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Glossary of Physical Organic Chemistry

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GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY

Abstract. This Glossary contains definitions, explanatory notes, and sources for terms used in physical organic chemistry. Its aim is to provide guidance on the terminology of physical organic chemistry, with a view to achieving a consensus on the meaning and applicability of useful terms and the abandonment of unsatisfactory ones. Owing to the substantial progress in the field, this 2021 revision of the Glossary is much expanded relative to the previous edition, and it includes terms from cognate fields.

INTRODUCTION TO THE 2021 REVISION
General Remarks

The first Glossary of Terms Used In Physical Organic Chemistry was published in provisional form in 1979 [1] and in revised form in 1983, incorporating modifications agreed to by IUPAC Commission III.2 (Physical Organic Chemistry) [2].

A further revision was undertaken under the chairmanship of Paul Müller, which was published in 1994 [3]. The work was coordinated with that of other Commissions within the Division of Organic Chemistry. In 1999 Gerard P. Moss, with the assistance of Charles L. Perrin, converted this glossary to a World Wide Web version [4]. The Compendium of Chemical Terminology [5] (Gold Book) incorporated many of the terms in the later version.

This Glossary has now been thoroughly revised and updated, to be made available as a Web document. The general criterion adopted for the inclusion of a term in this Glossary has been its wide use in the present or past literature of physical-organic chemistry and related fields, with particular attention to those terms that have been ambiguous. It is expected that the terms in this Glossary will be incorporated within the on-line version of the IUPAC Gold Book, which is the merged compendium of all glossaries [5].

The aim of this Glossary is to provide guidance on the terminology of physical-organic chemistry, with a view to achieving a far-reaching consensus on the definitions of useful terms and the abandonment of unsatisfactory ones. According to Antoine Lavoisier "Comme ce sont les mots qui conservent les idées et qui les transmettent, il en résulte qu'on ne peut perfectionner le langage sans perfectionner la science, ni la science sans le langage," (As it is the words that preserve the ideas and convey them, it follows that one cannot improve the language without improving science, nor improve

science without improving the language.") [6]. Our approach has been to take or update entries from the previous glossary, whereas new terms were added by virtue of their usage in the current literature and the diverse knowledge of the members of the Task Force.

The Task Force is pleased to acknowledge the generous contributions of many scientists who helped by proposing or defining new terms or by criticizing or modifying existing ones. The following members of the Task Force have contributed to this revision:

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Arrangement, Abbreviations, and Symbols

The arrangement is alphabetical, terms with Greek letters following those in the corresponding Latin ones. Italicized words in the body of a definition, as well as those cited at the end, point to relevant cross-references. Literature references direct the reader either to the original literature where the term was originally defined or to pertinent references where it is used, including other IUPAC glossaries, where definitions may differ from those here.

Definitions of techniques not directly used for measurements in physical-organic chemistry are not included here but may be consulted in specialized IUPAC texts, including the IUPAC Recommendations for Mass Spectrometry [7], the Glossary of Terms Used In Theoretical Organic Chemistry [8], the Glossary of Terms Used in Photochemistry 3rd edition [9], the Glossary of Terms Used in Photocatalysis and Radiation Catalysis [10] and the Basic Terminology of Stereochemistry [11].

1
2
3   1   In accordance with IUPAC recommendations [12] the symbol ‡ to indicate
4   2   transition state ("double dagger") is used as a prefix to the appropriate quantities, e.g.,
5   3 $\Delta^{\ddagger}G$ rather than $\Delta G^{\ddagger}$. In equations including a logarithmic function the procedure
6   4   recommended by IUPAC was adopted, i.e., to divide each dimensioned quantity by its
7   5   units. Since this procedure often introduces a cluttering of the equations, we have in
8   6   some cases chosen a short-hand notation, such as ln $\{k(T)\}$, where the curly brackets
9   7   indicate an argument of dimension one, corresponding to $k(T)/[k(T)]$, where the square
10   8   brackets indicate that the quantity is divided by its units, as recommended in [12].
11   9
12   10   **Note on the identification of new and/or revised terms.**
13   11   Terms that are found in the previous version of this Glossary [3,4] and currently
14   12   incorporated in the IUPAC "Gold Book" [5] are identified with a reference to the Glossary
15   13   of Terms used in Physical Organic Chemistry (1994), i.e., [3], whereas revised terms
16   14   are designated as rev[3]. Minor changes such as better wording, additional cross-
17   15   referencing, or reorganization of the text without changing the concept are, in general,
18   16   not considered revisions. However, the improved version should replace the older one
19   17   in the "Gold Book". New terms and terms from other IUPAC documents are not
20   18   identified as such. In many cases new references have been added in the definitions.
21   19
22   20
23   21

1 **A factor**

2 Arrhenius factor

3 (SI unit same as rate constant: s^{-1} for first-order reaction).

4 Pre-exponential factor in the *Arrhenius equation* for the temperature dependence of a

5 reaction rate constant.

6   *Note 1:* According to collision theory, A is the frequency of collisions with the correct

7 orientation for reaction.

8   *Note 2:* The common unit of A for second-order reactions is dm^3 mol^{-1} s^{-1}.

9   See also *A value*, *energy of activation*, *entropy of activation*.

10   See [12,13].

11   rev[3]

12

13 **A value**

14 Steric substituent parameter expressing the conformational preference of an equatorial

15 substituent relative to an axial one in a monosubstituted cyclohexane.

16   *Note 1*: This parameter equals $\Delta_r G^o$ for the equatorial to axial equilibration,

17 in kJ mol^{-1}. For example, A_{CH3} is 7.28 kJ mol^{-1}, a positive value because an axial

18 methyl group is destabilized by a *steric effect*.

19   *Note 2*: The values are also known as Winstein-Holness A values.

20   See [3,14,15].

21

22 **abstraction**

23 Chemical reaction or transformation, the main feature of which is the bimolecular

24 removal of an atom (neutral or charged) from a molecular entity.

25   *Examples*:

26       $CH_3COCH_3 + (i\text{-}C_3H_7)_2N^- \rightarrow [CH_3COCH_2]^- + (i\text{-}C_3H_7)_2NH$

27   (hydron abstraction from acetone)

28       $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$

29   (hydrogen atom abstraction from methane)

30   See *detachment*.

31   [3]

32

33 **acceptor parameter** (*A*)

34 acceptor number (deprecated). Unit and dimension 1.

35 Quantitative measure, devised by Gutmann [16] of the *Lewis acidity* of a solvent, based

36 on the ^{31}P chemical shift of dissolved triethylphosphine oxide (triethylphosphane oxide).

37   *Note:* The term acceptor number, designated by AN, is a misnomer and ought to be

38 called acceptor parameter, *A,* because it is an experimental value [17].

39   rev[3]

40

1
2
3   1   **acid**
4
5   2   *Molecular entity* or *chemical species* capable of donating a hydron (proton) or capable
6   3   of forming a bond with the electron pair of a Lewis base.
7
8   4   See *Brønsted acid, Lewis acid, Lewis base*.
9
10   5   See also *hard acid*.
11
12   6   [3]
13
14   7
15   8   **acidity**
16   9   (1) Of a compound:
17   10   Tendency of a *Brønsted acid* to act as a *hydron* (proton) donor, or tendency of a *Lewis*
18   11   *acid* to form *Lewis adduct*s and *π-adduct*s.
19   12   *Note*: Acidity can be quantitatively expressed by the acid dissociation constant of the
20   13   compound in water or in some other specified medium, by the association constants for
21   14   formation of Lewis adducts and π-adducts, or by the enthalpy or Gibbs energy of
22   15   deprotonation in the gas phase.
23   16   (2) Of a medium, usually one containing Brønsted acids:
24   17   Tendency of the medium to hydronate a specific reference base.
25   18   *Note 1*: The acidity of a medium is quantitatively expressed by the appropriate *acidity*
26   19   *function*.
27   20   *Note 2*: Media having an acidity greater than that of 100 % H_2SO_4 are often called
28   21   *superacid*s.
29   22   See [18].
30   23   rev[3]
31   24
32   25   **acidity function**
33   26   Measure of the thermodynamic *hydron*-donating or -accepting ability of a solvent
34   27   system, or a closely related thermodynamic property, such as the tendency of the *lyate*
35   28   *ion* of the solvent system to form *Lewis adduct*s.
36   29   *Note 1*: Acidity functions are not unique properties of the solvent system alone but
37   30   depend on the solute (or family of closely related solutes) with respect to which the
38   31   thermodynamic tendency is measured.
39   32   *Note 2*: Commonly used acidity functions are extensions of pH to concentrated acidic
40   33   or basic solutions. Acidity functions are usually established over a range of
41   34   compositions of such a system by UV/Vis spectrophotometric or NMR measurements
42   35   of the degree of hydronation (or Lewis adduct formation) for the members of a series of
43   36   structurally similar indicator bases (or acids) of different strength: the best known of
44   37   these is the Hammett acidity function H_o (for primary aromatic amines as indicator
45   38   bases).
46   39   For detailed information on other acidity functions, on *excess acidity*, on the
47   40   evaluation of acidity functions, and on the limitations of the concept, see [19,20,21,22].

1   [3]

2

3 **activated complex**

4   See *activated state.*

5   rev[3]

6

7 **activated state**

8 In theories of unimolecular reactions an energized *chemical species*, often

9 characterized by the superscript ‡, where the excitation is specific and the molecule is

10 poised for reaction.

11   *Note 1*: Often used as a synonym for *activated complex* or *transition state*, but not

12 restricted to transition-state theory.

13   *Note 2*: This is distinct from an energized *molecule*, often characterized by the

14 superscript *, in which excitation energy is dispersed among internal degrees of

15 freedom.

16   *Note 3:* This is not a *complex* according to the definition in this Glossary.

17   See also *transition state*, *transition structure*.

18

19 **activation energy**

20   See *energy of activation*.

21   See [12], section 2.12.

22   [3]

23

24 **activation strain model**

25   See *distortion interaction model*.

26

27 **addition reaction**

28 *Chemical reaction* of two or more reacting *molecular entities*, resulting in a product

29 containing all atoms of all components, with formation of two chemical bonds and a net

30 reduction in bond multiplicity in at least one of the reactants.

31   *Note 1*: The addition to an entity may occur at only one site (1,1-addition, *insertion*),

32 at two adjacent sites (1,2-addition) or at two non-adjacent sites (1,3- or 1,4-addition,

33 etc.).

34   *Examples*

35

36    $R_3C–H + H_2C\textbf{:} \rightarrow R_3C–CH_3$ (1,1-addition of a carbene)

37    $Br_2 + CH_2=CH–CH=CH_2 \rightarrow BrCH_2–CH(Br)–CH=CH_2$ (1,2-addition) +

38                  $BrCH_2–CH=CH–CH_2Br$ (1,4-addition)

39

Note 2: This is distinguished from *adduct* formation, which is less specific about bonding changes.

Note 3: The reverse process is called an *elimination* reaction.

