

Rradical (or free radical) : A molecular entity such as ·CH₃, ·SnH₃, Cl· possessing an unpaired electron. (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals. However, in the "isobolal analogy" (see HOFFMANN (1982)), the similarity between certain paramagnetic metal ions and radicals becomes apparent. At least in the context of physical organic chemistry, it seems desirable to cease using the adjective "free" in the general name of this type of *chemical species* and *molecular entity*, so that the term "free radical" may in future be restricted to those radicals which do not form parts of radical pairs. Depending upon the core atom that possesses the unpaired electron, the radicals can be described as carbon-, oxygen-, nitrogen-, metal-centred

radicals. If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed sigma or pi radicals. In the past, the term "radical" was used to designate a *substituent* group bound to a *molecular entity*, as opposed to "free radical", which nowadays is simply called radical. The bound entities may be called *groups* or *substituents*, but should no longer be called radicals. See also *biradical*.

Rust : The product of the corrosion of iron and steel in the presence of air and water.

Rusting : The corrosion of iron or iron-based alloys such as steel. Other metals may corrode, but only iron and steel rust.

The product of the concentrations of the products, divided by the product of the concentrations of the reactants, for a chemical reaction which is not necessarily at equilibrium. For example, the reaction quotient for $A + B = C + D$ is equal to $(C)(D) / ((A)(B))$, where the parentheses indicate concentrations. Each concentration is raised to a power equal to its stoichiometric coefficient in the expression. The reaction quotient for $A + 2B = 3C$ is equal to $(C)^3 / ((A)(B)^2)$. For gas phase reactions, partial pressures can be used in the reaction quotient in place of concentrations.

The relative standard deviation is a measure of precision, calculated by dividing the standard deviation for a series of measurements by the average measurement.

ρ -value (rho-value) : A measure of the susceptibility to the influence of *substituent* groups on the rate constant or equilibrium constant of a particular organic reaction involving a family of related *substrates*. Defined by Hammett for the effect of ring substituents in meta- and para-positions of aromatic side-chain reactions by the empirical " ρ σ -equation" of the general form $\lg(k_X/k_H) = \rho \sigma X$ in

which σ_x is a constant characteristic of the substituent X and of its position in the reactant molecule. More generally (and not only for aromatic series), ρ -values (modified with appropriate subscripts and superscripts) are used to designate the susceptibility of reaction series for families of various organic compounds to any substituent effects, as given by the modified set of σ -constants in an empirical ρ σ -correlation. Reactions with a positive ρ -value are accelerated (or the equilibrium constants of analogous equilibria are increased) by substituents with positive σ -constants. Since the sign of σ was defined so that substituents with a positive σ increase the acidity of benzoic acid, such substituents are generally described as attracting electrons away from the aromatic ring. It follows that reactions with a positive ρ -value are considered to involve a transition state (or reaction product) so that the difference in energy between this state and the reactants is decreased by a reduction in electron density at the reactive site of the substrate.

S

σ -adduct (sigma adduct) : The product formed by the attachment of an *electrophilic* or *nucleophilic* entering group or of a *radical* to a ring carbon of an aromatic species so that a new sigma bond is formed and the original *conjugation* is disrupted. (This has generally been called a " σ -complex", but adduct is more appropriate than complex according to the definitions given.) The term may also be used for analogous adducts to unsaturated (and conjugated) systems in general.

σ -constant (sigma constant) : Specifically the substituent constant for meta- and for para-substituents in benzene derivatives as defined by Hammett on the basis of the ionization constant of a substituted benzoic acid in water at 25 °C, i.e. $\lg(K_s/K_s^\circ)$, where K_s is the ionization constant of a *m*- or *p*-substituted benzoic acid and K_s° that of benzoic acid itself. The term is also used as a collective description for related electronic substituent constants based on other standard reaction series, of which, σ^+ , σ^- and σ° are typical; also constants which represent dissected electronic effects such as σ_I and σ_R . For this purpose it might be better always to spell out the term in full, i.e. as "Hammett sigma constant", and restrict σ -constants to the scale of substituent constants which is based on benzoic acid. A large positive σ -value implies high electron-withdrawing power by inductive and/or resonance effect, relative to H; a large negative σ -value implies high electron-releasing power relative to H.

σ : In the valence bond theory, a sigma bond is a valence bond that is symmetrical around the imaginary line between the bonded atoms. Most single bonds are sigma bonds.

Salifiable : Capable of reacting with an acid to form a salt. Lavoisier classified lime, baryta, alumina, and silica as "salifiable earths".

Salt bridge : A permeable material soaked in a salt solution that allows ions to be transferred from one container to another. The salt solution remains unchanged during this transfer. *Example*: sodium sulphate used as a salt bridge in a galvanic cell.

A tube (often filled with ion-laced agar) that allows two solutions to be in electrical contact without mixing in an electrochemical cell.

A U-tube containing an electrolyte that connects the two compartments of a voltaic cell, allowing ion flow without extensive mixing of the different solutions.

Saponification : A reaction between a fat and a base that produces a soap.

Saponify; saponified; saponifies. The hydrolysis of esters using hot sodium hydroxide solution to produce the salt of a carboxylic acid. Usually saponification refers to the hydrolysis of esters of fatty acids to manufacture soaps.

Satp : Standard ambient pressure and temperature. Compare with STP and standard state. Used to describe a substance at standard pressure and a temperature of 25°C (298.15 K).

Saturated : A state in which a liquid can hold no more of a substance. If any more of the substance is added, it will not dissolve.

Saturated fat : A lipid that contains no carbon-carbon double bonds. Animal fats like butter and lard are composed of saturated fat. Saturated fats tend to be waxy or greasy solids.

Saturated hydrocarbon : A hydrocarbon in which the carbon atoms are held with single bonds. *Example*: ethane (C_2H_6).

Saturated solution : A solution that holds the maximum possible amount of dissolved material. When saturated, the rate of dissolving solid and that of recrystallisation solid are the same, and a condition of equilibrium is reached. The amount of material in solution varies with the temperature; cold solutions can hold less

dissolved solid material than hot solutions. Gases are more soluble in cold liquids than in hot liquids.

Compare with supersaturated solution. A solution which does not dissolve any more solute. When a saturated solution is placed in contact with additional solute, solute neither dissolves nor is deposited from a saturated solution.

Saturation transfer : A term used in nuclear magnetic resonance. When a nucleus is strongly irradiated, its spin population may partly be transferred to another nucleus by an exchange process.

Saytzeff rule : Dehydrohalogenation of secondary- and tertiary-alkyl halides proceeds by the preferential removal of the β -hydrogen from the carbon that has the smallest number of hydrogens. Originally formulated by A. Saytzeff (Zaitsev) to generalize the orientation in β -elimination reactions of alkyl halides, this rule has been extended and modified, as follows: When two or more olefins can be produced in an elimination reaction, the thermodynamically most *stable* alkene will predominate. Exceptions to the Saytzeff rule are exemplified by the *Hofmann rule*.

Scavenger : A substance that reacts with (or otherwise removes) a trace component (as in the scavenging of trace metal ions) or traps a reactive reaction *intermediate*.

Scientific method : An inefficient but highly successful method of knowledge construction based on experimental testing of hypotheses.

Scientific notation : Exponential notation. A system for reporting very small or very large numbers by writing the number as a decimal number between 1 and 10, multiplied by a power of 10. For example, 60200000000000000000000 is written in scientific notation as 6.02×10^{23} . 0.000323 is written in scientific notation as 3.23×10^{-4} .

Second (s) : The second (s) is the base unit of time in the SI system of units, defined as the duration of 9,192,631,770 cycles of the radiation associated with a certain color of light emitted by the cesium atom.

Second ionization energy : (IE,IP) second ionization potential. Compare with first ionization energy, adiabatic ionization energy, vertical ionization energy, electronegativity, and electron affinity. The energy needed to remove an electron from an isolated +1 ion. The third ionization energy would be the energy required to remove an electron from an isolated +2 ion, and so on.

Second law : Second law of thermodynamics. The second law states that every spontaneous process causes a net increase in the entropy of the universe. Many alternative statements are possible, including: Heat cannot be converted to work via an isothermal cycle. Heat cannot be converted to work with 100% efficiency. Heat cannot flow from a cold object to a warmer object without doing outside work.

Second law of thermodynamics : In any spontaneous process, there is always an increase in the entropy of the universe.

Second order reaction : Compare with zero order reaction and first order reaction. A reaction with a rate law that is proportional to either the concentration of a reactant squared, or the product of concentrations of two reactants.

Sediment : Material that settles out at the bottom of a liquid when it is still. A precipitate is one form of sediment.

Sedimentation : Separation of a dense material (usually a solid) from a less dense material (usually a liquid) by allowing the denser material to settle out of the mixture.

Selectivity : The discrimination shown by a reagent in competitive attack on two or more *substrates* or on two or more positions in the same substrate. It is quantitatively expressed by ratios of *rate constants* of the competing reactions, or by the decadic logarithms of such ratios.

Selectivity factor : A quantitative representation of *selectivity* in *aromatic* substitution reactions (usually *electrophilic*, for monosubstituted benzene derivatives). If the *partial rate factor*, f , expresses the reactivity of a specified position in the aromatic compound PhX relative to that of a single position in benzene, then the selectivity factor S_f (expressing discrimination between *p*- and *m*-positions in PhX) is defined as $S_f = \lg(f_p^X/f_m^X)$.

Semiconductor : A material of intermediate conductivity. Semiconductor devices often use silicon when they are made as part of diodes, transistors or integrated circuits. Elements intermediate between metals and non-metals are also sometimes called semiconductors. *Example*: germanium oxide, germanium.

Semipermeable membrane : A membrane that allows some but not all of the components in a mixture to pass through it. Semipermeable membranes are used in dialysis.

A thin material that acts as a fine sieve or filter, allowing small molecules to pass, but holding large molecules back.

Separating column : Used in chromatography. A tall glass tube containing a porous disc near the base and filled with a substance (for example, aluminium oxide, which is known as a stationary phase) that can adsorb materials on its surface. When a mixture is passed through the column, fractions are retarded by differing amounts, so that each fraction is washed through the column in sequence.

Separating funnel : A pear-shaped, glassware funnel designed to permit the separation of immiscible liquids by simply pouring off the more dense liquid while leaving the less dense liquid in the funnel.

Series circuit : An electrical circuit in which all of the components are joined end to end in a line.

Serine : (Ser, $\text{HOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$)

Shell : Compare with subshell. A set of electrons with the same principal quantum number. The number of electrons permitted in a shell is equal to $2n^2$. A shell contains n^2 orbitals, and n subshells.

The term used to describe the imaginary ball-shaped surface outside the nucleus of an atom that would be formed by a set of electrons of similar energy. The outermost shell is known as the valence shell. *Example*: neon has shells containing 2 and 8 electrons.

Shielding : In the context of NMR spectroscopy shielding is the effect of the electron shells of the observed and the neighbouring nuclei on the external magnetic field. The external field induces

circulations in the electron cloud. The resulting magnetic moment is oriented in the opposite direction to the external field, so that the local field at the central nucleus is weakened, although it may be strengthened at other nuclei (deshielding). The phenomenon is the origin of the structural dependence of the resonance frequencies of the nuclei.

Short term memory : Short term memory is a mechanism for storing temporary information, such as where you parked your car or numbers in a simple arithmetic problems.

SI : Systeme Internationale; International System. Le Système Internationale (SI) is a system of units introduced to remove barriers to international trade, based on the older metric system. It is now used in science and technical communications worldwide.

Side-arm boiling tube : A boiling tube with an integral glass pipe near its open end. The side arm is normally used for the entry or exit of a gas.

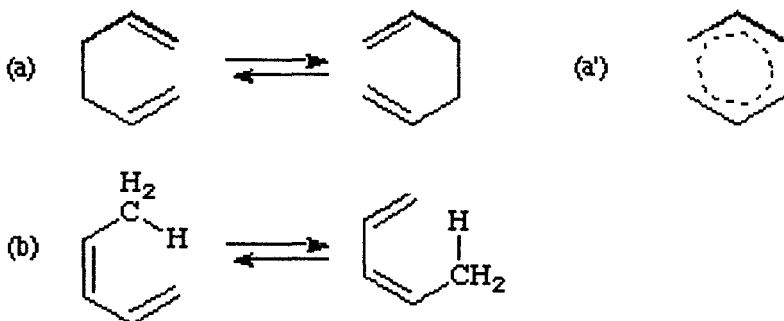
siemens (S, upside-down Ω) : Absolute ohm; ohm⁻¹; reciprocal ohm; mho.

Sigma bond : A bond formed from the overlap of either two s-orbitals or two hybrid orbitals such as sp³ or sp² orbitals. (σ bond) Compare with pi bond.

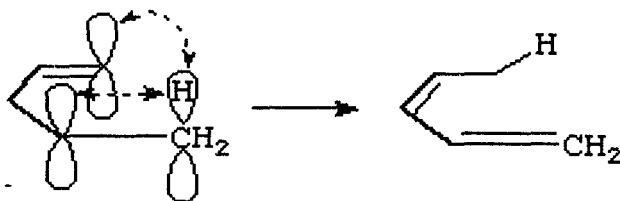
Sigma, pi (σ , π) : The terms are symmetry designations, pi molecular orbitals being antisymmetric with respect to a defining plane containing at least one atom (e.g. the molecular plane of ethene), and sigma molecular orbitals symmetric with respect to the same plane. In practice the terms are used both in this rigorous sense (for orbitals encompassing the entire molecule) and also for localized two-centre orbitals or bonds, and it is necessary to make a clear distinction between the two usages. In the case of two-centre bonds, a pi bond has a nodal plane that includes the internuclear bond axis, whereas a sigma bond has no such nodal plane. (A delta bond in organometallic or inorganic molecular species has two nodes.) *Radicals* are classified by analogy into sigma and pi radicals. Such two-centre orbitals may take part in molecular orbitals of sigma or pi symmetry. For example, the methyl group in propene contains three C-H bonds, each of which is of local sigma symmetry (i.e. without a

nodal plane including the internuclear axis), but these three "sigma bonds" can in turn be combined to form a set of group orbitals one of which has pi symmetry with respect to the principal molecular plane and can accordingly interact with the two-centre orbital of pi symmetry (pi bond) of the double-bonded carbon atoms, to form a molecular orbital of pi symmetry. Such an interaction between the CH₃ group and the double bond is an example of what is called *hyperconjugation*. This cannot rigorously be described as "sigma-pi conjugation" since sigma and pi here refer to different defining planes, and interaction between orbitals of different symmetries (with respect to the same defining plane) is forbidden.

Sigmatropic rearrangement : A *molecular rearrangement* that involves both the creation of a new sigma bond between atoms previously not directly linked and the breaking of an existing sigma bond. There is normally a concurrent relocation of pi bonds in the molecule concerned, but the total number of pi and sigma bonds does not change. The term was originally restricted to *intramolecular* pericyclic reactions, and many authors use it with this connotation. It is, however, also applied in a more general, purely structural, sense. If such reactions are *intramolecular*, their *transition state* may be visualized as an *association* of two fragments connected at their termini by two partial sigma bonds, one being broken and the other being formed as, for example, the two allyl fragments in (a'). Considering only atoms within the (real or hypothetical) cyclic array undergoing reorganization, if the numbers of these in the two fragments are designated *i* and *j*, then the rearrangement is said to be a sigmatropic change of order [*i,j*] (conventionally [*i*] <= [*j*]). Thus the rearrangement (a) is of order [3,3], whilst reaction (b) is a [1,5]sigmatropic shift of hydrogen. (N.B.: By convention square brackets [...] here refer to numbers of atoms, in contrast with current usage in the context of cycloaddition.)



The descriptors *a* and *s* (*antarafacial* and *suprafacial*) may also be annexed to the numbers *i* and *j*; (b) is then described as a [1s,5s] sigmatropic rearrangement, since it is suprafacial with respect both to the hydrogen atom and to the pentadienyl system :



The prefix "homo" (meaning one extra atom, interrupting conjugation - cf. "homoaromaticity") has frequently been applied to sigmatropic rearrangements, but is misleading. See also *cycloaddition*, *tautomerism*.

Significant figure : Significant digit; significant. A convention for recording measurements. Measurements are rounded so that they contain only the digits up to and including the first uncertain digit, when the number is written in scientific notation.

Silicate : A negatively charged ion containing silicon and oxygen, usually SiO_3^{-2} , $\text{Si}_2\text{O}_7^{-6}$, and $\text{Si}_3\text{O}_7^{-2}$.

A compound containing positively charged metal ions combined with negatively charged ions made of silicon and oxygen.

Silylene : Generic name for $\text{H}_2\text{Si:}$ and substitution derivatives thereof, containing an electrically neutral bivalent silicon atom with

two non-bonding electrons. (The definition is analogous to that given for *carbene*.)

The silanediyl group (H_2Si), analogous to the methylene group (H_2C).

Simple distillation : The distillation of a substance when only one volatile fraction is to be collected. Simple distillation uses a Liebig condenser arranged almost horizontally. When the liquid mixture is heated and vapours are produced, they enter the condenser and then flow away from the flask and can be collected. *Example*: simple distillation of ethanoic acid.

Single displacement : Single replacement reaction; single displacement reaction; single replacement. Compare with double displacement. A reaction of the form $\text{A} + \text{BC} = \text{B} + \text{AC}$. For example, zinc displaces hydrogen from hydrochloric acid in the following reaction: $\text{Zn(s)} + 2 \text{HCl(aq)} = \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$.

Single-electron transfer mechanism (SET) : A reaction *mechanism* characterized by the transfer of a single electron between the species occurring on the *reaction coordinate* of one of the *elementary steps*.

Single-step reaction : A reaction that proceeds through a single *transition state*.

Slag : A mixture of substances that are waste products of a furnace. Most slags are composed mainly of silicates.

Slater-type orbital : An approximate atomic orbital that attempts to allow for electron-electron repulsion by scaling the nuclear charge for each orbital.

Smelting : Roasting a substance in order to extract the metal contained in it.

Smog : A mixture of smoke and fog. The term is used to describe city fogs in which there is a large proportion of particulate matter (tiny pieces of carbon from exhausts) and also a high concentration of sulphur and nitrogen gases and probably ozone.

Smokeless fuel : A fuel which has been subjected to partial pyrolysis, such that there is no more loose particulate matter remaining. *Example*: Coke is a smokeless fuel.

Soap : A salt of a fatty acid. For example, sodium stearate is a soap made by neutralizing stearic acid. Commercial soaps are mixtures of fatty acid salts.

Sol : A colloid with solid particles suspended in a liquid. Examples are protoplasm, starch in water, and gels.

Solid : A solid is a relatively dense, rigid state of matter, with a definite volume and shape. Molecules in solids are often packed close together in regularly repeating patterns, and vibrate around fixed positions.

Solid/solid phase : A rigid form of matter which maintains its shape, whatever its container.

Solubility : A measure of the maximum amount of a substance that can be contained in a solvent.

Solubilities; equilibrium solubility; solubleness. The solubility of a substance is its concentration in a saturated solution. Substances with solubilities much less than 1 g/100 mL of solvent are usually considered insoluble. The solubility is sometimes called "equilibrium solubility" because the rates at which solute dissolves and is deposited out of solution are equal at this concentration.

Solubility product : (K_{sp}) K_{sp} . The equilibrium constant for a reaction in which a solid ionic compound dissolves to give its constituent ions in solution.

Solubilizing group : A group or substructure on a molecule that increases the molecule's solubility. Solubilizing groups usually make the molecule they are attached to ionic or polar. For example, hydrocarbon chains can be made water-soluble by attaching a carboxylic acid group to the molecule.

Soluble : Compare with insoluble.

Readily dissolvable in a solvent.

Soluble salt : An ionic compound that dissolves in a solvent (usually water).

Solute : A substance dissolved in a solvent to make a solution.

A substance that has dissolved. *Example*: sodium chloride in water.

Solution : A mixture of a liquid (the solvent) and at least one other substance of lesser abundance (the solute). Mixtures can be separated by physical means, for example, by evaporation and cooling.

Homogeneous mixture. Compare with heterogeneous mixture. A sample of matter consisting of more than one pure substance with properties that do not vary within the sample. Also called a homogeneous mixture.

Solvation : Any stabilizing interaction of a solute (or solute moiety) and the solvent or a similar interaction of solvent with groups of an insoluble material (i.e., the ionic groups of an ion-exchange resin). Such interactions generally involve electrostatic forces and *van der Waals forces*, as well as chemically more specific effects such as *hydrogen bond* formation.

Solvatochromic relationship : A *linear free-energy relationship* based on *solvatochromism*.

Solvatochromism : The (pronounced) change in position and sometimes intensity of an electronic absorption or emission band, accompanying a change in the polarity of the medium. Negative (positive) solvatochromism corresponds to a *hypsochromic* (*bathochromic*) shift with increasing solvent *polarity*.

Solvent : The main substance in a solution.

The most abundant component in a solution.

Solvent extraction : Solvent extraction is a method for separating mixtures by exploiting differences in the solubilities of the components. For example, a coffee machine extracts the soluble components of ground coffee with water, and leaves the insoluble components behind. The sample is shaken or mixed with solvent (or with two immiscible solvents) to effect the separation. The "like

dissolves like" is a useful guide for selecting solvents to use in the extraction. Nonpolar substances are usually successfully extracted into nonpolar solvents like hexane or methylene chloride. Polar and ionic substances are often extracted with water.

Solvent parameter : Quantitative measures of the capability of solvents for interaction with solutes. Such parameters have been based on numerous different physico-chemical quantities, e.g. *rate constants*, solvatochromic shifts in ultraviolet/visible spectra, solvent-induced shifts in infrared frequencies, etc. Some solvent parameters are purely empirical in nature, i.e. they are based directly on some experimental measurement. It may be possible to interpret such a parameter as measuring some particular aspect of solvent-solute interaction or it may be regarded simply as a measure of solvent *polarity*. Other solvent parameters are based on analysing experimental results. Such a parameter is considered to quantify some particular aspect of solvent capability for interaction with solutes.

Solvolysis : Generally, reaction with a solvent, or with a *lyonium ion* or *lyate ion*, involving the rupture of one or more bonds in the reacting solute. More specifically the term is used for *substitution*, *elimination* and *fragmentation* reactions in which a solvent species is the *nucleophile* ("alcoholysis" if the solvent is an alcohol, etc.).

Solvophobicity parameter : A *solvent parameter* defined by $S_p = 1 - M/M(\text{hexadecane})$ derived from the Gibbs energy of transfer ($\Delta_t G^\circ$) of a series of solutes from water to numerous aqueous-organic mixtures and to pure solvents: $\Delta_t G^\circ(\text{to solvent}) = MR_T + D$ where R_T is a solute parameter, and M and D characterize the solvent. The M values are used to define a solvent solvophobic effect so that S_p values are scaled from unity (water) to zero (hexadecane).

SOMO : A Singly Occupied Molecular Orbital (such as the half-filled *HOMO* of a radical).

Sonication : Irradiation with (often ultra)sound waves, e.g. to increase the rate of a reaction or to prepare vesicles in mixtures of surfactants and water.

Sorption : Assimilation of molecules of one substance by a material in a different phase. Adsorption (sorption on a surface) and absorption (sorption into bulk material) are two types of sorption phenomena.

Special salt effect : The initial steep rate increase observed in the *kinetic electrolyte effect* on certain solvolysis reactions, upon addition of some non-common ion salts, especially LiClO_4 .

Specific catalysis : The acceleration of a reaction by a unique *catalyst*, rather than by a family of related substances. The term is most commonly used in connection with specific hydrogen-ion or hydroxide-ion (*lyonium ion* or *lyate ion*) catalysis.

Specific gravity : specific gravities. Compare with density. The mass of a unit volume of a substance relative to the mass of a unit volume of water. Temperature must be specified when reporting specific gravities, since the density of the substance and of water change with temperature. Specific gravities are often reported relative to water at 4°C ; at that temperature, water has a density of 1.00000 g/mL and the specific gravity of a substance is equal to its density in g/mL .