See also *cheletropic reaction*, *cycloaddition, insertion*.

rev[3]

additivity principle

Hypothesis that each of several structural features of a *molecular entity* makes an independent, transferable, and additive contribution to a property of the substance concerned.

Note 1: 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 *chemical reaction*.

Note 2: The enthalpies of formation of series of compounds can be described by additivity schemes [23].

Note 3: Deviations from additivity may be remedied by including terms describing interactions between atoms or groups.
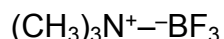
See *transferability* [24,25].

rev[3]

adduct

New *chemical species* AB, each *molecular entity* of which is formed by direct combination of two (or more) separate molecular entities A and B in such a way that there is no loss of atoms from A or B.

Example: adduct formed by interaction of a *Lewis acid* with a *Lewis base*:

$(CH_3)_3N^+{-}^-BF_3$

Note 1: Stoichiometries other than 1:1 are also possible, e.g., a bis-adduct (2:1).

Note 2: An *intramolecular* adduct can be formed when A and B are *groups* contained within the same molecular entity.

Note 3: If adduct formation is prevented by *steric hindrance*, *frustrated Lewis pair*s may result.
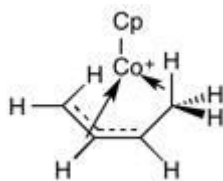
See also *addition reaction, frustrated Lewis pair, Lewis adduct, Meisenheimer adduct, π-adduct*.

rev[3]

agostic

Feature of a structure in which a hydrogen atom is bonded to both a main-group atom and a metal atom.

Example, [(1–3-η)-but-2-en-1-yl-η^2-C^4,H^4](η^5-cyclopentadienyl)cobalt(+1).

6   *Note*: The expression η-hydrido-bridged is also used to describe the bonding
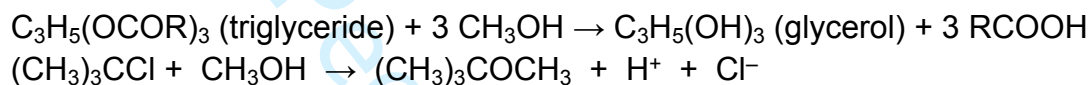7 arrangement with a bridging hydrogen, but this usage is deprecated.
8   See [26,27,28,29].
9   rev[3]

11 **alcoholysis**
12 Reaction with an alcohol solvent.
13   *Examples:*

15      $C_3H_5(OCOR)_3$ (triglyceride) + 3 $CH_3OH \rightarrow C_3H_5(OH)_3$ (glycerol) + 3 RCOOH
16      $(CH_3)_3CCl + CH_3OH \rightarrow (CH_3)_3COCH_3 + H^+ + Cl^-$

18   See *solvolysis*.
19   rev[3]

22 **allotropes**
23 Different structural modifications of an element, with different bonding arrangements of
24 the atoms.
25   *Examples* for carbon include diamond, *fullerenes*, graphite, and *graphene*.
26   See [29].

28 **allylic substitution reaction**
29 *Substitution* reaction on an allylic system with *leaving group* (*nucleofuge*) at position 1
30 and double bond between positions 2 and 3. The incoming group may become attached
31 to atom 1, or else the incoming group may become attached at position 3, with
32 movement of the double bond from 2,3 to 1,2.
33   *Example*:
34      $CH_3CH=CHCH_2Br + HOAc \rightarrow CH_3CH=CHCH_2OAc$ or $CH_3CH(OAc)CH=CH_2$

36   *Note*: This term can be extended to systems such as:

38      $CH_3CH=CH-CH=CH-CH_2Br \rightarrow CH_3CH(OAc)-CH=CH-CH=CH_2 +$
39              $CH_3CH=CH-CH(OAc)-CH=CH_2 + CH_3CH=CH-CH=CH-CH_2OAc$

1
2
3   1   and also to propargylic substitution, with a triple bond between positions 2 and 3 and
4   2   possible rearrangement to an allenic product.
5   3   rev[3]
6   4
7
8   5   **alternant**
9   6   Property of a *conjugated system* of π electrons whose atoms can be divided into two
10   7   sets (marked as "starred" and "unstarred") so that no atom of either set is directly linked
11   8   to any other atom of the same set.
12
13   9   *Examples*
14
15   10
16   11
17   12
18   13
19   14
20
21   15
22
23   16

alternant   nonalternant

(two unstarred atoms
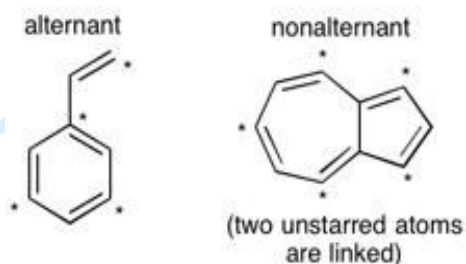are linked)

24   17   *Note 1:* According to several approximate theories (including *HMO theory*), the π
25   18   MOs for an alternant hydrocarbon are paired, such that for an orbital of energy $\alpha + x\beta$
26   19   there is another of energy $\alpha - x\beta$. The coefficients of paired molecular orbitals at each
27   20   atom are the same, but with opposite sign for the unstarred atoms, and the π electron
28
29   21   density at each atom in a neutral alternant hydrocarbon is unity.
30   22   See [30,31,32].
31   23   rev[3]
32
33   24
34
35   25   **ambident**
36   26   ambidentate, bidentate
37   27   Characteristic of a *chemical species* whose *molecular entities* each possess two
38   28   alternative, distinguishable, and strongly interacting reactive centres, to either of which
39
40   29   a *bond* may be made.
41   30   *Note 1*: Term most commonly applied to *conjugated nucleophiles*, for example an
42   31   enolate ion (which may react with *electrophiles* at either the α-carbon atom or the
43
44   32   oxygen) or a 4-pyridone, and also to the vicinally ambident cyanide ion and to cyanate
45   33   ion, thiocyanate ion, sulfinate ions, nitrite ion, and unsymmetrical hydrazines.
46
47   34
48
49
50
51
52   35
53   36
54   37   *Note 2*: Ambident electrophiles are exemplified by carboxylic esters RC(O)OR',
55
56   38   which react with nucleophiles at either the carbonyl carbon or the alkoxy carbon, and
57
58
59
60

1 by Michael acceptors, such as enones, that can react at either the carbonyl or the α-
2 carbon.
3   *Note 3*: Molecular entities containing two non-interacting (or feebly interacting)
4 reactive centres, such as dianions of dicarboxylic acids, are not generally considered
5 to be ambident or bidentate and are better described as bifunctional.
6   *Note 4*: The Latin root of the word implies two reactive centres, but the term has also
7 been applied to chemical species with more than two reactive centres, such as an acyl
8 thiourea, RCONHCSNHR', with nucleophilic O, S, and N. For such species the term
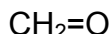9 polydentate (or multidentate) is more appropriate.
10   See [33,34,35,36].
11   [3]
12

13 **ambiphilic**
14 Both *nucleophilic* and *electrophilic*.
15   *Example*:
16     $CH_2=O$
17   See also *amphiphilic*, but the distinction between ambi (Latin: both) and amphi
18 (Greek: both) and the application to hydrophilic and lipophilic or to nucleophilic and
19 electrophilic is arbitrary.
20

21 **aminoxyl**
22 Compound having the structure
23     $R_2N-O^{\bullet} \leftrightarrow R_2N^{\bullet+}-O^-$
24   *Note*: The synonymous term 'nitroxyl radical' erroneously suggests the presence of
25 a nitro group; its use is deprecated.
26

27 **amphiphilic**
28 Both hydrophilic and lipophilic, owing to the presence in the molecule of a large organic
29 cation or anion and also a long hydrocarbon chain (or other combination of polar and
30 nonpolar groups, as in nonionic surfactants)
31   *Examples*:
32
33     $CH_3(CH_2)_nCO_2^-M^+$, $CH_3(CH_2)_nSO_3^-M^+$, $CH_3(CH_2)_nN(CH_3)_3^+X^-$ ($n > 7$).
34
35   *Note*: The presence of distinct polar (hydrophilic) and nonpolar (hydrophobic) regions
36 promotes the formation of *micelles* in dilute aqueous solution.
37   See also *ambiphilic*.
38   [3]
39

40 **amphiprotic (solvent)**

1 Feature of a self-ionizing solvent possessing characteristics of both *Brønsted acid* and

2 *base*.

   Examples: H_2O, CH_3OH.

4   [3]

5

amphoteric

7 Property of a *chemical species* that can behave as either an acid or as a base.

8   *Examples*: H_2O, HCO_3^- (hydrogen carbonate)

9   *Note*: This property depends upon the medium in which the species is investigated.

10 For example HNO_3 is an acid in water but becomes a base in H_2SO_4.

11   rev[3]

12

anchimeric assistance

14 *neighbouring group participation*

15   [3]

16

anionotropy

18 Rearrangement or *tautomerization* in which the migrating group moves with its electron

19 pair.

20   See [37].

21   [3]

22

annelation

24 Alternative, but less desirable term for *annulation*.

25   *Note*: The term is widely used in German and French languages.

26   [3]

27

annulation

29 *Transformation* involving fusion of a new ring to a molecule via two new bonds.

30   *Note*: Some authors use the term *annelation* for the fusion of an additional ring to an

31 already existing one, and annulation for the formation of a ring from an acyclic

32 precursor.

33   See [38,39].

34   See also *cyclization*.

35   [3]

36

annulene

38 Conjugated monocyclic hydrocarbon of the general formula C_nH_n (*n* even) with the

39 maximum number of noncumulative double bonds and without side chains.

1   *Note*: In systematic nomenclature an annulene may be named [*n*]annulene, where *n*
2   is the number of carbon atoms, e.g., [8]annulene for cycloocta-1,3,5,7-tetraene.
3   See [40].
4   See *aromatic*, *Hückel (4n + 2) rule*.
5   [3]

6

anomeric effect

8   Tendency of an electronegative substituent alpha to a heteroatom in a six-membered
9   ring to prefer the axial position, as in the *anomers* of glucopyranose.
10 *Note 1*: The effect can be generalized to the conformational preference of an
11 electronegative substituent X to be antiperiplanar to a lone pair of atom Y in a system
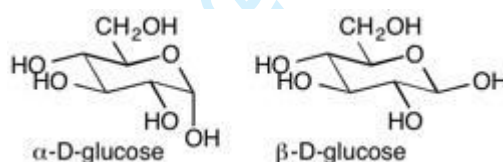12 R–Y–C–X with geminal substituents RY and X.
13 *Note 2:* The effect can be attributed, at least in part, to *n-σ^* delocalization* of the lone
14 pair on Y into the C–X σ^* orbital.
15 See [11,41,42,43,44].

16

anomers

18 The two stereoisomers (epimers) of a cyclic sugar or glycoside that differ only in the
19 *configuration* at C1 of aldoses or C2 of ketoses (the anomeric or acetal/ketal carbon).
20 *Example:*

21
22
23
24

α-D-glucose   β-D-glucose

25 See [11].
26 [3]

27

antarafacial, suprafacial

29 Two spatially different ways whereby bonding changes can occur when a part of a
30 molecule undergoes two changes in bonding (*bond*-making or bond-breaking), either
31 to a common centre or to two related centres external to itself. These are designated
32 as antarafacial if opposite faces of the molecule are involved, and suprafacial if both
33 changes occur at the same face. The concept of face is clear from the diagrams in the
34 cases of planar (or approximately planar) frameworks with interacting π orbitals.

35
36   antarafacial   suprafacial
37
38
39
40

1

2

3   1

4   2

6   3   For examples of the use of these terms see *cycloaddition*, *sigmatropic rearrangement*.

7   4   See also *anti*, σ, π.

9   5   rev[3]

10   6

11   7   ***anti***

13   8   Stereochemical relationship of two substituents that are on opposite sides of a

14   9   reference plane, in contrast to *syn*, which means "on the same side".

15 10   *Note 1*: Two substituents attached to atoms joined by a single *bond* are *anti* if the

17 11   torsion angle (dihedral angle) between the bonds to the substituents is greater than 90°,

18 12   in contrast to *syn* if it is less than 90°.

19 13   *Note 2*: A further distinction is made between antiperiplanar, synperiplanar, anticlinal

21 14   and synclinal.

22 15   See [11,45,46,47].

23 16   *Note 3*: When the terms are used in the context of *chemical reactions* or

25 17   *transformations*, they designate the relative orientation of substituents in the substrate

26 18   or product:

27 19   (1)   Addition to a carbon-carbon double bond:

29 20

30 21

42 30   (2)   Alkene-forming *elimination*:

43 31

49 32

50 33

51 34   (3)   Aldol reaction (where *syn* and *anti* designate the relative orientation of CH_3

53 35   and OH in the product)

54 36

1

2   *Note 4*: In examples (1) and (2) *anti* processes are always *antarafacial*, and *syn*

3 processes are *suprafacial*.

4   *Note 5*: In the older literature the terms *anti* and *syn* were used to designate

5 stereoisomers of oximes and related compounds. That usage was superseded by the

6 terms *trans* and *cis* or *E* and *Z*.

7   See [11].

8   rev[3]

9

10 **anti-Hammond effect**

11 If a structure lying off the *minimum-energy reaction path* (MERP) is stabilized, the

12 position of the *transition state* moves toward that structure.

13   See *Hammond Postulate, More O'Ferrall - Jencks diagram, perpendicular effect*.

14   rev[3]

15

16 **aprotic (solvent)**

17 *non-HBD solvent* (non-Hydrogen-Bond Donating solvent)

18 Solvent that is *not* capable of acting as a hydrogen-bond donor.

19   *Note*: Although this definition applies to both polar and nonpolar solvents, the

20 distinction between HBD and non-HBD (or between protic and aprotic) is relevant only

21 for polar solvents.

22   See *HBD solvent*.

23   rev[3]

24

25

26 **aquation**

27 Incorporation of one or more integral molecules of water into a species, with or without

28 displacement of one or more other atoms or groups.

29   *Example*: The incorporation of water into the inner *ligand* sphere of an inorganic

30 *complex*.

31   See [48].

32   See also *hydration*.

33   [3]

1

aromatic (*adj.*), **aromaticity** (*n.*)

(1) Having a chemistry typified by benzene (traditionally).

(2) Feature of a cyclically *conjugated molecular entity* whose electronic energy is significantly lower or whose stability is significantly greater (owing to *delocalization*) than that of a hypothetical localized structure (e.g., *Kekulé structure*).

   Note 1: If the molecular entity is of higher energy or less stable than a hypothetical localized structure, the entity is said to be antiaromatic.

   Note 2: A geometric parameter indicating bond-length equalization has been used as a measure of aromatic character, as expressed in the harmonic oscillator model of aromaticity [49].

   Note 3: The magnitude of the magnetically induced ring current, as observed experimentally by NMR spectroscopy or by the calculated nucleus-independent chemical shift (NICS) value, is another measure of aromaticity [50].

   Note 4: 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, whereby a cycle with ($4n+2$) electrons and a Möbius cycle with $4n$ electrons are aromatic. Reactions of molecules in the *ground state* involving antiaromatic transition states proceed much less easily than those involving aromatic transition states.

   See [51,52,53]. See 19 articles in [54].

   See also *Hückel (4n + 2) rule*, *Möbius aromaticity*.

   [3]

Arrhenius equation

Empirical expression for the temperature dependence of a reaction rate constant k as

   $k(T) = A \exp(-E_A/RT)$,

with A the pre-exponential factor (Arrhenius *A factor*) and E_A the Arrhenius *energy of activation*, both considered to be temperature-independent.

   rev[3]

aryne

Hydrocarbon derived from an arene by formal removal of two vicinal hydrogen atoms.

   Example: 1,2-didehydrobenzene (benzyne)

Note 1: 1,4-Didehydrobenzene ("p-benzyne *diradical*", structure above right). Despite common usage this is not an aryne because there is no triple bond, and the usage is deprecated.

Note 2: Arynes are usually *transient species*.

Note 3: The analogous heterocyclic compounds are called heteroarynes or hetarynes.

See [40,55].

rev[3]

association

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.

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

[3]

asymmetric induction

Preferential formation in a *chemical reaction* of one *enantiomer* or *diastereoisomer* over the other as a result of the influence of a *chiral centre* (*stereogenic centre*, *chiral feature*) in the substrate, reagent, *catalyst*, or environment.

Note: The term also refers to the formation of a new chiral centre or chiral feature preferentially in one *configuration* under such influence.

See [11].

rev[3]

atomic charge

Net charge due to the nucleus and the average electronic distribution in a given region of space. This region is considered to correspond to an atom in a *molecular entity*.

Note 1: The boundary limits of an atom in a polyatomic molecular entity cannot be defined, as they are not a quantum-mechanical observable. Therefore, different conceptual schemes of dividing a molecule into individual atoms will result in different atomic charges.

Note 2: The atomic charge on an atom should not be confused with its *formal charge*. For example, the N in NH_4^+ is calculated to carry a net negative charge even though its

1   1   formal charge is +1, and each H is calculated to carry a net positive charge even though

2   2   its formal charge is 0.

3   3   See [8].

4   4

5

6   5   **atomic orbital**

7   6   Wavefunction that depends explicitly on the spatial coordinates of only one electron

8   7   around a single nucleus.

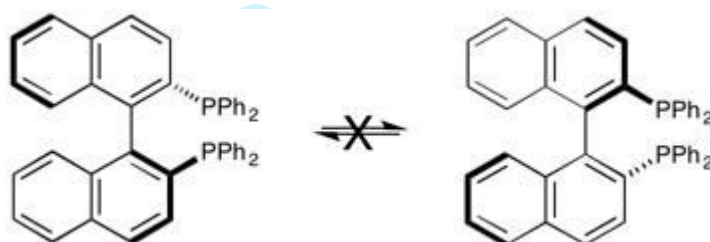9   8   See also *molecular orbital*.

10   9   See [8].

11   10   [3]

12   11

13   12   **atropisomers**

14   13   Stereoisomers that are enantiomeric owing to hindered rotation about a single bond.

15   14   *Example* (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, BINAP):

16   15

17   16

18   17

19   18

20   19

21   20

22   21

23   22   See [11].

24   23

25   24   **attachment**

26   25   *Transformation* by which one *molecular entity* (the *substrate*) is converted into another

27   26   by the formation of one (and only one) two-centre *bond* between the substrate and

28   27   another molecular entity and which involves no other changes in *connectivity* in the

29   28   substrate.

30   29   *Example*: formation of an acyl cation by attachment of carbon monoxide to a

31   30   *carbenium* ion (R^+):

32   31 $R^+ + CO \rightarrow (RCO)^+$

33   32   See also *colligation*.

34   33   rev[3]

35   34

36   35   **autocatalytic reaction**

37   36   *Chemical reaction* in which a product (or a reaction *intermediate*) also functions as

38   37   *catalyst*.

39   38   *Note*: In such a reaction the observed *rate of reaction* is often found to increase with

40   39   time from its initial value.

1   *Example*: acid-catalyzed bromination of acetophenone, PhCOCH$_3$, because the

2 reaction generates HBr, which functions as a catalyst.

3   rev[3]

4

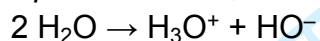5 **automerization**

6 degenerate rearrangement

7   [3]

8

9 **autoprotolysis**

10 *Proton transfer reaction* (*hydron* transfer reaction) between two identical *amphoteric*

11 molecules (usually of a solvent), one acting as a *Brønsted acid* and the other as a

12 *Brønsted base*.

13   *Example*:

14   2 H$_2$O → H$_3$O$^+$ + HO$^-$

15   [3]

16

17 **autoprotolysis constant**

18 Product of the activities of the species produced as the result of *autoprotolysis*.

19   *Example*: The autoprotolysis constant for water, K_w (or K_{AP}), is equal to the product

20 of the relative activities of the hydronium and hydroxide ions at equilibrium in pure water.

21

22         $K_w = a(H_3O^+)a(HO^-) = 1.0 \times 10^{-14}$ at 25 °C and 1 standard atmosphere.

23

24   *Note:* Since the relative activity $a(H_2O)$ of water at equilibrium is imperceptibly

25 different from unity (with mole fraction as the activity scale and pure un-ionized water

26 as the standard state), the denominator in the expression for the thermodynamic

27 equilibrium constant $K_w°$ for autoprotolysis has a value very close to 1.

28

29         $$K_w° = \frac{a(H^3O^+)a(HO^-)}{a(H_2O)^2}$$

30

31 Furthermore, owing to the low equilibrium extent of dissociation, and if infinite dilution

32 is selected as the standard state, the activity coefficients of the hydronium and

33 hydroxide ions in pure water are very close to unity. This leads to the relative activities

34 of H$_3$O$^+$ and HO$^-$ being virtually identical with the numerical values of their molar

35 concentrations, if the molar scale of activity is used and an activity of 1 mol dm^{-3} is

36 chosen as the standard state. Thus

37

38     $K_w \approx [H_3O^+][HO^-]$

39

1   where $[H_3O^+]$ and $[HO^-]$ are the numerical values of the molar concentrations. The

2   autoprotolysis constant has the unit (and dimension) 1 because each relative activity

3   has dimension 1, being a quotient of an absolute activity (including units) divided by a

4   common unit standard state activity (including units).

5   See [56,57].

6   rev[3]

7

8   **α (alpha)**

9   (1) Designation applied to the carbon to which a functional group is attached.

10   (2) In carbohydrate nomenclature a stereochemical designation of the *configuration* at

11   the anomeric carbon.

12   (3) Parameter in a *Brønsted relation* expressing the sensitivity of the rate of protonation

13   to *acidity*.

14   (4) Parameter in *Leffler's relation* expressing the sensitivity of changes in Gibbs

15   activation energy to changes in overall Gibbs energy for an elementary reaction.