Specific heat : The heat required to raise the temperature of 1 g of a substance by 1°C is called the specific heat of the substance. Specific heat is an intensive property with units of $\text{J g}^{-1} \text{ K}^{-1}$.

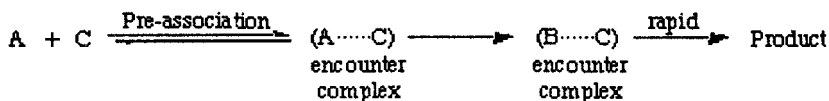
Specific heat capacity : The amount of energy required to raise the temperature of one gram of a substance by one degree Celsius (or Kelvin).

Specific volume : The volume of a unit mass of substance. For example, the specific volume of water at 4°C is 1.00000 mL/g . Specific volume is the reciprocal of density.

Spectator ion : A spectator ion is an ion that appears as both a reactant and a product in an ionic equation. For example, in the ionic equation $\text{Ag}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) = \text{AgCl}(\text{s}) + \text{Na}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ the sodium and nitrate ions are spectator ions.

Spectator mechanism : A *pre-association* mechanism in which one of the *molecular entities*, C, is already present in an *encounter*

pair with A during formation of B from A, but does not assist the formation of B, e.g.



The formation of B from A may itself be a bimolecular reaction with some other reagent. Since C does not assist the formation of A, it is described as being present as a spectator, and hence such a mechanism is sometimes referred to as a spectator mechanism.

Spectrophotometer : An instrument for measuring the amount of light absorbed by a sample.

Spectrophotometry : Spectrophotometric. Determination of the concentration of a material in a sample by measurement of the amount of light the sample absorbs.

Spectroscope : Spectrometer. An instrument for measuring the spectrum of light or radiation.

Spectroscopy : Spectrometry; spectroscopic. Spectroscopy is analysis of the interaction between electromagnetic radiation and matter. Different types of radiation interact in characteristic ways with different samples of matter; the interaction is often unique and serves as a diagnostic "fingerprint" for the presence of a particular material in a sample. Spectroscopy is also a sensitive quantitative technique that can determine trace concentrations of substances.

Spectrum : A sequence of colors produced by passing light through a prism or diffraction grating.

A range of wavelengths of electromagnetic radiation.

A plot that shows how some intensity-related property of a beam of radiation or particles depends on another property that is related to dispersal of the beam by a prism, a magnet, or some other device. For example, a plot of light absorbance vs. wavelength is an absorption spectrum; a plot of ion abundance vs. mass is a mass spectrum.

Spin : Electrons have an intrinsic angular momentum that is similar to what would be observed if they were spinning. Electron spin is sometimes called a "twoness" property because it can have two values, referred to as "spin up" and "spin down". Nuclei can have spins of their own.

Spin density : The unpaired *electron density* at a position of interest, usually at carbon, in a *radical*. It is often measured experimentally by electron paramagnetic resonance (EPR, ESR (electron spin resonance)) spectroscopy through hyperfine coupling constants of the atom or an attached hydrogen.

Spin label : A *stable* paramagnetic group (typically a nitryl radical) that is attached to a part of a *molecular entity* whose microscopic environment is of interest and may be revealed by the electron spin resonance (ESR) spectrum of the spin label. When a simple paramagnetic molecular entity is used in this way without covalent attachment to the molecular entity of interest it is frequently referred to as a "spin probe".

Spin pair : ($\uparrow\downarrow$) paired spins; electron pair; paired electrons. Compare with unpaired spin.

Spin trapping : In certain reactions in solution a *transient radical* will interact with a diamagnetic reagent to form a more *persistent* radical. The product radical accumulates to a concentration where detection and, frequently, identification are possible by EPR/ESR spectroscopy. The key reaction is usually one of *attachment*; the diamagnetic reagent is said to be a "spin trap", and the persistent product radical is then the "spin adduct". The procedure is referred to as spin trapping, and is used for monitoring reactions involving the intermediacy of *reactive* radicals at concentrations too low for direct observation. Typical spin traps are C-nitroso compounds and nitrones, to which reactive radicals will rapidly add to form nitryl radicals. A quantitative development, in which essentially all reactive radicals generated in a particular system are intercepted, has been referred to as "spin counting". Spin trapping has also been adapted to the interception of radicals generated in both gaseous and solid phases. In these cases the spin adduct is in practice transferred to a liquid solution for observation in

order to facilitate interpretation of the EPR/ESR spectra of the radicals obtained.

Spontaneous : Spontaneity; spontaneous process; spontaneous reaction. A spontaneous process occurs because of internal forces; no external forces are required to keep the process going, although external forces may be required to get the process started. For example, the burning of wood is spontaneous once the fire is started. The combination of water and carbon dioxide to reform the wood and oxygen is NOT spontaneous!

Spontaneous process : A process that occurs without outside intervention. Spontaneity is independent of rate. To be spontaneous a process must increase the entropy of the universe.

Stabilizer : A substance that makes a mixture more stable. Antioxidants and antiozonants are examples of stabilizers; stabilizers are added to paints to prevent the components of the mixture from separating over time.

Stable : As applied to *chemical species*, the term expresses a thermodynamic property, which is quantitatively measured by relative molar standard Gibbs energies. A chemical species A is more stable than its isomer B if $\Delta_r G^\circ > 0$ for the (real or hypothetical) reaction $A \longrightarrow B$, under standard conditions. If for the two reactions $P \longrightarrow X + Y$ ($\Delta_r G_1^\circ$) $Q \longrightarrow X + Z$ ($\Delta_r G_2^\circ$) $\Delta_r G_1^\circ > \Delta_r G_2^\circ$, P is more stable relative to the product Y than is Q relative to Z. Both in qualitative and quantitative usage the term stable is therefore always used in reference to some explicitly stated or implicitly assumed standard. The term should not be used as a synonym for *unreactive* or "less reactive" since this confuses thermodynamics and kinetics. A relatively more stable chemical species may be more *reactive* than some reference species towards a given reaction partner.

Standard deviation : (s,BESD, σ) The standard deviation is a statistical measure of precision. The best estimate of the standard deviation s for small data sets is calculated using

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N-1}}$$

where x_i is the measurement from the i -th run, \bar{x} is the mean of all the measurements, and N is the number of measurements. For very large data sets, the standard deviation is the root-mean-square deviation from the true mean, and is usually written as σ to distinguish it from the best estimate standard deviation s used for small data sets.

Standard enthalpy change : (ΔH°) standard enthalpy. A change in enthalpy associated with a reaction or transformation involving substances in their standard states.

Standard enthalpy of formation : (ΔH_f°) standard heat of formation; heat of formation; enthalpy of formation. The change in enthalpy when one mole of compound is formed from its elements in their most stable form and in their standard states.

Standard enthalpy of reaction : (ΔH_{rxn}°) standard heat of reaction. A change in enthalpy associated with a reaction involving substances in their standard states.

Standard entropy of reaction : (ΔS_{rxn}°) entropy of reaction. A change in entropy associated with a reaction involving substances in their standard states. A superscript circle ($^\circ$) distinguishes standard enthalpy changes from enthalpy changes which involve reactants and products that are not in their standard states.

Standard hydrogen electrode : SHE. A platinum electrode that runs the half reaction $2\text{H}^+(\text{aq}, 1\text{M}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}, 1\text{atm})$, chosen as a reference for cell voltages. The electrode potential of the standard hydrogen electrode is defined to be zero volts.

Standard molar entropy : (S°) The entropy of one mole of a substance in its standard state.

Standard molar volume : The volume of 1 mole of an ideal gas at STP, equal to 22.414 liters.

Standard pressure : (P° or P°) Standard pressure is a pressure of 1 bar. Before 1982, the standard pressure was 1 atm (1 atm = 1.01325 bar).

Standard reduction potential : (E°) The voltage associated with a reduction process at standard state. The reduction potential of $2\text{H}^+(\text{aq}, 1\text{M}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}, 1\text{atm})$ is taken as exactly zero volts.

Standard solution : A solution of precisely known concentration.

Standard state : ($^{\circ}$ or $^{\circ}$) A set of conditions defined to allow convenient comparison of thermodynamic properties. The standard state for a gas is the state of the pure substance in the gaseous phase at the standard pressure, with the gas behaving ideally. The standard state for liquids and solids is the state of the most stable form of the substance at the standard pressure. Temperature is not included in the definition of standard state and must be specified, but when not given a temperature of 25°C is usually implied.

Standard state : The most stable form of a substance at 298 K and 1 atmosphere of pressure.

Starch : A polymer of glucose that has alpha-1,4-glycoside linkages.

A polysaccharide used by plants to stockpile glucose molecules. The most common forms are amylose and amylopectin.

State (of a system) : The condition of the system at a given time; it is usually defined by an equation which is called an equation of state.

State function : A property that depends only on the condition or "state" of the system, and not on the path used to obtain the current conditions. Energy, enthalpy, temperature, volume, pressure, and temperature are examples of state functions; heat and work are examples of non-state functions.

A property that is independent of the pathway; this function can be used to define or specify the state of the system.

State of matter : There are three common states of matter: gases, liquids, and solids. States of matter differ in the way the molecules are arranged at the molecular level, but not in the structure of the molecules themselves. Other states (the plasma and Bose-Einstein condensate states) are uncommon on Earth.

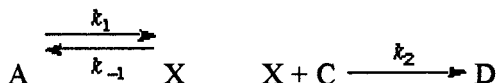
Stationary phase : A stationary phase is a substance that shows different affinities for different components in a sample mixture in a separation of the mixture by chromatography. The mobile phase (a

solution containing the sample) flows over or through the stationary phase to effect the separation.

Stationary state : In quantum mechanics: A state that does not evolve with time.

In kinetics: See *steady state*.

Steady state (or stationary state) : In a kinetic analysis of a complex reaction involving *unstable* intermediates in low concentration, the rate of change of each such *intermediate* is set equal to zero, so that the rate equation can be expressed as a function of the concentrations of *chemical species* present in macroscopic amounts. For example, assume that X is an unstable intermediate in the reaction sequence :



Conservation of mass requires that: $[A] + [X] + [D] = [A]_0$ which, since $[A]_0$ is constant, implies: $-d[X]/dt = d[A]/dt + d[D]/dt$. Since $[X]$ is negligibly small, the rate of formation of D is essentially equal to the rate of disappearance of A, and the rate of change of $[X]$ can be set equal to zero. Applying the steady state approximation ($d[X]/dt = 0$) allows the elimination of $[X]$ from the kinetic equations, whereupon the rate of reaction is expressed :

$$d[D]/dt = -d[A]/dt = \frac{k_1 k_2 [A][C]}{k_{-1} + k_2 [C]}$$

Note: The steady-state approximation does not imply that $[X]$ is even approximately constant, only that its absolute rate of change is very much smaller than that of $[A]$ and $[D]$. Since according to the reaction scheme $d[D]/dt = k_2 [X][C]$, the assumption that $[X]$ is constant would lead, for the case in which C is in large excess, to the absurd conclusion that formation of the product D will continue at a constant rate even after the reactant A has been consumed. (2) In a stirred flow reactor a steady state implies a regime so that all concentrations are independent of time.

Steel : An alloy of iron and carbon. Steel contains anywhere between 0.2% carbon (for soft wire and sheet steel) and 1.5% carbon (for cutting tools), with small amounts of many other elements often present.

Stepwise reaction : A *chemical reaction* with at least one reaction *intermediate* and involving at least two consecutive *elementary reactions*. See also *composite reaction*.

Steradian : (str) A solid angle with vertex at the center of a sphere of radius r that encompasses an area of r^2 on the surface of the sphere.

Stereochemistry : Stereochemistry is the study of how the properties of a compound are affected by the spatial positions of groups within its molecules. Stereochemistry is also concerned with determining the structure of stereoisomers.

Stereoelectronic : Pertaining to the dependence of the properties (especially the energy) of a *molecular entity* in a particular electronic state (or of a *transition state*) on relative nuclear geometry. The electronic ground state is usually considered, but the term can apply to excited states as well. Stereoelectronic effects are ascribed to the different alignment of electronic orbitals in different arrangements of nuclear geometry.

Stereoelectronic control : Control of the nature of the products of a *chemical reaction* (or of its rate) by *stereoelectronic* factors. The term is usually applied in the framework of an orbital approximation. The variations of *molecular orbital* energies with relative nuclear geometry (along a *reaction coordinate*) are then seen as consequences of variations in basis-orbital overlaps.

Stereoisomer : Molecules with the same atoms and bond structure, but different three dimensional arrangements of atoms. For example, the CH_3 groups in $\text{CH}_3\text{CH}=\text{CHCH}_3$ can be placed on the same side of the double bond in one stereoisomer and on opposite sides in another.

Stereoisomers : Molecules that have the same molecular formula, the same sequence of bonds, but different spatial arrangements. Geometric isomers and optical isomers are both types of stereoisomers.

Stereoselectivity, stereoselective : Stereoselectivity is the preferential formation in a *chemical reaction* of one stereoisomer over another. When the stereoisomers are enantiomers, the phenomenon is called enantioselectivity and is quantitatively expressed by the enantiomer excess; when they are diastereoisomers, it is called diastereoselectivity and is quantitatively expressed by the diastereomer excess. Reactions are termed (100%) stereoselective if the discrimination is complete or partially ($x\%$) stereoselective if one product predominates. The discrimination may also be referred to semiquantitatively as high or low stereoselectivity.

Stereospecificity, stereospecific : A reaction is termed stereospecific if starting materials differing only in their *configuration* are converted into stereoisomeric products. According to this definition, a stereospecific process is necessarily *stereoselective* but not all stereoselective processes are stereospecific. Stereospecificity may be total (100%) or partial. The term is also applied to situations where reaction can be performed with only one stereoisomer. For example the exclusive formation of *trans*-1,2-dibromocyclohexane upon bromination of cyclohexene is a stereospecific process, although the analogous reaction with (*E*)-cyclohexene has not been performed.

The term has also been applied to describe a reaction of very high stereoselectivity, but this usage is unnecessary and is discouraged. [For the use of the term "stereospecific polymerization"]

Steric effect : The effect on a chemical or physical property (structure, rate or equilibrium constant) upon introduction of substituents having different steric requirements. The steric effect in a reaction is ascribed to the difference in steric energy between, on the one hand, reactants and, on the other hand, a *transition state*, (or products). A steric effect on a rate process may result in a rate increase ("steric acceleration") or a decrease ("steric retardation"). (The adjective "steric" is not to be confused with stereochemical.) Steric effects arise from contributions ascribed to *strain* as the sum of (1) non-bonded repulsions, (2) bond angle strain, and (3) bond stretches or compressions. For the purpose of *correlation analysis* or *linear free-energy relations* various scales of steric parameters have been proposed, notably *A values*, Taft's E_s and Charton's ν scales. In

a reactant molecule RY and an appropriate reference molecule R⁰Y, the "primary steric effect" of R is the direct result of differences in compressions which occur because R differs from R⁰ in the vicinity of the reaction centre Y. A "secondary steric effect" involves the differential moderation of electron delocalization by non-bonded compressions. Some authors make a distinction between "steric" effects attributed to van der Waals repulsions alone, and "strain" effects, attributed to deviations of bond angles from "ideal" values.

Steric hindrance : The original term for a *steric effect* arising from crowding of substituents.

Steric-approach control : Control of *stereoselectivity* of a reaction by steric hindrance towards attack of the reagent, which is directed to the less hindered face of the molecule. Partial bond making is strong enough at the *transition state* for steric control to take place. This suggests that the transition state should not be close to products.

Stoichiometric coefficient : The coefficients given before substances in a balanced chemical equation. For example, the stoichiometric coefficient of carbon dioxide in the following reaction is $4 : 2 \text{C}_2\text{H}_6(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{CO}_2 + 6 \text{H}_2\text{O}$

Stoichiometry : Ratios of atoms in a compound.

Ratios of moles of compounds in a reaction.

A branch of chemistry that quantitatively relates amounts of elements and compounds involved in chemical reactions, based on the law of conservation of mass and the law of definite proportions.

Stopped flow : A technique for following the kinetics of reactions in solution (usually in the millisecond time range) in which two reactant solutions are rapidly mixed by being forced through a mixing chamber. The flow of the mixed solution along a uniform tube is then suddenly arrested. At a fixed position along the tube the solution is monitored (as a function of time following the stoppage of the flow) by some method with a rapid response (e.g. photometry).

STP : standard temperature and pressure. Compare with SATP and standard state. Used to describe a substance at standard pressure and a temperature of 0°C (273.15 K).

Strain : Strain is present in a *molecular entity* or *transition structure* if the energy is enhanced because of unfavourable bond lengths, bond angles, or dihedral angles ("torsional strain") relative to a standard. It is quantitatively defined as the standard enthalpy of a structure relative to a strainless structure (real or hypothetical) made up from the same atoms with the same types of bonding. (The enthalpy of formation of cyclopropane is 53.6 kJ mol^{-1} , whereas the enthalpy of formation based on three "normal" methylene groups, from acyclic models, is -62 kJ mol^{-1} . On this basis cyclopropane is destabilized by ca. 115 kJ mol^{-1} of strain energy).

Stripping : Stripping is a technique for removing volatile components in a mixture by bubbling a stream of an chemically unreactive gas (like nitrogen) through the sample, and then 'scrubbing' the nitrogen through a solution or solid adsorbent that can recover the volatile materials.

Strong acid : A strong acid is an acid that completely dissociates into hydrogen ions and anions in solution. Strong acids are strong electrolytes. There are only six common strong acids: HCl (hydrochloric acid), HBr (hydrobromic acid), HI (hydroiodic acid), H_2SO_4 (sulfuric acid), HClO_4 (perchloric acid), and HNO_3 (nitric acid).

Strong base : A strong base is an base that completely dissociates into ions in solution. Strong bases are strong electrolytes. The most common strong bases are alkali metal and alkaline earth metal hydroxides.

Strong electrolyte : A strong electrolyte is a solute that completely dissociates into ions in solution. Solutions of strong electrolytes conduct electricity. Most soluble ionic compounds are strong electrolytes.

Strong ligand : Strong field ligand. A ligand that causes a large crystal field splitting which results in a low-spin complex.

Structural formula. A structural formula is a diagram that shows how the atoms in a molecule are bonded together. Atoms are represented by their element symbols and covalent bonds are represented by lines. The symbol for carbon is often not drawn. Most structural formulas don't show the actual shape of the molecule

(they're like floor plans that show the layout but not the 3D shape of a house).

Structural isomers : They organic compounds that have the same som formula, meaning the same number of carbons , hydrogens or other type ot atoms. They differ from each other in the way the atoms are connected. Examples are n-butane and 2-methylpropane or ethanol and dimethylether.

Subjacent orbital : The Next-to-Highest Occupied Molecular Orbital ("NHOMO", also called "HOMO-") and the Second Lowest Unoccupied Molecular Orbital (SLUMO). Subjacent orbitals are sometimes found to play an important role in the interpretation of molecular interactions according to the *frontier orbital* approach.

Sublimation : Sublimate; sublimating. Conversion of a solid directly into a gas, without first melting into a liquid.

The process by which a substance goes directly from the solid to the gaseous state without passing through the liquid state.

Subshell : Sublevel. A set of electrons with the same azimuthal quantum number. The number of electrons permitted in a subshell is equal to $2\ell + 1$.

Substituent : An atom or *group* of bonded atoms that can be considered to have replaced a hydrogen atom (or two hydrogen atoms in the special case of bivalent groups) in a parent *molecular entity* (real or hypothetical).

Substitution : Substitution reaction. A reaction in which an atom or fragment within a molecule is replaced with another.

Substitution reaction : A *reaction*, *elementary* or *stepwise*, in which one atom or *group* in a *molecular entity* is replaced by another atom or group. For example, $\text{CH}_3\text{Cl} + \text{OH}^- \longrightarrow \text{CH}_3\text{OH} + \text{Cl}^-$

Substrate : A *chemical species*, the reaction of which with some other chemical reagent is under observation (e.g., a compound that is transformed under the influence of a *catalyst*). The ter should be used with care. Either the context or a specific statem should always make it clear which chemical species in a reactic regarded as the substrate. See also *transformation*.

A substance that is acted upon by an enzyme during a biochemical reaction.

Successor complex : The radical ion pair which forms by the transfer of an electron from the donor D to the acceptor A after these species have diffused together to form the *precursor* or *encounter complex* : $A + D \longrightarrow (A \cdot D) \longrightarrow (A \cdot^- D^+)$

Sugar : A carbohydrate with a characteristically sweet taste. Sugars are classified as monosaccharides, disaccharides, or trisaccharides.

Sulphate (SO_4^{2-}) : The SO_4^{2-} ion, formed by reaction of sulfuric acid with a base.

A compound containing the SO_4^{2-} ion.

Sulphite (SO_3^{2-}) : The SO_3^{2-} ion, formed by reaction of sulfurous acid with a base.

A compound containing the SO_3^{2-} ion.

Sulphuric acid (H_2SO_4) : Oil of vitriol; sulphuric acid. An oily, corrosive liquid that acts as a strong acid when dissolved in water. Sulfuric acid has so many industrial uses that sulfuric acid production was once used as an index of industrial productivity. Salts of sulfuric acids are called sulfates.

Sulphurous acid (H_2SO_3) : A colorless liquid that acts as a weak acid when dissolved in water, sometimes used as a bleach. Salts of sulfurous acid are called sulfites.

Supercooling : Supercooled; supercool. Liquids at temperatures below their normal freezing points are said to be "supercooled".

Supercritical fluid : A fluid state that occurs when the pressure and temperature exceed the substance's critical pressure and critical temperature. Supercritical fluids fill their containers like gases but dissolve substances like liquids, which makes them very useful as solvents. Their density and other properties are intermediate between gases and liquids.

Superoxide : Superoxide ion. A binary compound containing oxygen in the $-1/2$ oxidation state. For example, KO_2 is potassium superoxide, an ionic compound containing the superoxide ion, O_2^- .

Supersaturated solution : supersaturated. A supersaturated solution has concentration of solute that is higher than its solubility. A crystal of solute dropped into a supersaturated solution grows; excess solute is deposited out of the solution until the concentration falls to the equilibrium solubility.

Supramolecule : A system of two or more *molecular entities* held together and organized by means of intermolecular (noncovalent) binding interactions.

Surface tension : The work required to expand the surface of a liquid by unit area.

Surfactant : A material that spreads along a surface, changing the properties of the surface. For example, soap spreads over a water surface and lowers its surface tension.

Surroundings : In thermodynamics, the surroundings refer to the universe outside the system.

Everything in the universe surrounding a thermodynamic system.

Suspension : A heterogenous mixture in which droplets or particles are suspended in a liquid.

Swain-Lupton equation : A dual parameter approach to the correlation analysis of substituent effects, which involves a field constant (F) and a resonance constant (R). The original treatment was modified later.

Swain-Scott equation : The *linear free-energy relation* of the form $\lg(k/k_0) = sn$ applied to the variation of *reactivity* of a given *electrophilic* substrate towards a series of nucleophilic reagents. n is characteristic of the reagent (i.e. a measure of its *nucleophilicity*) and s is characteristic of the substrate (i.e. a measure of its sensitivity to the nucleophilicity of the reagent). A scale of n values is based on the rate coefficients k for the reaction of methyl bromide with nucleophiles in water at 25 °C, s being defined as 1.00 for these reactions and n being defined as 0.00 for the hydrolysis of methyl bromide. (Other scales have been devised).

Symbiosis : The term was originally applied to describe the maximum flocking of either hard or soft *ligands* in the same complexes. For hydrocarbon molecules, symbiosis implies that those containing a maximum number of C-H bonds (e.g. CH₄) or C-C bonds (e.g. Me₄C) are the most stable.