16   See [11].

17   rev[3]

18

19   **α-effect**

20   Positive deviation of an α nucleophile (one bearing an unshared pair of electrons on an

21   atom adjacent to the nucleophilic site) from a Brønsted-type plot of lg $\{k_{nuc}\}$ vs. pK_a. The

22   argument in the lg function should be of dimension 1. Thus, reduced *rate coefficient*s

23   should be used. Here $\{k_{nuc}\} = k_{nuc}/[k_{nuc}]$ is the reduced k_{nuc}.

24   *Note 1*: More generally, it is the influence on the reactivity at the site adjacent to the

25   atom bearing a lone pair of electrons.

26   *Note 2*: The term has been extended to include the effect of any substituent on an

27   adjacent reactive centre, e.g., the α-silicon effect.

28   See [58,59,60].

29   See also *Brønsted relation*.

30   rev[3]

31

32   **α-elimination**

33   1,1-elimination

34   *Transformation* of the general type

35

36   RR'ZXY → RR'Z + XY (or X + Y, or X$^+$ + Y$^-$)

37

38   where the central atom Z is commonly carbon.

39   See also *elimination*.

40   rev[3]

1

Baldwin's rules

Set of empirical rules for closures of 3- to 7-membered rings.

Note: The favoured pathways are those in which the length and nature of the linking chain enable the terminal atoms to achieve the proper geometry and *orbital* overlaps for reaction.

Example: Hex-5-en-1-yl radical undergoes 5-exo-trig cyclization to cyclopentylmethyl radical rather than 6-endo-trig cyclization to cyclohexyl radical.
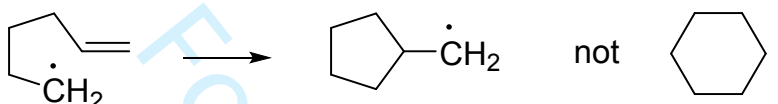
See [61,62].

rev[3]

base

Chemical species or *molecular entity* having an available pair of electrons capable of forming a *bond* with a *hydron* (proton) (see *Brønsted base*) or with the vacant orbital of some other species (see *Lewis base*).

See also *hard base*, *superbase*.

[3]

basicity

(1) Tendency of a *Brønsted base* to act as *hydron* (proton) acceptor.

Note 1: The basicity of a *chemical species* is normally expressed by the *acidity* or acid-dissociation constant of its conjugate acid (see *conjugate acid-base pair*).

Note 2: To avoid ambiguity, the term pK_{aH} should be used when expressing basicity by the acid-dissociation constant of its conjugate acid. Thus the pK_{aH} of NH_3 is 9.2, while its pK_a, expressing its acidity, is 38.

(2) Tendency of a *Lewis base* to act as a *Lewis acid* acceptor.

Note 3: For Lewis bases, basicity is expressed by the association constants of *Lewis adduct*s and *π-adduct*s, or by the enthalpy of an acid/base reaction.

Note 4: Spectroscopic shifts induced by acid/base adduct formation can also be used as a measure of the strength of interaction.

See [63].

rev[3]

bathochromic shift (effect)

Shift of a spectral band to lower frequencies (longer wavelengths).

1 *Note*: This is informally referred to as a red shift and is opposite to a *hypsochromic*

2 *shift* ("blue shift"), but these historical terms are discouraged because they apply only

3 to visible transitions.

4   See [9].

5   [3]

6

7 **Bell-Evans-Polanyi principle**

8 Linear relation between energy of activation (E_A) and enthalpy of reaction ($\Delta_r H$),

9 sometimes observed within a series of closely related reactions.

10

11 $E_A = a + b\,\Delta_r H$

12

13 See [64,65,66,67].

14 rev[3]

15

16 **benzyne**

17 1,2-Didehydrobenzene (a C_6H_4 *aryne* derived from benzene) and its derivatives formed

18 by substitution.

19   *Note*: The terms *m*- and *p*-benzyne are occasionally used for 1,3- and 1,4-

20 didehydrobenzene, respectively, but these are incorrect because there is no triple bond.

21   See [40,55].

22   [3]

23

24 **bidentate**

25 Feature of a *ligand* with two potential binding sites.

26

27 **bifunctional catalysis**

28 Catalysis (usually of *hydron* transfer) by a *chemical species* involving a mechanism in

29 which two *functional groups* are implicated in the *rate-limiting step*, so that the

30 corresponding *catalytic coefficient* is larger than that expected for catalysis by a

31 chemical species containing only one of these functional groups.

32   *Example*: Hydrogen carbonate is a particularly effective *catalyst* for the hydrolysis of

33 4-hydroxybutyranilide (*N*-phenyl-4-hydroxybutanamide), because it catalyzes the

34 breakdown of the tetrahedral intermediate to expel aniline:

35

Note: The term should not be used to describe a *concerted process* involving the action of two different catalysts.

See [68,69,70,71,72].

rev[3]

bifurcation

Feature on a *potential-energy surface* whereby a *minimum-energy reaction path* (MERP) emanating from a saddle point (corresponding to a *transition structure*) splits in two and leads to alternative products without intervening minima or secondary barriers to overcome. A bifurcation arises when the curvature of the surface in a direction perpendicular to the MERP becomes zero and then negative; it implies the existence of a lower-energy transition structure with a *transition vector* orthogonal to the original MERP.

See [73,74].

bimolecular

See *molecularity*.

[3]

binding site

Specific region (or atom) in a *molecular entity* that is capable of entering into a stabilizing interaction with another atomic or molecular entity.

Example: an active site in an enzyme that interacts with its *substrate*.

Note 1: Typical modes of interaction are by *covalent bonding*, *hydrogen bonding*, *coordination*, and *ion-pair* formation, as well as by dipole-dipole interactions, dispersion forces, hydrophobic interactions, and desolvation.

Note 2: Two binding sites in different molecular entities are said to be complementary if their interaction is stabilizing.

[3]

1 **biradical**

2 *diradical*

3   See [9].

4   rev[3]

5

6 **blue shift**

7 Informal expression for *hypsochromic shift*, but this historical term is discouraged

8 because it applies only to visible transitions.

9   rev[3]

10

11 **Bodenstein approximation**

12   See *steady state*.

13   [3]

14

15 **bond**

16 Balance of attractive and repulsive forces between two atoms or groups of atoms,

17 resulting in sufficient net stabilization to lead to the formation of an aggregate

18 conveniently considered as an independent *molecular entity*.

19   *Note*: The term usually refers to the *covalent bond*.

20   See [75].

21   See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.

22   rev[3]

23

24 **bond dissociation**

25   See *heterolysis*, *homolysis*.

26   *Note*: In ordinary usage the term refers to homolysis. If not, it should be specified as

27 heterolytic.

28   [3]

29

30 **bond-dissociation energy**

31 D_e

32 (SI unit: kJ mol^{-1})

33 Energy required to break a given *bond* of some specific *molecular entity* by *homolysis*

34 from its potential-energy minimum.

35   *Note:* This is the quantity that appears in the *Morse potential*.

36   See also *bond-dissociation enthalpy*.

37   rev[3]

38

39 **bond-dissociation enthalpy**

40 DH^0, $\Delta_{diss}H^0$

1   (SI unit: kJ mol^{-1})
2   Standard molar enthalpy required to break a given *bond* of some specific *molecular*
3   *entity* by *homolysis*.
4   *Example*: For $CH_4 \rightarrow CH_3\cdot + H\cdot$ the bond-dissociation enthalpy is symbolized as
5    $DH^0(CH_3–H)$.
6   *Note:* Although DH^0 is commonly used, $\Delta_{diss}H^0$ is more consistent with the notation
7   for other thermodynamic quantities.
8   See also *bond-dissociation energy*, *bond energy*, *heterolytic bond-dissociation*
9   *enthalpy*.
10

11   **bond energy**
12   D_0
13   (SI unit: kJ mol^{-1})
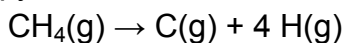14   Enthalpy of bond dissociation at 0 K.
15   See *bond-dissociation enthalpy*.
16   rev[3]
17

18   **bond enthalpy (mean bond enthalpy, mean bond energy)**
19   Average value of the gas-phase *bond-dissociation enthalpies* (usually at a temperature
20   of 298 K) for all *bond*s of the same type within the same *chemical species*.
21   *Example*: For methane, the mean bond enthalpy is 415.9 kJ mol^{-1}, one-fourth the
22   enthalpy of reaction for
23           $CH_4(g) \rightarrow C(g) + 4\ H(g)$
24   *Note*: More commonly, tabulated mean bond energies (which are really enthalpies)
25   are values of bond enthalpies averaged over a number of selected chemical species
26   containing that type of bond, such as 414 kJ mol^{-1} for C–H bonds in a group of R_3CH
27   (R = H, alkyl).
28   See [76].
29

30   **bond order**
31   Theoretical index of the degree of bonding between two atoms, relative to that of a
32   normal single *bond*, i.e., the bond provided by one localized electron pair.
33   *Example*: In ethene the C–C bond order is 2, and the C–H bond order is 1.
34   *Note 1*: In valence-bond theory it is a weighted average of the bond orders between
35   the respective atoms in the various resonance forms. In molecular-orbital theory it is
36   calculated from the weights of the atomic orbitals in each of the occupied molecular
37   orbitals. For example, in valence-bond theory the bond order between adjacent carbon
38   atoms in benzene is 1.5; in *Hückel molecular orbital theory* it is 1.67.
39   *Note 2:* Bond order is often derived from the electron distribution.

1
2
3   1   *Note 3:* The Pauling bond order *n* (as often used in the *bond-energy-bond-order*
4
5   2   *model*) is a simple function of change in bond length *d*, where the value of the coefficient
6   3   *c* is often 0.3 Å (for *n* > 1) or 0.6 Å (for *n* < 1).
7
8
9   5 $n = \exp[(d_1 - d_n)/c]$
10   6   rev[3]
11
12
13   8   **bond-energy-bond-order model** (BEBO):
14   9   Empirical procedure for estimating *activation energy*, involving relationships among
15 10 bond length, *bond-dissociation energy*, and *bond order*.
16 11   See [13,77].
17
18
19 13 **bond-stretch isomers**
20 14 Two (or more) molecules with the same spin multiplicity but with different lengths for
21 15 one or more bonds.
22 16   *Note*: This feature arises because the potential-energy surface, which describes how
23 17 the energy of the molecule depends on geometry, shows two (or more) minima that are
24 18 not merely symmetry-related.
25 19   See [78,79,80,81].
26
27
28 21 **borderline mechanism**
29 22 Mechanism intermediate between two extremes, for example a *nucleophilic substitution*
30 23 intermediate between S_N1 and S_N2, or intermediate between electron transfer and S_N2.
31 24   [3]
32
33
34 26 **Born-Oppenheimer approximation**
35 27 Representation of the complete *wavefunction* as a product of electronic and nuclear
36 28 parts, $\Psi(r,R) = \psi_{el}(r,R)\ \psi_{nuc}(R)$, so that the two wavefunctions can be determined
37 29 separately by solving two different Schrödinger equations.
38 30   See [8].
39
40 32 **Bredt's rule**
41 33 Prohibition of placing a double bond with one terminus at the *bridgehead* atom of a
42 34 polycyclic system unless the rings are large enough to accommodate the double bond
43 35 without excessive *strain*.
44 36   *Example*: Bicyclo[2.2.1]hept-1-ene (A), which is capable of existence only as a
45 37 *transient species*, although its higher homologues, bicyclo[3.3.1]non-1-ene (B) and
46 38 bicyclo[4.2.1]non-1(8)-ene (C), with double bond at the bridgeheads, have been
47 39 isolated.