Synchronization (principle of nonperfect synchronization) : This principle applies to reactions in which there is a lack of synchronization between bond formation or bond rupture and other *primitive changes* that affect the stability of products and reactants, such as *resonance*, *solvation*, electrostatic, *hydrogen bonding* and *polarizability* effects. The principle states that a product-stabilizing factor whose development lags behind bond changes at the *transition state*, or a reactant-stabilizing factor whose loss is ahead of bond changes at the transition state, increases the *intrinsic barrier* and decreases the "intrinsic rate constant" of a reaction. For a product-stabilizing factor whose development is ahead of bond changes, or reactant factors whose loss lags behind bond changes, the opposite relations hold. The reverse effects are observable for factors that destabilize a reactant or product.

Synchronous : A *concerted* process in which the *primitive changes* concerned (generally bond rupture and bond formation) have progressed to the same extent at the *transition state* is said to be synchronous. The term figuratively implies a more or less synchronized progress of the changes. However, the progress of the bonding change (or other primitive change) has not been defined quantitatively in terms of a single parameter applicable to different bonds or different bonding changes. The concept is therefore in general only qualitatively descriptive and does not admit an exact

definition except in the case of concerted processes involving changes in two identical bonds.

synthesis. Synthesize; synthetic reaction. Formation of a complex product from simpler reactants. For example, water can be synthesized from oxygen and hydrogen gas: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell)$.

Synthetic : Synthetic material; artificial; artificial substance. A substance manufactured by chemical synthesis.

System : In thermodynamics, the system is the part of the universe that is of interest.

That part of the universe on which attention is to be focused.

Systematic error : Determinate error. Compare with random error, gross error and mistake. Systematic errors have an identifiable cause and affect the accuracy of results.

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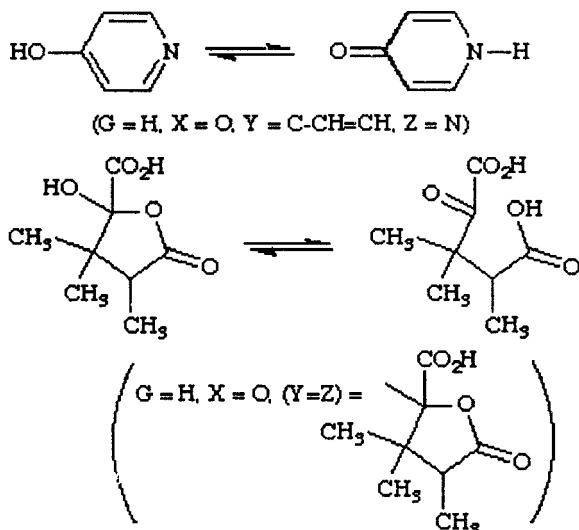
Tryptophan. Trp; α -amino- β -indolylpropionic acid. A naturally occurring amino acid with a heterocyclic group on its side chain.

Tacticity : Literally, arrangement or system. Used to describe the arrangement of substituents on a polymer chain.

Taft equation : Various equations are associated with R.W. Taft, but the term is most often used to designate the family of equations that emerged from Taft's analysis of the reactivities of aliphatic esters, and which involved the polar substituent constant σ^* and the steric substituent constant E_s , $\lg k = \lg k_0 + \rho^* \sigma^* + \delta E_s$, or the one-parameter forms applicable when the role of either the polar term or the steric term may be neglected. Nowadays σ^* is usually replaced by the related constant σ_1 .

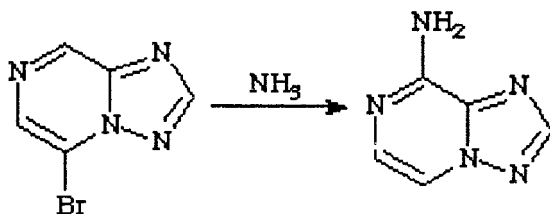
Tautomer : A structure formed by facile motion of a hydrogen from one site to another within the same molecule.

Tautomerism : Isomerism of the general form $G-X-Y=Z \rightleftharpoons X=Y-Z-G$ where the isomers (called tautomers) are readily interconvertible; the atoms connecting the groups X,Y,Z are typically any of C, H, O, or S, and G is a group which becomes an *electrofuge* or *nucleofuge* during isomerization. The commonest case, when the electrofuge is H^+ , is also known as "prototropy". Examples, written so as to illustrate the general pattern given above, include: Keto-enol tautomerism, such as $H-O-C(CH_3)=CH-CO_2Et$ (enol) $\rightleftharpoons (CH_3)C(=O)-CH_2-CO_2Et$ (keto) ($G = H$, $X = O$, $Y = CCH_3$, $Z = CHCO_2Et$) $ArCH_2-N=CHAr' \rightleftharpoons ArCH=N-CH_2Ar'$ ($G = H$, $X = CHAr$, $Y = N$, $Z = CHAr'$) The grouping Y may itself be a three-atom (or five-atom) chain extending the conjugation, as in

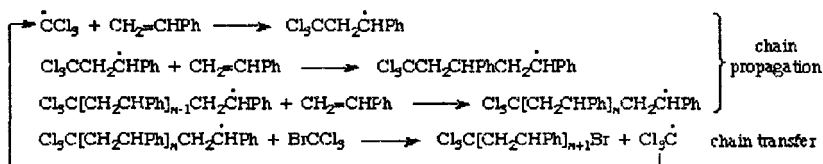


Tautomerization : The *isomerization* by which tautomers are interconverted. It is a *heterolytic* molecular re-arrangement and is frequently very rapid.

Tele-substitution : A *substitution reaction* in which the *entering group* takes up a position more than one atom away from the atom to which the *leaving group* was attached.



Telomerization : The formation of an *addition oligomer*, having uniform end groups $\text{X}'\dots\text{X}''$, by a *chain reaction* in which a *chain transfer* limits the length of the polymer ("telomer") produced. An example is the polymerization of styrene in bromotrichloromethane solution ($\text{X}' = \text{CCl}_3$, $\text{X}'' = \text{Br}$), where $\text{Cl}_3\text{C}\cdot$ radicals are formed in the initiation step to produce $\text{Cl}_3\text{C}[\text{CH}_2\text{CHPh}]_n\text{Br}$, with n greater than 1 and often less than ca. 10 :



Temperature : Compare with heat and thermodynamic temperature. Temperature is an intensive property associated with the hotness or coldness of an object. It determines the direction of spontaneous heat flow (always from hot to cold).

An intensive property that measures the extent to which an object can be labeled "hot" or "cold."

Temperature is proportional to the average random kinetic energy of ideal gases..

Temporary hardness : Temporary water hardness. Compare with permanent hardness and water hardness. The component of total water hardness that can be removed by boiling the water. $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ are responsible for temporary hardness.

Teoretical yield : Maximum yield; stoichiometric yield. Compare with actual yield and percent yield. The amount of product obtained when all of the limiting reagent reacts.

Teratogen : A substance that can cause deformities in embryos. Dioxin is a teratogen.

Terminal : The end of a polymer molecule.

A point at which electrical connections can easily be made or broken.

Terminal reaction : A reaction that ends a cycle or chain of other chemical reactions.

Termination : The steps in a *chain reaction* in which reactive *intermediates* are destroyed or rendered inactive, thus ending the chain.

Terminus : The end of a polymer molecule.

Tertiary structure : The interactions between the side chains on amino acids in a protein that help determine the structure of the protein.

Tetrahedral complex : A complex in which four ligands are bound to the metal atom and arranged toward the corners of a tetrahedron.

Tetrahedral hole : A hole in a closest-packed structure surrounded by four atoms or ions arranged toward the corners of a tetrahedron.

Tetrahedral intermediate : A reaction *intermediate* in which the bond arrangement around an initially double-bonded carbon atom (typically a carbonyl carbon atom) has been transformed from trigonal to tetrahedral. For example, aldol in the *condensation reaction* of acetaldehyde (but most tetrahedral intermediates have a more fleeting existence).

Tetrahedron : A geometry that resembles a trigonal-based pyramid.

Tetravalent : Literally, able to form four bonds. Carbon is tetravalent because it forms four bonds in virtually all of its compounds.

Thermal : Pertaining to heat.

Thermal conductor : An object that conducts heat easily from one side to the other, or from one end to the other.

Thermal energy : Energy an object possesses by virtue of its temperature. For example, 1 g of water at 15°C has 4.184 J more energy than 1 g of water at 14°C.

Thermal insulator : An object, such as a blanket or a fur coat, that tends to slow down the rate at which heat is transferred from one object to another.

Thermal neutron : Also known as a slow neutron.

Thermionic emission : The emission of electrons or ions by a hot object. For example, the filament in a mass spectrometer spits out energetic electrons that ionize atoms and molecules in the sample.

Thermistor : A device that senses temperature changes by using a resistor with an electrical resistance that falls when temperature rises.

Thermochemical equation : An compact equation representing a chemical reaction that describes both the stoichiometry and the energetics of the reaction. For example, the thermochemical equation $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$, $\Delta H = -2220 \text{ kJ}$ means "When one mole of gaseous CH_4 is burned in two moles of oxygen gas, one mole of CO_2 gas and 2 moles of steam are produced, and 2220 kilojoules of heat are released."

Thermochemistry : The study of the heat given off or absorbed in a chemical reaction.

Thermocouple : A device that senses temperature changes by using a pair of joined wires made of dissimilar metals that produces a voltage that changes with temperature.

Thermodynamic control (of product composition) : The term characterizes conditions that lead to reaction products in a proportion governed by the equilibrium constant for their interconversion and/or for the interconversion of reaction *intermediates* formed in or after the *rate-limiting step*. (Some workers prefer to describe this phenomenon as "equilibrium control").

Thermodynamic control : Describes a chemical reaction that forms the most stable product, not the product of the fastest reaction.

Thermodynamic equilibrium : A system is at thermodynamic equilibrium if the energy it gains from its surroundings is exactly balanced by the energy it loses, no matter how much time is allowed to pass.

Thermodynamics : The study of energy and its interconversions.

Thermodynamics : The study of the relationship between heat, work, and other forms of energy.

Thermoelectron : An electron emitted by a very hot object.

Thermolysis : The uncatalysed cleavage of one or more covalent *bonds* resulting from exposure of a compound to a raised temperature, or a process in which such cleavage is an essential part.

Thermometer : An instrument for measuring temperature.

Thermometry : The science of temperature measurement.

Thermonuclear reaction : A nuclear reaction that only occurs at extremely high temperatures.

Thermoplastic. Compare with thermosetting. A polymer that softens or melts on heating, and becomes rigid again on cooling. Thermoplastic polymer chains are not cross-linked. Polystyrene is a thermoplastic.

Thermosetting : Thermosetting plastic. Compare with thermoplastic. A polymer that solidifies on heating and cannot be remelted. The setting action results from crosslinking of the polymer chains at high temperature- a process that is not reversed by cooling and reheating.

Thin layer chromatography : (TLC) Compare with chromatography. A technique for separating components in a mixture on the basis of their differing polarities. A spot of sample is placed on a flat sheet coated with silica and then carried along by a solvent that soaks the sheet. Different components will move different distances over the surface. TLC is a useful screening technique in clinical chemistry; for example, it can be used to detect the presence of drugs in urine.

Thin-layer chromatography : Chromatography in which a solvent is passed over a solid support that has been applied as a thin layer to a glass or plastic plate.

Thio- : A prefix that describes compounds in which a sulfur atom can be found where an oxygen atom is expected. The sulfate ion, for example, has the formula SO_4^{2-} , whereas the thiosulfate ion has the formula $\text{S}_2\text{O}_3^{2-}$.

A prefix that means, "replace an oxygen with sulfur". For example, sulfate ion is SO_4^{2-} ; thiosulfate ion is $\text{S}_2\text{O}_3^{2-}$. Cyanate ion is OCN^- ; thiocyanate ion is SCN^- .

Third law : Third law of thermodynamics. The entropy of a perfect crystal is zero at absolute zero.

The entropy of a perfect crystal at 0 K is zero.

The notion that the entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

Thixotropic fluid : Thixotropy. A liquid that becomes less viscous when stirred. Paint and printing inks are thixotropic fluids; they are formulated so that they flow more freely when brushed or rolled. -amino- β -3b-hydroxybutyric-20acid"

Threonine : ($\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{NH}_2)\text{COOH}$) α -amino- β -hydroxybutyric acid. A naturally occurring amino acid with a hydroxyl group on its side chain. Closely related to serine.

Titrant : The substance that quantitatively reacts with the analyte in a titration. The titrant is usually a standard solution added carefully to the analyte until the reaction is complete. The amount of analyte is calculated from the volume of titrant required for complete reaction.

Titration : A procedure for determining the amount of some unknown substance (the analyte) by quantitative reaction with a measured volume of a solution of precisely known concentration (the titrant).

A technique used to determine the concentration of a solute in a solution.

Titration curve : A plot that summarizes data collected in a titration. A linear titration curve plots moles of analyte (or, some quantity proportional to moles of analyte) on the Y axis, and the volume of titrant added on the X axis. Nonlinear plots use the log of the concentration of the analyte instead. Nonlinear titration curves are often used for neutralization titrations (pH vs. mL NaOH solution). Logs are used to exaggerate the rate of change of concentration on the plot, so that the endpoint can be determined from the point of maximal slope.

Torquoselectivity : The term refers to the preference for "inward" or "outward" rotation of substituents in conrotatory or disrotatory electrocyclic ring opening reactions.

Torr : Torr; mm Hg. A unit of pressure, defined so that 760 Torr is exactly 1 atmosphere. A Torr is equivalent to 1 mm Hg on barometer readings taken at 0°C; at other temperatures, the conversion from mm Hg to Torr is approximately $p(\text{Torr}) = p(\text{mm Hg}) \times (1 - 1.8 \times 10^{-4}t)$, where t is in °C.

A unit of pressure equal to the pressure exerted by a column of mercury 1 milli-meter tall. By definition, 1 torr = 1 mmHg.

A unit of pressure, also called millimeters of mercury (mm Hg); 760 torr = 1 atm.

Toxicology : The study of poisons, including identification, isolation, biological effects, mechanism of action, and development of antidotes.

Trans : Literally, across. Describes isomers of compounds in which similar substituents lie on opposite sides of a double bond or on opposite sides of a transition metal.

Transcription : The process by which the message encoded in DNA is transcribed to form a sequence of m-RNA that can be used as a template to make proteins.

Transferability : Transferability assumes invariance of properties, associated conceptually with an atom or a fragment present in a variety of molecules. The property, such as *electronegativity*, nucleophilicity, NMR *chemical shift*, etc. is held as retaining a similar value in all these occurrences.

Transformation : The conversion of a *substrate* into a particular product, irrespective of reagents or *mechanisms* involved. For example, the transformation of aniline ($\text{C}_6\text{H}_5\text{NH}_2$) into *N*-phenylacetamide ($\text{C}_6\text{H}_5\text{NHCOCH}_3$) may be effected by use of acetyl chloride or acetic anhydride or ketene. A transformation is distinct from a reaction, the full description of which would state or imply all the reactants and all the products.

Transient (chemical) species : Relating to a short-lived reaction *intermediate*. It can be defined only in relation to a time scale fixed by the experimental conditions and the limitations of the technique employed in the detection of the intermediate. The term is a relative one. Transient species are sometimes also said to be

"metastable". However, this latter term should be avoided, because it relates a thermodynamic term to a kinetic property, although most transients are also thermodynamically *unstable* with respect to reactants and products. See also *persistent*.

Transition coordinate : The reaction coordinate at the transition state corresponding to a vibration with an imaginary frequency. Motion along it in the two opposite senses leads towards the reactants or towards the products. See also *reaction coordinate*, *transition state*.

Transition metal : Metals in the block of elements that serve as a transition between the two columns on the left side of the table, where s orbitals are filled, and the six columns on the right, where p orbitals are filled.

Metals in the block of elements that serve as a transition between the two columns on the left side of the table, where s orbitals are filled, and the six columns on the right, where p orbitals are filled.

Transition element; outer transition element. An element with an incomplete *d* subshell. Elements which have common cations with incomplete *d* subshells are also considered transition metals. Elements with incomplete *f* subshells are sometimes called "inner transition elements".

Transition state : In theories describing *elementary reactions* it is usually assumed that there is a transition state of more positive molar Gibbs energy between the reactants and the products through which an assembly of atoms (initially composing the *molecular entities* of the reactants) must pass on going from reactants to products in either direction. In the formalism of "transition state theory" the transition state of an elementary reaction is that set of states (each characterized by its own geometry and energy) which an assembly of atoms, when randomly placed there, would have an equal probability of forming the reactants or of forming the products of that elementary reaction. The transition state is characterized by one and only one imaginary frequency. The assembly of atoms at the transition state has been called an *activated complex*. (It is not a *complex* according to the definition in this Glossary.) It may be noted that the calculations of reaction rates by the transition state method

and based on calculated *potential-energy surfaces* refer to the potential energy maximum at the saddle point, as this is the only point for which the requisite separability of transition state coordinates may be assumed. The ratio of the number of assemblies of atoms that pass through to the products to the number of those that reach the saddle point from the reactants can be less than unity, and this fraction is the "transmission coefficient" κ . (There are also reactions, such as the gas-phase *colligation* of simple *radicals*, that do not require "activation" and which therefore do not involve a transition state.)

The state of highest energy during a reaction. Also called activated complex. During the transition state bond breaking and bond formation occurs.

Transition state analogue : A substrate designed to mimic the properties or the geometry of the *transition state* of reaction.

Transition structure : A saddle point on a *potential-energy surface*. It has one negative force constant in the harmonic force constant matrix.

Translation : The process by which the information coded in a sequence of m-RNA is translated into a sequence of amino acids in a protein.

Translational motion : The net movement of an atom, ion, or molecule through a gas, liquid, or solid.

Transmittance : (T) percent transmittance; transmission. Compare with absorbance. The transmittance is the fraction of radiant intensity transmitted by a sample, $T = I/I_0$ where T is the transmittance and I, I_0 are the radiant intensity of the radiation after and before passing through the sample. The percent transmittance is the transmittance times 100%.

Transuranium element : transuranic; transuranic element. An element with an atomic number higher than 92 (uranium's atomic number). Transuranium elements are unstable and occur in extremely low concentrations (if at all) in nature. Most are made artificially.

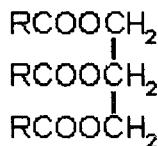
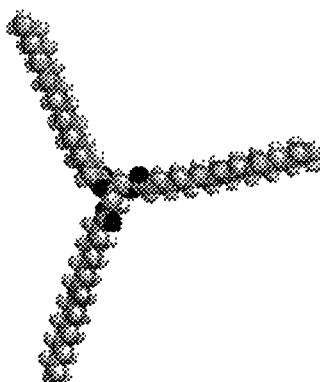
Transuranium elements : Elements with atomic numbers larger than that of uranium.

Trapping : The interception of a *reactive* molecule or reaction *intermediate* so that it is removed from the system or converted into a more *stable* form for study or identification.

Triad : Three elements (such as F, Cl, and Br) with similar chemical properties.

Triglyceride : A triester of glycerol and fatty acids found in fats and oils. Also known as a triacylglycerol.

A triglyceride is an ester of glycerol and three fatty acids. Most animal fats are composed primarily of triglycerides. In the structures below, the fatty acids attached to the glycerol are represented by 'R'. The fatty acids can be the same or different.



Trigonal bipyramidal : Trigonal bipyramidal shape; trigonal bipyramidal geometry. A molecular shape that results when there are five bonds and no lone pairs on the central atom in the molecule. Three of the bonds are arranged along the atom's equator, with 120° angles between them; the other two are placed at the atom's axis. Axial bonds are at right angles to the equatorial bonds. The PCl_5 molecule has a trigonal bipyramidal molecular geometry.

A geometry in which two atoms, ions, or molecules are added to a trigonal planar system along an axis perpendicular to the triangular plane.

Trigonal planar : A geometry in which three atoms, ions, or molecules are coordinated to a central atom and arranged toward the corners of an equilateral triangle.

A molecular shape that results when there are three bonds and no lone pairs around the central atom in the molecule. The pairs are arranged along the central atom's equator, with 120° angles between them. The carbonate ion (CO_3^{2-}) has a trigonal planar geometry.

Trigonal pyramidal : A molecular shape that results when there are three bonds and one lone pair on the central atom in the molecule. NH_3 is a trigonal pyramidal molecule.

Trigonal pyramidal geometry : A geometry in which a central atom at the apex of a pyramid is coordinated to three atoms, ions or molecules to form a pyramid.

Triple bond : (\equiv) A covalent bond that involves 3 bonding pairs. In the valence bond theory, one of the bonds in a triple bond is a sigma bond and the other two are pi bonds. For example, the central bond in acetylene is a triple bond: $\text{H}-\text{C}\equiv\text{C}-\text{H}$.

The combination of temperature and pressure in a phase diagram at which the substance can simultaneously exist as a gas, a liquid, and a solid.

The temperature and pressure at which the solid, liquid, and gaseous forms of a substance are at equilibrium.

Triprotic : Used to describe acids, such as H_3PO_4 , that can donate three protons or bases, such as the PO_3^{3-} ion, that can accept three protons.

Tritium : A radioisotope of hydrogen with two neutrons and one proton in its nucleus.

t-RNA : Transfer RNA. The relatively small polynucleotide that carries amino acids and recognizes the codon on m-RNA that specifies the amino acid to be incorporated at a particular point on a protein chain.

Trueness : Compare with accuracy. Trueness is the closeness of an average measurement to a "true" value, while accuracy is the closeness of a single measurement to the true value.

T-shape : A molecular shape that results when there are 3 bonds and 2 lone pairs ^{*} around the central atom in the molecule. The atoms bonded to the central atom lie at the ends of a "T" with 90° angles between them. ICl_3 has a T-shaped molecular geometry.

T-shaped geometry : A molecular geometry whose shape resembles the letter T.

Tetrahedral : A molecular shape that results when there are four bonds and no lone pairs around the central atom in the molecule. The atoms bonded to the central atom lie at the corners of a tetrahedron with 109.5° angles between them. The ammonium ion (NH_4^+) has a tetrahedral molecular geometry.

Tunnelling : The process by which a particle or a set of particles crosses a barrier on its potential energy surface without having the energy required to surmount this barrier. Since the rate of tunnelling decreases with increasing reduced mass, it is significant in the context of *isotope effects* of hydrogen isotopes.

Tyndall effect : Light passing through a colloid is scattered by suspended particles. The light beam becomes clearly visible; this phenomenon is called the Tyndall effect. For example, car headlight beams can be seen in fog, but the beams are invisible in clear air. -amino-β-3p-hydroxyphenylpropionic-20acid">**tyrosine**. Tyr; α-amino-β-p-hydroxyphenylpropionic acid. A naturally occurring amino acid with a phenol group on its side chain.

U

Umpolung : Any process by which the normal alternating donor and acceptor reactivity pattern of a chain, which is due to the presence of O or N heteroatoms, is interchanged. Reactivity umpolung is most often achieved by temporary exchange of heteroatoms (N, O) by others, such as P, S, and Se. The original meaning of the term has been extended to the reversal of any commonly accepted reactivity pattern. For example, reaction of $R-C\equiv CX$ ($X = \text{halide}$) as a synthon for " $R-C\equiv C^+$ " (i.e. *electrophilic* acetylene) is an umpolung of the normal more common acetylide, $R-C\equiv C^-$ (i.e. *nucleophilic*) reactivity.

Unreactive : Failing to react with a specified *chemical species* under specified conditions. The term should not be used in place of *stable*, since a relatively more stable species may nevertheless be more *reactive* than some reference species towards a given reaction partner.