1
2
3
4   A   B   C
5
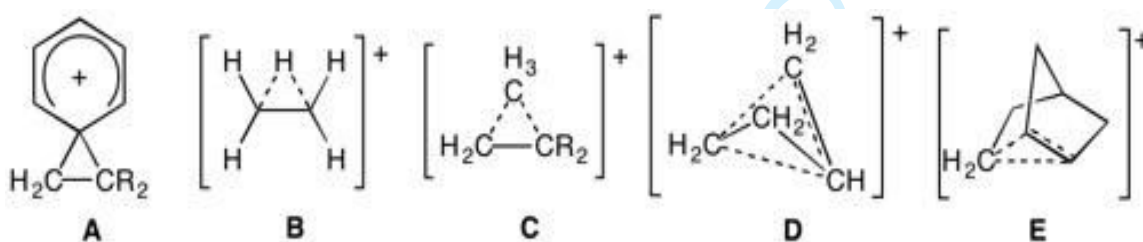6 See [82,83,84,85].
7 For limitations see [86].
8 *Note*: For an alternative formulation, based on the instability of a *trans* double bond
9 in a small ring (fewer than 8 atoms), see [87].
10 rev[3]
11
12 **bridged carbocation**
13 *Carbocation* (real or hypothetical) in which there are two (or more) carbon atoms that
14 could in alternative *Lewis formula*s be designated as carbenium centres but which is
15 instead represented by a structure in which a group (a hydrogen atom or a hydrocarbon
16 residue, possibly with substituents in non-involved positions) bridges these potential
17 carbenium centres.
18 *Note*: Electron-sufficient bridged carbocations are distinguished from electron-
19 deficient bridged carbocations. Examples of the former, where the bridging uses π
20 electrons, are phenyl-bridged ions (for which the trivial name phenonium ion has been
21 used), such as **A**. These ions are straightforwardly classified as *carbenium ion*s. The
22 latter type of ion necessarily involves three-centre bonding because the bridging uses
23 σ electrons. The hydrogen-bridged carbocation **B** contains a two-coordinate hydrogen
24 atom, whereas structures **C**, **D**, and **E** (the 2-norbornyl cation) contain five-coordinate
25 carbon atoms.
26

27   **A**   **B**   **C**   **D**   **E**
28
29 See [88].
30 See also *carbonium ion*, *multi-centre bond*, *neighbouring group participation*.
31 For the definitive X-ray structure of the norbornyl cation see [89].
32 rev[3]
33
34
35
36 **bridgehead (atom)**

1 Atom that is part of two or more rings in a polycyclic molecule and that is separated
2 from another bridgehead atom by bridges all of which contain at least one other atom.
3 *Example:* C1 and C4 in bicyclo[2.2.1]heptane, but not C4a and C8a in
4 decahydronaphthalene.
5

bridging ligand
7 *Ligand* attached to two or more, usually metallic, central atoms.
8 See [29].
9 [3]
10

Brønsted acid (Brönsted acid)
12 *Molecular entity* capable of donating a *hydron* (proton) to a base (i.e., a hydron donor),
13 or the corresponding *chemical species*.
14 *Examples*: H_2O, H_3O^+, CH_3COOH, H_2SO_4, HSO_4^-, HCl, CH_3OH, NH_3.
15 See also *conjugate acid-base pair*.
16 [3]
17

Brønsted base (Brönsted base)
19 *Molecular entity* capable of accepting a *hydron* (proton) from a Brønsted acid (i.e., a
20 hydron acceptor), or the corresponding *chemical species*.
21 *Examples*: HO^-, H_2O, $CH_3CO_2^-$, HSO_4^-, SO_4^{2-}, Cl^-, CH_3O^-, NH_2^-.
22 See also *conjugate acid-base pair*.
23 [3]
24

Brønsted relation (Brönsted relation)
26 Either of the equations
27

28 $$\lg(\{k_{HA}\}/p) = C\ +\ \alpha\,\lg(q\{K_{HA}\}/p)$$
29

30 $$\lg(\{k_A\}/q)\ = C\ -\ \beta\,\lg(q\{K_{HA}\}/p)$$
31

32 where α, β, and C are constants for a given reaction series (α and β are called Brønsted
33 exponents or Brønsted parameters). The arguments in the lg functions should be of
34 dimension 1. Thus, reduced *rate coefficients* should be used: $\{k_A\} = k_A/[k_A]$ and $\{k_{HA}\} =$
35 $k_{HA}/[k_{HA}]$, which are the reduced catalytic coefficients of reactions whose rates depend
36 on the concentrations of acid HA or of its conjugate base A^-, $\{K_{HA}\} = K_{HA}/[K_{HA}]$ is the
37 reduced acid dissociation constant of HA, p is the number of equivalent acidic protons
38 in HA, and q is the number of equivalent basic sites in A^-. The chosen values of p and
39 q should always be specified. (The charge designations of HA and A^- are only
40 illustrative.).

Note 1: The equations are often written without reduced variables, whereupon the slope α or β, obtained from a graph or least-squares analysis, is correct because it is the derivative of a logarithmic quantity, of dimension 1.

Note 2: The Brønsted relation is often termed the Brønsted catalysis law. Although justifiable on historical grounds, use of 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).

Note 3: The term pseudo-Brønsted relation is sometimes used for reactions that involve *nucleophilic catalysis* instead of acid-base catalysis. Various types of Brønsted parameters have been proposed such as β_{nuc} or β_{lg} for nucleophile or leaving group, respectively.

See also *linear free-energy relation* (*linear Gibbs energy relation*).

rev[3]

Bunnett-Olsen equations

Relations between $lg([SH^+]/[S]) + H_o$ and $H_o + lg\{[H^+]\}$ for base S in aqueous acid solutions, 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. and where ϕ is an empirical parameter that is determined by the slope of the linear correlation of $lg([SH^+]/[S]) - lg\{[H^+]\}$ vs. $H_o + lg\{[H^+]\}$.

$$lg([SH^+]/[S]) - lg\{[H^+]\} = (\phi - 1)(H_o + lg\{[H^+]\}) + pK_{SH+}$$

$$lg([SH^+]/[S]) + H_o = \phi (H_o + lg\{[H^+]\}) + pK_{SH+}$$

Arguments in the lg functions should be of dimension 1. Thus, concentrations should be divided by the respective unit (unless they are eliminated as in the ratio of two concentrations), i.e., the reduced quantity should be used, indicated by curly brackets.

Note 1: These equations avoid using (or defining) an acidity function for each family of bases, including those for which such a definition is not possible. In many cases, ϕ (or $\phi - 1$) values for base families defining an acidity function are very similar. Broadly, the value of ϕ is related to the degree of solvation of SH$^+$.

Note 2: These equations are obsolete, and the *Cox-Yates equation*, with the equivalent parameter m^* (= $1 - \phi$), is now preferred.
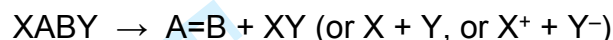
See [21,90].

See also *Cox-Yates equation*.

rev[3]

β, β_{nuc}, β_{lg}

1 Parameter in a *Brønsted relation* expressing the sensitivity of the rate of deprotonation

2 to *basicity*.

3 *Note*: β_{nuc} and β_{lg} are used to correlate *nucleophilic* reactivity and leaving-group

4 ability, respectively.

5

6 **β-elimination**

7 1,2-elimination

8 *Transformation* of the general type

9

10 $\quad$ XABY $\rightarrow$ A=B + XY (or X + Y, or X$^+$ + Y$^-$)

11

12 where the central atoms A and B are commonly, but not necessarily, carbon.
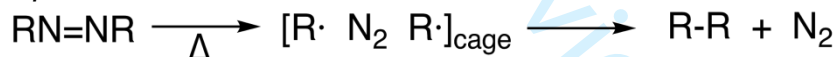
13 $\quad$ See also *elimination*.

14

15 **cage**

16 Aggregate of molecules, generally solvent molecules in the condensed phase, that

17 surrounds fragments formed by thermal or photochemical dissociation.

18 $\quad$ *Note*: Because the cage hinders the separation of the fragments by diffusion, they

19 may preferentially react with one another ("cage effect") although not necessarily to re-
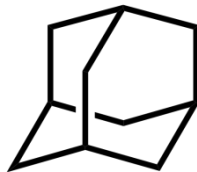
20 form the precursor species.

21 $\quad$ *Example:*

22 $\quad$ RN=NR $\xrightarrow{\Delta}$ [R· N_2 R·]$_{cage}$ $\longrightarrow$ R-R + N_2

23 $\quad$ See also *geminate recombination*.

24 $\quad$ [3]

25

26 **cage compound**

27 Polycyclic compound capable of encapsulating another compound

28 $\quad$ *Example* (adamantane, where the central cavity is large enough to encapsulate He,

29 Ne, or Na$^+$):

30

31

32

33

34

35 $\quad$ *Note:* A compound whose cage is occupied is called an *inclusion complex*.

36 $\quad$ See [91,92].

37 $\quad$ rev[3]
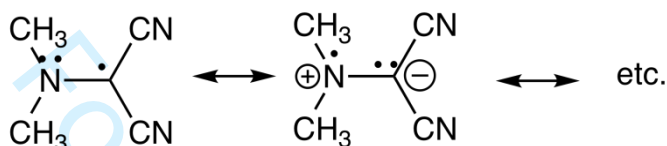
38

39

40 **canonical form**

1 resonance form

2   rev[3]

3

4 captodative effect

5 Combined action of an electron-withdrawing ("captor") substituent and an electron-

6 releasing ("dative") substituent, both attached to a *radical* centre, on the stability of a
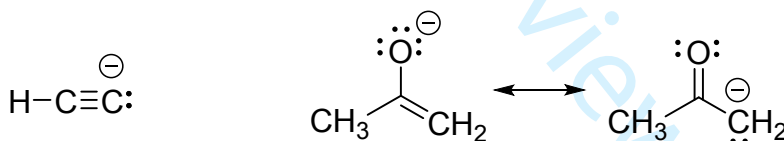
7 carbon-centred radical.

8   *Example*:

9

10

11

12

13

14   See [93,94,95].

15   rev[3]

16

17 carbanion

18 Generic name for an anion containing an even number of electrons and having an

19 unshared pair of electrons on a carbon atom which satisfies the *octet rule* and bears a

20 negative *formal charge* in its *Lewis structure* or in at least one of its *resonance form*s.

21   *Examples:*

22

23

24   See also *radical ion*.

25   See [40,96].

26   rev[3]

27

28 carbene

29 Generic name for the species H_2C: ("methylidene") and substitution derivatives thereof,

30 containing an electrically neutral bivalent carbon atom with two nonbonding electrons.