Unstable : The opposite of *stable*, i.e. the *chemical species* concerned has a higher molar Gibbs energy than some assumed standard. The term should not be used in place of *reactive* or *transient*, although more reactive or transient species are frequently also more unstable. (Very unstable chemical species tend to undergo exothermic *unimolecular* decompositions. Variations in the structure of the related chemical species of this kind generally affect the energy of the *transition states* for these decompositions less than they affect the stability of the decomposing chemical species. Low stability may therefore parallel a relatively high rate of unimolecular decomposition.)

Ultraviolet light : Ultraviolet; ultraviolet radiation; ultraviolet region; UV. Electromagnetic radiation with wavelength longer than

that of x-rays but shorter than that of visible light. Ultraviolet light can break some chemical bonds and cause cell damage.

Uncertainty principle : Heisenberg's uncertainty principle; Heisenberg principle; indeterminacy; indeterminancy principle. The exact momentum and exact location of a particle cannot be specified. Werner Heisenberg stated that the product of uncertainties in location and momentum measurements can never be smaller than $h/4\pi$, where h is Planck's constant.

Unimolecular reaction : A reaction that involves isomerization or decomposition of a single molecule.

Unit : A standard for comparison in measurements. For example, the meter is a standard length which may be compared to any object to describe its length. The basis for comparing a measurement with a standard reference, such as the units known as "inches" or "feet."

Unit cell : The simplest repeating unit in a crystal. The simplest arrangement of atoms or molecules that regularly repeats in a crystal structure.

Universal indicator : A universal indicator is an indicator which undergoes several color changes over a wide range of pH. The color is used to "indicate" pH directly. Universal indicators are usually mixtures of several indicators.

Unpaired spin : (\uparrow) unpaired electron. A single electron occupying an orbital.

Unsaturated compound : An organic compound with molecules containing one or more double bonds.

Unsaturated fat : A lipid containing one or more carbon-carbon double bonds. Unsaturated fats tend to be oily liquids and are obtained from plants.

Unsaturated solution : A solution with a concentration lower than its equilibrium solubility.

Uncertainty : The limit on the precision of a measurement. Analytical balances, for example, can weigh an object with an uncertainty of ± 0.001 or ± 0.0001 grams.

Unimolecular : Describes a step in a chemical reaction in which one molecule is consumed.

Unit factor : A ratio, or factor, equal to one that is constructed from an equality. The fact that 12 inches is equivalent to one foot can be used to construct two unit factors: $(12 \text{ in})/(1 \text{ ft})$ or $(1 \text{ ft})/(12 \text{ in})$. Used in dimensional analysis.

Unsaturated fatty acid : A long-chain carboxylic acid that contains one or more $\text{C}=\text{C}$ double bonds.

Unsaturated hydrocarbon : A hydrocarbon that contains $\text{C}=\text{C}$ double bonds and/or $\text{C}\equiv\text{C}$ triple bonds, and therefore contains less hydrogen than a saturated hydrocarbon.



Vacuum : Absolute vacuum. Compare with partial vacuum.
A volume which contains no matter.

Valence : The maximum number of univalent atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted.

The number of hydrogen atoms that typically bond to an atom of an element. For example, in H_2O , oxygen has a valence of 2; carbon in CH_4 has a valence of four.

Valence band : The highest energy band in a solid that contains electrons.

In the valence bond theory, a valence bond is a chemical bond formed by overlap of half-filled atomic orbitals on two different atoms.

Valence electron : Electrons that can be actively involved in chemical change; usually electrons in the shell with the highest value of n . For example, sodium's ground state electron configuration is $1s^2 2s^2 2p^6 3s^1$; the $3s$ electron is the only valence electron in the atom. Germanium (Ge) has the ground state electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$; the $4s$ and $4p$ electrons are the valence electrons.

Electrons in the outermost or highest-energy orbitals of an atom. The electrons that are gained or lost in a chemical reaction.

Valence isomer : A constitutional isomer interrelated with another by *pericyclic reactions*. For example, Dewar benzene, prismane and benzvalene are valence isomers of benzene.

Valence shell : The shell corresponding to the highest value of principal quantum number in the atom. The valence electrons in this shell are on average farther from the nucleus than other electrons; they are often directly involved in chemical reaction.

Valence shell electron pair repulsion theory : VSEPR. A model that explains the shapes of molecules by assuming that electron pairs arrange themselves around atoms in a way that minimizes electron-electron repulsions. v-aminoisovaleric-20acid"

Valine : $((\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH})$ Val; α -aminoisovaleric acid. A naturally occurring aliphatic amino acid with a nonpolar isopropyl side chain.

Valence tautomerization : The term describes simple reversible and generally rapid *isomerizations* or *degenerate rearrangements* involving the formation and rupture of single and/or double bonds, without *migration* of atoms or *groups*; e.g.



Valence-bond theory : A model of the bonding in covalent compounds based on the assumption that atoms in these compounds are held together by the sharing of pairs of valence electrons by adjacent atoms.

Valence-shell electron-pair repulsion theory (VSEPR) : A model in which the repulsion between pairs of valence electrons is used to predict the shape or geometry of a molecule.

Van der Waals equation : A semiempirical equation that describes the relationship between pressure (P), volume (V), temperature (T), and moles of gas (n) for a real gas. The equation is $(P + n^2a/V^2)(V - nb) = nRT$, where a and b are constants that include the effects of molecular attractions and molecular volume. a and b are usually fitted to experimental data for a particular gas.

An equation that corrects for the two erroneous assumptions in the ideal gas equation that the volume occupied by the gas

particles is negligibly small and that there is no force of attraction between gas particles.

Van der Waals force : A force acting between nonbonded atoms or molecules. Includes dipole-dipole, dipole-induced dipole, and London forces.

The attractive or repulsive forces between *molecular entities* (or between groups within the same molecular entity) other than those due to *bond* formation or to the electrostatic interaction of ions or of ionic *groups* with one another or with neutral molecules. The term includes: *dipole-dipole*, *dipole-induced dipole* and *London* (instantaneous induced dipole-induced dipole) *forces*. The term is sometimes used loosely for the totality of nonspecific attractive or repulsive intermolecular forces.

The weak forces of attraction between atoms or molecules that explain why gases condense to form liquids and solids when cooled.

Van der Waals radius : Van der Waals radii. One half the distance between two nonbonded atoms, when attractive and repulsive forces between the atoms are balanced.

Vapor pressure : The pressure of the gas that collects above a liquid in a closed container.

The partial pressure of a gas in equilibrium with a condensed form (solid or liquid) of the same substance.

Vapor pressure depression : The decrease in the vapor pressure of a solvent that occurs when a solute is added to form a solution.

Vapor pressure lowering : Vapour pressure depression; vapor pressure depression. A colligative property of solutions. The vapor pressure of a solution is always lower than the vapor pressure of the pure solvent; the ratio of solution to pure solvent vapor pressures is approximately equal to the mole fraction of solvent in the solution.

Variable : Compare with independent variable and dependent variables. A quantity that can have many possible values. In designing experiments, variables that affect measurements must be

identified and controlled. For example, an experiment that measures reaction rates must control temperature, because temperature is a variable that can change the rate of reaction.

Vertical ionization energy : Compare with adiabatic ionization energy. The energy required to remove an electron from an atom, molecule, or ion in the gas phase without moving any nuclei. The vertical ionization energy is greater than or equal to the adiabatic ionization energy.

Vibrational motion : The motion of a molecule that results in the stretching or bending of one or more bonds in the molecule.

Vinyl : polyethylene. A polymer made by linking ethylene ($\text{CH}_2=\text{CH}_2$) or substituted ethylene molecules together.

Viscosity : (η) coefficient of viscosity. The resistance a liquid exhibits to flow. Experimentally, the frictional force between two liquid layers moving past each other is proportional to area of the layers and the difference in flow speed between them. The constant of proportionality is called "viscosity" or "coefficient of viscosity", and is given the symbol η . The time required for a liquid to drain out of a capillary tube is directly proportional to its viscosity. The poise is a non-SI unit frequently used to express viscosities.

A measure of the resistance of a liquid or gas to flow.
Viscous liquids, such as molasses, flow very slowly.

Visible light : Visible light is electromagnetic radiation with a wavelength between 400 and 750 nm.

Vital force : A mythical force that was once assumed to explain the difference between animate (organic) and inanimate (inorganic) objects.

Vitamin : A substance that is critical for proper functioning of a living organism that the organism is unable to produce in sufficient quantities for itself.

Literally, vital amines. A wide range of compounds that are either water-soluble or fat-soluble and are necessary components of the diet of higher organisms, such as mammals.

Vlence bond theory : B theory; VB. A theory that explains the shapes of molecules in terms of overlaps between half-filled atomic orbitals, or half filled "hybridized" orbitals (which are a mixture of atomic orbitals).

Volatile : volatility. A solid or liquid material that easily vaporizes. A material with a significant vapor pressure.

Volt : (V) The SI unit of electrical potential. One volt equals one joule per coulomb.

The unit of electrical potential defined as one joule of work per coulomb of charge transferred.

Voltage : (V) A measured electric potential, in volts.

Voltaic cell : A device in which chemical energy from a spontaneous redox reaction is changed to electrical energy that can be used to do work; also called a galvanic cell.

An electrochemical cell that uses a spontaneous chemical reaction to do work. Also known as a galvanic cell.

Galvanic cell. An electrochemical cell that spontaneously generates electrical energy.

Voltaic pile : An early battery consisting of disks of dissimilar metals (usually zinc and copper) separated by moist paper or cloth soaked in an electrolyte solution.

Voltammeter : An instrument for measuring voltages and amperages.

Voltmeter : An instrument that measures cell potential by drawing electric current through a known resistance.

Volume : (V) The amount of space an object takes up.

The amount of space a container can hold. The SI unit of volume is the cubic meter (m^3); the liter is a popular unit of volume in chemistry.

Volume of activation, $\Delta^\ddagger V$ A quantity derived from the pressure dependence of the *rate constant* of a reaction (mainly used for reactions in solution), defined by the equation $\Delta^\ddagger V = -RT(\partial \ln k / \partial p)T$ providing that the rate constants of all reactions (except first-

order reactions) are expressed in pressure-independent concentration units, such as mol dm^{-3} at a fixed temperature and pressure. The volume of activation is interpreted, according to *transition state* theory as the difference between the partial molar volumes of the transition state (${}^{\ddagger}V$) and the sums of the partial volumes of the reactants at the same temperature and pressure, i.e., $\Delta {}^{\ddagger}V = {}^{\ddagger}V - \sum (rV_R)$ where r is the order in the reactant R and V_R its partial molar volume.

Volume percent : The percent of the total volume of a mixture due to a particular component.

Volume percentage : [(v/v)-] Volume percentages express the concentration of a component in a mixture or an element in a compound. For example, 95% ethanol by volume contains 95 mL of ethanol in 100 mL of solution (NOT in 100 mL of water!)

Vulcanization : vulcanization of rubber. A process of combining rubber with sulfur or other substances that causes the polymer chains to crosslink, making them stronger and more elastic.



Water : (H_2O) dihydrogen monoxide; H_2O . A colorless, tasteless liquid with some very peculiar properties that stem from the bent H-O-H structure of its molecules.

Water gas : A mixture of CO , CO_2 , and H_2 produced from the reaction of red-hot coal with steam.

Blue gas; synthesis gas. A fuel gas used in industrial synthesis of organic chemicals, and in welding, glassmaking, and other high-temperature industrial applications. Water gas made by passing steam over a bed of hot coal or coke. It consists mainly of carbon monoxide (CO) and hydrogen (H_2), contaminated with small amounts of CO_2 , N_2 , CH_4 , and O_2 .

Water hardness : Hard water. Compare with water softener. Hard water is water contaminated with compounds of calcium and magnesium. Dissolved iron, manganese, and strontium compounds can also contribute to the "total hardness" of the water, which is usually expressed as ppm CaCO_3 . Water with a hardness over 80 ppm CaCO_3 is often treated with water softeners, since hard water produces scale in hot water pipes and boilers and lowers the effectiveness of detergents.

Water of crystallization : Water of hydration. Water that is stoichiometrically bound in a crystal; for example, the waters in copper sulfate pentahydrate.

Water softener : Soft water; water softening. Compare with water hardness. A material that lowers water hardness when dissolved in water. For example, sodium carbonate ("washing soda") softens water by precipitating Ca^{2+} ions as CaCO_3 . Zeolites soften water by exchanging Ca^{2+} ions with Na^+ ions.

Water softening : Compare with water softener and water hardness. Removal of Ca^{2+} and Mg^{2+} from water to prevent undesirable precipitation reactions from occurring in plumbing, pools, washwater, and boilers.

Water-dissociation equilibrium constant (K_w) : The product of the equilibrium concentration of the H_3O^+ and OH^- ions in an aqueous solution: $K_w = 1.0 \times 10^{-14}$ at 25°C .

Wave : A phenomenon that does not have mass and therefore does not occupy space. Waves travel through space.

An oscillating motion that moves outward from the source of some disturbance (ripples running away from a pebble tossed in a pond). Waves transmit the energy of the disturbance away from its source.

Wave function : A mathematical equation that describes orbitals in which electrons reside.

(Ψ) A mathematical function that gives the amplitude of a wave as a function of position (and sometimes, as a function of time and/or electron spin). Wavefunctions are used in chemistry to represent the behavior of electrons bound in atoms or molecules.

Wavelength : The distance between adjacent peaks (or adjacent troughs) on a wave. Varying the wavelength of light changes its color; varying the wavelength of sound changes its pitch.

The distance between repeating points on a wave.

Wavenumber : The number of wave crests per unit distance. Wavenumber is the reciprocal of wavelength. Wavenumbers are used extensively in infrared spectroscopy, and usually have units of cm^{-1} .

Wave-particle duality : The observation that electrons; photons; and other very small entities behave like particles in some experiments and like waves in others. Compare with quantum.

The principle that all objects in motion are simultaneously particles and waves. Most objects have a wavelength that is too small to be detected. Very light objects, such as photons and electrons, can have wavelengths large enough to give these objects some of the properties of waves.

Wax : An ester formed from long-chain fatty acids and alcohols that is usually solid at room temperature.

Weak acid : An acid that dissociates only slightly in water. An acid for which the acid-dissociation equilibrium constant is significantly smaller than one.

Compare with strong acid. An acid that only partially dissociates into hydrogen ions and anions in solution. Weak acids are weak electrolytes. Recognize weak acids by learning the six common strong acids; any acid that doesn't appear on the list of strong acids is usually a weak acid.

Weak base : A base that only partially dissociates into ions in solution. Weak bases are weak electrolytes. Ammonia is an example of a weak base; the reaction $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) = \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ is reversible.

Weak electrolyte : A weak electrolyte is a solute that incompletely dissociates into ions in solution. For example, acetic acid partially dissociates into acetate ions and hydrogen ions, so that an acetic acid solution contains both molecules and ions. A solution of a weak electrolyte can conduct electricity, but usually not as well as a strong electrolyte because there are fewer ions to carry the charge from one electrode to the other.

Weak ligand : Weak field ligand. Compare with strong field ligand. A ligand that causes a small crystal field splitting which results in a high-spin complex.

Weight (W) : Weight is the force exerted by an object in a gravitational field. The weight of an object (W) arises from its mass (m): $W = mg$ where g is the acceleration due to gravity (about 9.8 m/s^2 on Earth).

A measure of the gravitational force of attraction of the earth acting on an object.

Weight percent : The percent by weight of an element in a compound, or the percent by weight of one component in a mixture.

Wetting : wet. Covering with a surface with thin film of liquid. Liquid beads up on a surface if it cannot wet it.

Work (w) : Mechanical energy equal to the product of the force applied to an object times the distance the object is moved.

Compare with heat. Work is the energy required to move an object against an opposing force. Work is usually expressed as a force times a displacement. Dropping a stone from a window involves no work, because there is no force opposing the motion (unless you consider air friction...). Pushing against a stone wall involves no work, unless the stone wall actually moves.

Work of expansion : The work done when a system that consists of a gas expands against its surroundings.



Xenobiotic : A substance which is not normally found in a living thing.

Xenon : Xe. Element 54, a colorless, inert gas used to fill cathode ray tubes.

X-ray : A high-energy, short-wavelength form of electromagnetic radiation.

A very high energy form of electromagnetic radiation (though not as high energy as gamma rays). X-rays typically have wavelengths from a few picometers up to 20 nanometers. X-rays easily penetrate soft tissue, which makes them useful in medical imaging and in radiation therapy.

X-ray crystallography : Determination of three dimensional arrangement of atoms in a crystal by analysis of x-ray diffraction patterns.

X-ray diffraction pattern : Interference patterns created by x-rays as they pass through a solid material. Studying x-ray diffraction patterns gives detailed information on the three-dimensional structure of crystals, surfaces, and atoms.

X-ray spectrum : x-ray spectra. A set of characteristic x-ray frequencies or wavelengths produced by a substance used as a target in an x-ray tube. Each element has a characteristic x-ray spectrum, and there is a strong correlation between atomic number and the frequencies of certain lines in the x-ray spectrum.

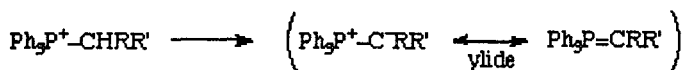
X-ray tube : A cathode ray tube that focuses energetic streams of electrons on a metal target, causing the metal to emit x-rays.



Yield : Experimental yield; actual yield. The amount of product actually obtained in a chemical reaction.

Ylem : The primordial substance out of which the elements were synthesized in the first moments after the creation of the universe.

Ylide : A *chemical species* produced (actually or notationally) by loss of a *hydron* from an atom directly attached to the central atom of an "*onium ion*", e.g.



Ytterbium : Yb. Element 70, atomic weight 173.04, a very rare, malleable metal used in special alloys for X-ray sources.

Yttrium : Y. Element 39, atomic weight 88.90585, a dark gray metal that is used in alloys and nuclear technology for its high neutron transparency. Yttrium compounds are used in the manufacture of color tv screens, superconducting ceramics, and fireproof bricks.

Yukawa-Tsuno equation : A multiparameter extension of the *Hammett equation* to quantify the role of enhanced *resonance* effects on the reactivity of *meta*- and *para*-substituted benzene derivatives, e.g. $\lg k = \lg k_0 + \rho \sigma + r (\sigma^+ - \sigma)$ The parameter *r* gives the enhanced resonance effect on the scale $(\sigma^+ - \sigma)$, or $(\sigma^- - \sigma)$, respectively.



Zeeman effect : The splitting of spectral lines when an external magnetic field is applied.

Zeolite : Addition compounds of the type $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$, with calcium sometimes replacing or present with the sodium. The sodium in the zeolite exchanges with calcium in water, making zeolites useful for water softening. The porous structure of zeolites also makes them effective molecular sieves[†] used as gas adsorbents and drying agents. Artificial zeolites are used as ion exchange resins[‡].

Zero order reaction : A reaction with a reaction rate that does not change when reactant concentrations change.

Zero point energy : A minimum possible energy for an atom or molecule predicted by quantum mechanics. Electrons stay in motion and bonds continue to vibrate even at absolute zero because of zero point energy.

Zero-order reaction : A reaction whose rate is not proportional to the concentration of any of the reactants.

Zeroth law of thermodynamics : A law stating that two objects in thermal equilibrium with a third object are in thermal equilibrium with each other.

Zeta potential : Electrokinetic potential. Electric potential across all phase boundaries between solids and liquids. In colloids, the zeta potential is the potential across the ion layer around a charged colloidal particle. Neutralizing the zeta potential can cause the colloid to precipitate.

Zinc : Zn. Element 30, atomic weight 65.37, a reactive gray metal that dissolves in acids, used to galvanize metals and in many alloys (e. g. brass and bronze).

Zincography : Process of etching unprotected parts of a zinc plate with strong acids to produce a printing surface.

Zirconium : Zr. Element 40, atomic weight 91.22, a hard, grayish, highly flammable crystalline metal that dissolves in hot concentrated acids. Used in steel manufacture and in nuclear reactor chambers because of its transparency to neutrons. Its silicate is used to make zircon used as a gemstone.

Zone refining : A method for purifying solids based on the fact that solutes tend to concentrate in the liquid when a solution is frozen. A solid bar is drawn slowly over a heat source and melted in a narrow band; impurities are carried along in the melted band until the end of the bar is reached.

Zucker-Hammett hypothesis : This hypothesis states that, if in an acid catalyzed reaction, $\lg k_1$ (first-order rate constant of the reaction) is linear in H_0 (Hammett *acidity function*), water is not involved in the *transition state* of the *rate-controlling step*. However, if $\lg k_1$ is linear in $\lg[H^+]$, then water is involved. This has been shown to be incorrect by Hammett himself.

Z-value : An index of the *ionizing power* of a solvent based on the frequency of the longest wavelength electronic absorption maximum of 1-ethyl-4-methoxycarbonylpyridinium iodide in the solvent. The Z-value is defined by $Z = 2.859 \times 10^4/\lambda$ where Z is in kcal mol^{-1} and λ is in nm.

Zwitterion : A particle that contains both positively charged and negatively charged groups. For example, amino acids ($\text{NH}_2\text{-CHR-COOH}$) can form zwitterions ($^+\text{NH}_3\text{-CHR-COO}^-$)

Zwitterion : Literally, a mongrel or hybrid ion. A molecule that contains both negative and positive charges, such as the $\text{H}_3\text{N}^+\text{CHR-COO}^-$ form of an amino acid.

Zwitterionic compound : A neutral compound having electrical charges of opposite sign, delocalized or not on adjacent or nonadjacent atoms. Zwitterionic compounds have no uncharged canonical representations. Sometimes referred to as inner salts,

ampholytes, dipolar ions (a misnomer). For example: $\text{H}_3\text{N}^+\text{CH}_2\text{C}(=\text{O})\text{O}^-$, glycine.

Zymase : Enzymes present in yeast that catalyze fermentation of sugar into alcohol and carbon dioxide.

Zymogen : proenzyme. A protein that may be converted into an enzyme.

Y

Y chromosome : One of the two sex chromosomes, X and Y. The sex chromosome associated with male characteristics, occurring with one X chromosome in the male sex chromosome pair.

YAC (yeast artificial chromosome) : A cloning vector used to clone DNA fragments (up to 400 kb); it is constructed from the telomeric, centromeric, and replication origin sequences needed for replication in yeast cells. The inserts can be much larger than those accepted by other vectors such as plasmids or cosmids.

OR

Constructed from yeast DNA, it is a vector used to clone large DNA fragments.

Yeast : Any unicellular fungi of genus *Saccharomyces* which reproduces by budding and can ferment carbohydrates.

OR

Unicellular fungi, which usually grow by budding. The brewing and baking industries rely on the ability of yeasts to produce enzymes that convert sugar into alcohol and carbon dioxide.

Yellow marrow : Specialized lipid storage tissue within bone cavities.

Ylem : A form of matter hypothesized by proponents of the big bang theory to have existed before the formation of the chemical elements.

Yolk : The nutritive material of an ovum, consisting primarily of protein and fat.

Yolk sac : A membranous sac attached to the embryo containing yolk.

Z

Zinc : Prostate gland function, growth of reproductive organs. Healthy immune system, healing of wounds. Acuity of taste & smell.

Zinc-finger protein : A secondary feature of some proteins containing a zinc atom; a DNA-binding protein.

Zoogleal film : A complex population of organisms that form a “slime growth” on a trickling-filter media and break down the organic matter in wastewater.

Zoogleal mass : Jelly-like masses of bacteria found in both the trickling filter and activated sludge processes.

Zoology : The biological science of animals or the scientific study of animals.

Zooplankton : Tiny, free-floating organisms in aquatic systems. Unlike phytoplankton, zooplankton cannot produce their own food, and so are consumers.

Zoosemiotics : The scientific study of animal communication.

Zygote : The cell produced at fertilization by the union of gametes; the individual derived from this cell.

Zygote : The product of gamete fusion. In organisms with a haploid life cycle, the zygote immediately undergoes **meiosis**, but in organisms with a multicellular diploid stage, the zygote is merely the first stage in the diploid portion of the life cycle.