31   *Note 1*: The nonbonding electrons may have antiparallel spins (singlet state) or

32 parallel spins (*triplet state*).

33   *Note 2*: Use of the alternative name "methylene" as a generic term is not

34 recommended.

35   See [40].

36   See also *diradical*.

37   [3]

38

carbenium ion

Generic name for a *carbocation* whose electronic structure can be adequately described by two-electron-two-centre bonds.

Note 1: The name implies a hydronated carbene or a substitution derivative thereof.

Note 2: The term is a replacement for the previously used term *carbonium ion*, which now specifies a carbocation with penta- or higher-coordinate carbons. The names provide a useful distinction between tricoordinate and pentacoordinate carbons.

Note 3: To avoid ambiguity, the name should be avoided as the root for the nomenclature of *carbocation*s. For example, the term "ethylcarbenium ion" might refer to either $CH_3CH_2^+$ (ethyl cation, ethylium) or $CH_3CH_2CH_2^+$ (propyl cation, propylium).

See [40,97].

rev[3]

carbenoid

Carbene-like *chemical species* but with properties and *reactivity* differing from the free carbene, arising from additional substituents bonded to the carbene carbon.

Example: $R_1R_2C(Cl)M$ (M = metal)

rev[3]

carbocation

Positive ion containing an even number of electrons and with a significant portion of the excess positive charge located on one or more carbon atoms.

Note 1: This is a general term embracing *carbenium ion*s, all types of *carbonium ion*s, vinyl cations, etc.

Note 2: Carbocations may be named by adding the word "cation" to the name of the corresponding *radical* [97,98].

Note 3: Such names do not imply structure (e.g., whether three-coordinated or five-coordinated carbon atoms are present) [98].

See also *bridged carbocation*, *radical ion*.

See [40].

[3]

carbonium ion

(1) Carbocation that contains at least one carbon atom with a *coordination number* of five or greater.

(2) Carbocation whose structure cannot adequately be described by only two-electron two-centre *bond*s.

Example: methanium (CH_5^+).

Note 1: In most of the earlier literature this term was used for all types of carbocations, including those that are now defined as a (tricoordinate) *carbenium ion*.

Note 2: To avoid ambiguity, the term should be avoided as the root for the nomenclature of *carbocation*s. For example, the name "ethylcarbonium ion" might refer to either $CH_3CH_2^+$ (ethyl cation) or $CH_3CH_2CH_2^+$ (propyl cation).

See [98,99].

rev[3]

carbyne

methylidyne

Generic name for the species HC·: and substitution derivatives thereof, such as EtOCO–C·: (2-ethoxy-2-oxoethylidyne), containing an electrically neutral univalent carbon atom with three non-bonding electrons.

Note: Use of the alternative name "methylidyne" as a generic term is not recommended.

[3]

Catalán solvent parameters

Quantitative measure of solvent polarity, based on the solvent's hydrogen-bond-donor ability, hydrogen-bond-acceptor ability, polarizability, and dipolarity.

See [100,101].

See also *solvent parameter*.

catalyst

Substance that increases the rate of a *chemical reaction* (owing to a change of mechanism to one having a lower Gibbs energy of activation) without changing the overall standard Gibbs energy change (or position of equilibrium).

Note 1: The catalyst is both a reactant and product of the reaction, so that there is no net change in the amount of that substance.

Note 2: 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.

Note 3: The requirement that there be no net change in the amount of catalyst is sometimes relaxed, as in the base catalysis of the bromination of ketones, where base is consumed, but this is properly called *pseudo-catalysis*.

Note 4: *Catalysis* can be classified as homogeneous, in which only one phase is involved, and heterogeneous, in which the reaction occurs at or near an interface between phases.

Note 5: Catalysis brought about by one of the products of a reaction is called autocatalysis.

Note 6: The terms catalyst and catalysis should not be used when the added substance reduces the rate of reaction (see *inhibition*).

1
2
3   1   *Note 7*: The above definition is adequate for isothermal-isobaric reactions, but under
4   2   other experimental conditions the state function that is lowered by the catalyst is not the
5   3   Gibbs activation energy but the quantity corresponding to those conditions (e.g., the
6   4   Helmholtz energy under isothermal-isochoric conditions).
7
8   5   See [13].
9
10   6   See also *autocatalytic reaction*, *bifunctional catalysis*, *catalytic coefficient*, *electron-*
11   7   *transfer catalysis*, *general acid catalysis*, *general base catalysis*, *intramolecular*
12   8   *catalysis*, *micellar catalysis*, *Michaelis-Menten kinetics*, *phase-transfer catalysis*,
13   9   *pseudo-catalysis*, *rate of reaction*, *specific catalysis*.
14
15   10   rev[3]
16
17   11
18   12   **catalytic antibody (abzyme)**
19   13   monoclonal antibody with enzymatic activity
20
21   14   *Note 1*: A catalytic antibody acts by binding its antigen and catalyzing a chemical
22   15   reaction that converts the antigen into desired products. Despite the existence of natural
23   16   catalytic antibodies, most of them were specifically designed to catalyze desired
24   17   chemical reactions.
25
26   18   *Note 2:* Catalytic antibodies are produced through immunization against a transition-
27   19   state analogue for the reaction of interest. The resulting antibodies bind strongly and
28   20   specifically the transition-state analogue, so that they become *catalyst*s for the desired
29   21   reaction.
30
31   22   *Note 3*: The concept of catalytic antibodies and the strategy for obtaining them were
32   23   advanced by W. P. Jencks [102]. The first catalytic antibodies were finally produced in
33   24   1986 [103,104].
34
35   25

36   26   **catalytic coefficient**
37   27   If the *rate of reaction* v is expressible in the form
38
39   28

40   29 $v = (k_0 + \Sigma k_i[C_i]^{ni})\ [A]^a\ [B]^b...$
41
42   30

43   31   where A, B, ... are reactants and C_i represents one of a set of catalysts, then the
44   32   proportionality factor k_i is the catalytic coefficient of the particular *catalyst* C_i.
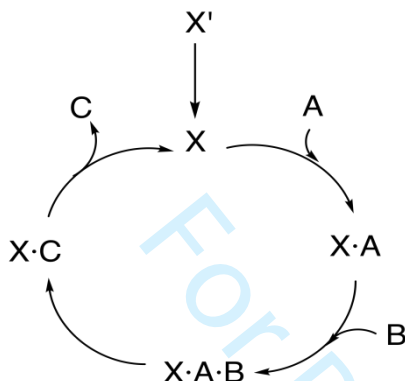45
46   33   *Note*: Normally the partial *order of reaction* (n_i) with respect to a catalyst will be unity,
47   34   so that k_i is an $(a + b+...+1)^{th}$-order *rate coefficient*.
48
49   35   [3]
50
51   36

52   37

53   38

54   39   **catalytic cycle**
55
56
57
58
59
60

Sequence of reaction steps in the form of a loop. One step is binding of a reactant to the active *catalyst* (sometimes formed from a precatalyst), and another step is the release of product and regeneration of catalyst.

Example: A + B → C, catalyzed by X formed from precatalyst X'.
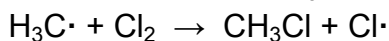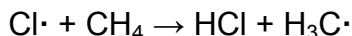

cation/π interaction

Noncovalent attractive force between a positive ion (metal cation, protonated *Brønsted base*, etc.) and a π electron system.
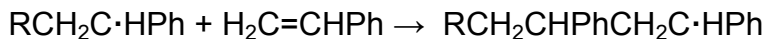
See [105].

chain reaction

Reaction in which one or more reactive *reactive intermediates* (frequently *radicals*) are continuously regenerated through a repetitive cycle of elementary steps ("propagation steps").

Example: Chlorination of methane by a radical *mechanism*, where Cl· is continually regenerated in the chain-propagation steps:

$$Cl· + CH_4 \rightarrow HCl + H_3C·$$

$$H_3C· + Cl_2 \rightarrow CH_3Cl + Cl·$$

Note: In chain polymerization reactions, *reactive intermediates* of the same types, generated in successive steps or cycles of steps, differ in molecular mass, as in

$$RCH_2C·HPh + H_2C=CHPh \rightarrow RCH_2CHPhCH_2C·HPh$$
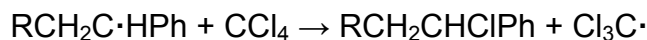
See [106].

See also *chain transfer*, *initiation*, *termination*.

[3]

chain transfer

Chemical reaction during a chain polymerization in which the active centre is transferred from the growing macromolecule to another molecule or to another site on the same molecule, often by abstraction of an atom by the *radical* end of the growing macromolecule.

1   *Note 1*: The growth of the polymer chain is thereby terminated but a new radical,
2 capable of chain propagation and polymerization, is simultaneously created. For the
3 example of alkene polymerization cited for a *chain reaction*, the reaction

4       $RCH_2C \cdot HPh + CCl_4 \rightarrow RCH_2CHClPh + Cl_3C \cdot$

5 represents a chain transfer, the radical $Cl_3C \cdot$ inducing further polymerization:
6   *Note 2*: Chain transfer also occurs in other chain reactions, such as cationic or
7 anionic polymerization, in which case the abstraction is by the reactive cationic or
8 anionic end of the growing chain.
9   See [106].
10   See also *telomerization*.
11   [3]
12

13 **charge density**
14   See *electron density*.
15   See [12].
16   [3]
17

18 **charge-transfer (CT) complex**
19 Ground-state *adduct* that exhibits an electronic absorption corresponding to light-
20 induced transfer of electronic charge from one region of the adduct to another.
21   See [9].
22   rev[3]
23

24 **chelation**
25 Formation or presence of *bond*s (or other attractive interactions) between a single
26 central atom (or ion) and two or more separate *binding site*s within the same *ligand*.
27   *Note 1*: A *molecular entity* in which there is chelation (and the corresponding
28 *chemical species*) is called a chelate, while the species that binds to the central atom
29 is called a chelant.
30   *Note 2*: The terms *bidentate*, tridentate, ... *multident*ate are used to indicate the
31 number of potential binding sites of the ligand, at least two of which must be used by
32 the ligand in forming a chelate. For example, the bidentate ethylenediamine forms a
33 chelate with Cu^{+2} in which both nitrogen atoms of ethylenediamine are bonded to
34 copper.
35   *Note 3*: The use of the term is often restricted to metallic central atoms or ions.
36   *Note 4*: The phrase "separate binding sites" is intended to exclude cases such as
37 $[PtCl_3(CH_2=CH_2)]^-$, ferrocene, and (benzene)tricarbonylchromium, in which ethene, the
38 cyclopentadienyl group, and benzene, respectively, are considered to present single
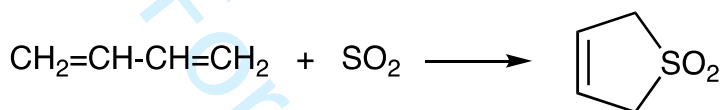39 binding sites to the respective metal atom.
40   See also *ambident*, *cryptand*.

1   See also [29].

2   [3]

3

4 **cheletropic reaction**

5 *Cycloaddition* across the terminal atoms of a π system with formation of two new σ

6 bonds to a single atom of a monocentric reagent. There is formal loss of one π bond in

7 the substrate and an increase in *coordination number* of the relevant atom of the

8 reagent.

9   *Example: addition* of sulfur dioxide to butadiene:

$$CH_2=CH-CH=CH_2 \;+\; SO_2 \;\longrightarrow\; \overset{\big|\big|}{\bigcirc}SO_2$$

10

11   *Note*: The reverse of this type of reaction is designated "cheletropic elimination".

12   See [107].

13   [3]

14

15 **chelotropic reaction**

16 Alternative (and etymologically more correct) name for *cheletropic reaction*.

17   See [51].

18   [3]

19

20 **chemical flux, ϕ**

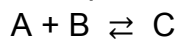21 Unidirectional *rate of reaction*, applicable to the progress of component reaction steps

22 in a complex system or to the progress of reactions in a system at dynamic equilibrium

23 (in which there are no observable concentration changes with time), excluding the

24 reverse reaction and other reaction steps.

25   *Note 1*: Chemical flux is a derivative with respect to time, and has the dimensions of

26 amount of substance per volume transformed per time.

27   For example, for the mechanism

28         $A + B \rightleftarrows C$

29         $C + D \rightarrow E$

30   ϕ_1 is the chemical flux due to forward reaction step 1, or the rate of formation of C or

31 the rate of loss of A or B due to that step, and similarly for ϕ_{-1} and ϕ_2.

32   *Note 2*: The sum of all the chemical fluxes leading to C is designated the "total

33 chemical flux into C" (symbol $\Sigma\phi_C$), and the sum of all the chemical fluxes leading to

34 destruction of C is designated the "total chemical flux out of C" (symbol $\Sigma\phi_{-C}$), and

35 similarly for A and B. It then follows for this example that $\Sigma\phi_C = \phi_1$ and $\Sigma\phi_{-C} = \phi_{-1} + \phi_2$,

36   *Note 3*: The net rate of appearance of C is then given by

1
2
3   1
4
5   2 $d[C]/dt = \Sigma\phi_C - \Sigma\phi_{-C}$
6
7   3
8
9   4   *Note 4*: In this system ϕ_1 (or $\Sigma\phi_C$) can be regarded as the hypothetical rate of
10   5   formation of C due to the single (unidirectional) reaction 1 proceeding in the assumed
11   6   absence of all other reactions, and $\Sigma\phi_{-C}$ can be regarded as the hypothetical rate of
12   7   destruction of C due to the two (unidirectional) reactions −1 and 2.
13   8   *Note 5*: Even when there is no net reaction, chemical flux can often be measured by
14   9   NMR methods.
15   10   See [1].
16   11   See also *order of reaction*, *rate-limiting step*, *steady state*.
17   12   rev[3]
18   13
19
20   14   **chemical reaction**
21   15   Process that results in the interconversion of *chemical species*.
22   16   *Note 1*: This definition includes experimentally observable interconversions of
23   17   *conformer*s and *degenerate rearrangement*s.
24   18   *Note 2*: Chemical reactions may be *elementary reaction*s or *stepwise reaction*s.
25   19   *Note 3*: Detectable chemical reactions normally involve sets of *molecular entities*, as
26   20   indicated by this definition, but it is often conceptually convenient to use the term also
27   21   for changes involving single molecular entities (i.e., "microscopic chemical events"),
28   22   whose reactions can now be observed experimentally.
29   23   See also *identity reaction*.
30   24   rev[3]
31   25
32
33   26   **chemical relaxation**
34   27   Passage of a perturbed system toward or into chemical equilibrium.
35   28   *Note 1*: A *chemical reaction* at equilibrium can be disturbed from equilibrium by a
36   29   sudden change of some external parameter such as temperature, pressure, or electric-
37   30   field strength.
38   31   *Note 2*: In many cases, and in particular when the displacement from equilibrium is
39   32   slight, the progress of the system towards equilibrium can be expressed as a first-order
40   33   process
41   34

        35       $$c(t) - (c_{eq})_2 = [(c_{eq})_1 - (c_{eq})_2] \exp(-t/\tau)$$

        36

        37   where $(c_{eq})_1$ and $(c_{eq})_2$ are the equilibrium amount concentrations of one of the chemical
        38   species before and after the change in the external parameter, and $c(t)$ is its amount
        39   concentration at time t. The time parameter τ, called relaxation time, is related to the

1 *rate coefficients* of the chemical reaction involved. Such measurements are commonly
2 used to follow the kinetics of very fast reactions.
3 *Note 3: Relaxation,* or the passage toward equilibrium, is more general than chemical
4 relaxation, and includes relaxation of nuclear spins.
5 See [108,109].
6 See *relaxation*.
7 rev[3]

8

chemical shift (NMR)
9
10 δ
11 Variation of the resonance frequency of a nucleus in nuclear magnetic resonance
12 (NMR) spectrometry as a consequence of its environment.
13 *Note 1*: The chemical shift of a nucleus X, δ_X, expressed as its frequency, ν_X, relative
14 to that of a standard, ν_{ref}, and defined as

15

16 $$\delta_X = (\nu_X - \nu_{ref})/\nu_{ref}$$

17

18 For ^{1}H and ^{13}C NMR the reference signal is usually that of tetramethylsilane (SiMe$_4$).
19 *Note 2:* Chemical shift is usually reported in "parts per million" or ppm, where the
20 numerator has unit Hz, and the denominator has unit MHz, like the spectrometer's
21 operating frequency.
22 *Note 3*: For historical reasons that predate Fourier-transform NMR, if a resonance
23 signal occurs at higher frequency than a reference signal, it is said to be downfield, and
24 if resonance occurs at lower frequency, the signal is upfield. Resonances downfield
25 from SiMe$_4$ have positive δ-values, and resonances upfield from SiMe$_4$ have negative
26 δ-values. These terms have been superseded, and deshielded and shielded are
27 preferred for downfield and upfield, respectively.
28 See [110].
29 See also *shielding*.
30 rev[3]

31

chemical species
32
33 Ensemble of chemically identical *molecular entities* that can explore the same set of
34 molecular energy levels on the time scale of an experiment. The term is applied equally
35 to a set of chemically identical atomic or molecular structural units in a solid array.
36 *Note 1*: For example, conformational *isomer*s may be interconverted sufficiently
37 slowly to be detectable by separate NMR spectra and hence to be considered to be
38 separate chemical species on a time scale governed by the radiofrequency of the
39 spectrometer used. On the other hand, in a slow chemical reaction the same mixture of
40 conformers may behave as a single chemical species, i.e., there is virtually complete

1 equilibrium population of the total set of molecular energy levels belonging to the two
2 conformers.
3   *Note 2*: Except where the context requires otherwise, the term is taken to refer to a
4 set of molecular entities containing isotopes in their natural abundance.
5   *Note 3*: The definition given is intended to embrace not only cases such as graphite
6 and sodium chloride but also a surface oxide, where the basic structural units may not
7 be capable of isolated existence.
8   *Note 4*: In common chemical usage, and in this Glossary, generic and specific
9 chemical names (such as *radical* or hydroxide ion) or chemical formulae refer either to
10 a chemical species or to a *molecular entity*.
11   [3]
12

chemically induced dynamic nuclear polarization (CIDNP)
14 Non-Boltzmann nuclear spin-state distribution produced in thermal or photochemical
15 reactions, usually from *colligation* and diffusion or *disproportionation* of *radical pair*s,
16 and detected by NMR spectroscopy as enhanced absorption or emission signals.
17   See [111,112].
18   rev[3]
19

chemiexcitation
21 Generation, by a chemical reaction, of an electronically excited molecular entity from
22 reactants in their ground electronic states.
23   See [9].
24   [3]
25

chemoselectivity
27 Feature of a chemical reagent that reacts preferentially with one of two or more different
28 functional groups.
29   *Note 1*: A reagent has a high chemoselectivity if reaction occurs with only a limited
30 number of different functional groups. For example, sodium tetrahydridoborate ($NaBH_4$)
31 is a more chemoselective reducing agent than is lithium tetrahydridoaluminate ($LiAlH_4$).
32 The concept has not been defined in more quantitative terms.
33   *Note 2*: The term is also applied to reacting molecules or intermediates that exhibit
34 selectivity towards chemically different reagents.
35   *Note 3*: Usage of the term chemospecificity for 100 % chemoselectivity is
36 discouraged.
37   See [113].
38   See also *regioselectivity*, *stereoselectivity*, *stereospecificity*.
39   [3]
40

chemospecificity

obsolete

  See *chemoselectivity*.

  [3]

chirality

Property of a structure that is not superimposable on its mirror image.

  See [11,46].

  [3]

chirality centre

chiral centre (superseded)

Atom with attached groups such that the arrangement is not superimposable on its mirror image.

  Note: Often this is a tetrahedral atom with four different groups attached, such as CH_3BrClF, or C2 of $CH_3CHBrCH_2CH_3$, or the sulfur of $CH_3S(=O)Ph$, where the lone pair is considered as a fourth group.

  See [11].

  See also *stereogenic centre*.

  [3]

chiral feature

Structural characteristic rendering a molecule *chiral*.

  Examples: four different substituents on a carbon atom (*chirality centre)*, conformational helix, chiral axis (as in allenes XCH=C=CHX).

chiral recognition

Attraction between molecules through noncovalent interactions that exhibit complementarity only between partners with specific chirality.

  See also *molecular recognition.*

chromophore

Part (atom or group of atoms) of a *molecular entity* in which the electronic transition responsible for a given spectral band is approximately localized.

  Note 1: The term arose originally to refer to the groupings that are responsible for a dye's colour.

  Note 2: The electronic transition can often be assigned as involving n, π, π^*, σ, and/or σ^* orbitals whose energy difference falls within the range of the visible or UV spectrum.

  Note 3: The term has been extended to vibrational transitions in the infrared.

  See [9,114,115].

1
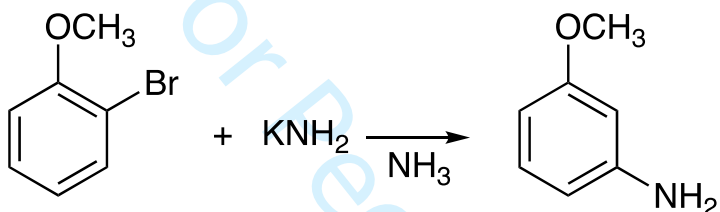
2

1   [3]

2

3   **CIDNP**

4   Acronym for *chemically induced dynamic nuclear polarization*.

5   [3]

6

7   **cine-substitution**

8   *Substitution* reaction (generally *aromatic*) in which the entering group takes up a

9   position adjacent to that occupied by the *leaving group*.

10   *Example*:

11

12

13

14   See also *tele-substitution*.

15   [3]

16

17   **classical carbocation**

18   *Carbocation* whose electronic structure can be adequately described by two-electron-

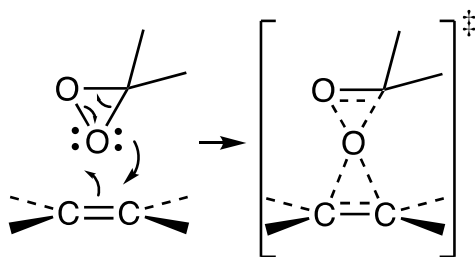19   two-centre bonds, i.e., synonymous with *carbenium ion*.

20

21   **clathrate**

22   See *host*, *inclusion compound*.

23   [3]

24

25   **coarctate**

26   *Feature of a *concerted* *transformation* in which the primary changes in bonding occur

27   within a cyclic array of atoms but in which two nonbonding *atomic orbital*s on an atom

28   interchange roles with two bonding orbitals.

29   *Example:* epoxidation with dimethydioxirane

30

1

2   *Note:* Because the atomic orbitals that interchange roles are orthogonal, such a
3   reaction does not proceed through a fully *conjugated transition state* and is thus not a
4   pericyclic reaction. It is therefore not governed by the rules that express *orbital*
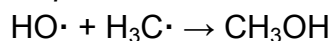5   *symmetry* restrictions applicable to pericyclic reactions.
6   See [116].
7   See also *pseudopericyclic*.

8

9   **colligation**
10 Formation of a covalent bond by combination or recombination of two *radical*s.
11   *Note*: This is the reverse of *unimolecular homolysis*.
12   *Example*:
13          $HO\cdot + H_3C\cdot \rightarrow CH_3OH$
14   [3]

15

16 **collision complex**
17 Ensemble formed by two reaction partners, where the distance between them is equal
18 to the sum of the van der Waals radii of neighbouring atoms.
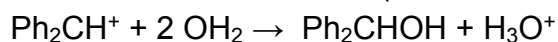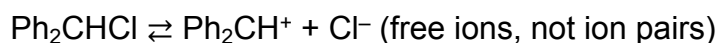19   See also *encounter complex*.
20   [3]

21

22 **common-ion effect (on rates)**
23 Reduction in the *rate* of certain reactions of a *substrate* RX in solution [by a path that
24 involves a *pre-equilibrium* with formation of R^+ (or R^-) ions as reaction intermediates]
25 caused by the addition to the reaction mixture of an electrolyte solute containing the
26 "common ion" X^- (or X^+).
27   *Example*: the rate of solvolysis of chlorodiphenylmethane in acetone-water is
28 reduced by the addition of salts of the common ion Cl^-, which causes a decrease in the
29 *steady-state* concentration of the diphenylmethyl cation:

30

31          $Ph_2CHCl \rightleftarrows Ph_2CH^+ + Cl^-$ (free ions, not ion pairs)
32          $Ph_2CH^+ + 2\ OH_2 \rightarrow\ Ph_2CHOH + H_3O^+$

33

1   *Note*: This retardation due to a common ion should be distinguished from the
2   acceleration due to a salt effect of all ions.
3   rev[3]
4

5   **compensation effect**
6   Observation that a plot of $T\Delta_r S$ vs. $\Delta_r H$ (frequently $T\Delta^{\ddagger}S$ vs. $\Delta^{\ddagger}H$) for a series of reactions
7   with a range of different substituents (or other unique variable such as solvent or
8   dissolved salt), are straight lines of approximately unit slope, so that, e.g., the terms
9    $\Delta^{\ddagger}H$ and $T\Delta^{\ddagger}S$ partially compensate, and $\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S$ shows less variation than
10   $\Delta^{\ddagger}H$ or $T\Delta^{\ddagger}S$ separately.
11   *Note*: Frequently such $\Delta^{\ddagger}S$ vs. $\Delta^{\ddagger}H$ correlations are statistical artifacts, arising if
12   entropy and enthalpy are extracted from the variation of an equilibrium constant or a
13   *rate constant* with temperature, so that the slope and intercept of the van't Hoff plots
14   are correlated. The problem is avoided if the equilibrium constant and the enthalpy are
15   measured independently, for example by spectrophotometry and calorimetry,
16   respectively.
17   See [117,118,119,120].
18   See also *isoequilibrium relationship, isokinetic relationship*.
19   rev[3]
20

21   **complex**
22   *Molecular entity* formed by loose *association* involving two or more component
23   molecular entities (ionic or uncharged), or the corresponding *chemical species*. The
24   attraction between the components is often due to hydrogen-bonding or van der Waals
25   attraction and is normally weaker than a covalent *bond*.
26   *Note 1*: The term has also been used with a variety of meanings in different contexts:
27   it is therefore best avoided when a more explicit alternative is applicable, such as *adduct*
28   when the association is a consequence of bond formation.
29   *Note 2*: In inorganic chemistry the term "coordination entity" is recommended instead
30   of "complex" [29,121].
31   See also *activated complex*, *adduct*, *charge transfer complex*, *electron-donor-*
32   *acceptor complex*, *encounter complex*, *inclusion complex*, *σ-adduct*, *π-adduct*,
33   *transition state*.
34   [3]
35

36   **composite reaction**
37   *Chemical reaction* for which the expression for the rate of disappearance of a reactant
38   (or rate of appearance of a product) involves *rate constant*s of more than a single
39   *elementary reaction*.

1 Examples: "opposing reactions" (where rate constants of two opposed chemical
2 reactions are involved), "parallel reactions" (for which the rate of disappearance of any
3 reactant is governed by the rate constants relating to several simultaneous reactions
4 that form different products from a single set of reactants), and *stepwise reaction*s.
5 [3]
6

7 **comproportionation**
8 Any *chemical reaction* of the type A' + A" → 2 A
9 *Example*:
10 $Pb + PbO_2 + 2 H_2SO_4 \rightarrow 2 PbSO_4 + 2 H_2O$ (in a lead battery)
11
12 *Note:* Other stoichiometries are possible, depending on the *oxidation number*s of the
13 species.
14 Reverse of *disproportionation*. The term "symproportionation" is also used.
15 See [122].
16 rev[3]
17

18 **concerted**
19 Feature of a process in which two or more primitive changes occur within the same
20 *elementary reaction*. Such changes will normally be "energetically coupled".
21 *Note 1*: The term "energetically coupled" means that the simultaneous progress of
22 the primitive changes involves a *transition state* of lower energy than that for their
23 successive occurrence.
24 *Note 2*: In a concerted process the primitive changes may be *synchronous* or
25 asynchronous.
26 See also *bifunctional catalysis*, *potential-energy surface*.
27 [3]
28

29 **condensation**
30 Reaction (usually stepwise) in which two or more reactants (or remote reactive sites
31 within the same *molecular entity*) yield a product with accompanying formation of water
32 or some other small molecule, e.g., ammonia, ethanol, acetic acid, hydrogen sulfide.
33 *Note 1*: The *mechanism* of many condensation reactions has been shown to
34 comprise consecutive *addition* and *elimination* reactions, as in the base-catalysed
35 formation of (*E*)-but-2-enal (crotonaldehyde) from acetaldehyde, via dehydration of 3-
36 hydroxybutanal (aldol). The overall reaction in this example is known as the aldol
37 condensation.
38 *Note 2*: The term is sometimes also applied to cases where the formation of water
39 or other simple molecule does not occur, as in "benzoin condensation".
40 [3]

1

2 **condensed formula**

3 Linear representation of the structure of a *molecular entity* in which bonds are omitted.

4   *Example*: methyl 3-methylbutyl ether (isoamyl methyl ether,

5 $(CH_3)_2CHCH_2CH_2OCH_3$, sometimes condensed further to $(CH_3)_2CH[CH_2]_2OCH_3$)

6   *Note*: This term is sometimes also called a *line formula*, because it can be written on

7 a single line, but the line formula explicitly shows all bonds.

8

9 **configuration (electronic)**

10 Distribution of the electrons of an atom or a *molecular entity* over a set of one-electron

11 wavefunctions called *orbital*s, according to the Pauli principle.

12   *Note*: From one configuration several states with different multiplicities may result.

13 For example, the ground electronic configuration of the oxygen molecule (O_2) is

14       $1\sigma_g^2, 1\sigma_u^2, 2\sigma_g^2, 2\sigma_u^2, 1\pi_u^4, 3\sigma_g^2, 1\pi_g^2$

15 resulting in

16       $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$ multiplets

17   See [8,9].

18   [3]

19

20 **configuration (molecular)**

21 Arrangement in space of the atoms of a *molecular entity* that distinguishes it from any

22 other molecular entity having the same molecular formula and *connectivity* and that is

23 not due to conformational differences (rotation about single bonds).

24   See [11].

25   [3]

26

27 **conformations**

28 Different spatial arrangements of a molecular entity that can be interconverted by

29 rotation about one or more formally single bonds.

30   *Note 1*: Different conformations are often not considered to be stereoisomeric,

31 because interconversion is rapid.

32   *Note 2*: Different or equivalent spatial arrangements of *ligands* about a central atom,

33 such as those interconverted by pyramidal inversion (of amines) or Berry

34 pseudorotation (as of PF_5) and other "polytopal rearrangements", are sometimes

35 considered conformations, but they are properly described as *configuration*s.

36   See [11].

37   rev[3]

38

39 **conformational isomers**

40 conformers

conformer

Conformation of a *molecular entity* that corresponds to a minimum on the potential-energy surface of that molecular entity.

Note: The distinction between conformers and isomers is the height of the barrier for interconversion. Isomers are stable on macroscopic timescales because the barrier for interconversion is high, whereas a conformer cannot persist on a macroscopic timescale because the interconversion between conformations is achieved rapidly.

See [11].

conjugate acid

Brønsted acid BH^+ formed on protonation (hydronation) of the base B.

Note 1: B is called the conjugate base of the acid BH^+.

Note 2: 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, and so do NH_4^+ and its conjugate base NH_3.
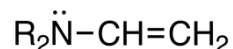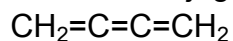
rev[3]

conjugated system, conjugation

Molecular entity whose structure may be represented as a system of alternating multiple and single (or σ) bonds: e.g.,

$$CH_2=CH–CH=CH_2 \text{ or } CH_2=CH–C\equiv N$$

Note: In such systems, conjugation is the interaction of one p-orbital with another p-orbital (or d-orbital) across an intervening σ bond, including the analogous interaction involving a p-orbital containing an unshared electron pair, e.g.,

$$R_2\ddot{N}-CH=CH_2$$

or the interaction across a double bond whose π system does not interact with the p orbitals of the conjugated system, as in

$$CH_2=C=C=CH_2$$

See also *cross-conjugation*, *delocalization*, *resonance, through-conjugation*.

[3]

connectivity

Description of which atoms are bonded to which other atoms.

Note: Connectivity is often displayed in a *line formula* or other structure showing which atoms are bonded to which other atoms, but with minimal or no indication of *bond* multiplicity.

Example: The connectivity of propyne is specified by CH_3CCH.

1
2
3   1   rev[3]
4
5   2
6   3   **conrotatory**
7
8   4   Stereochemical feature of an *electrocyclic reaction* in which the substituents at the
9   5   interacting termini of the conjugated system rotate in the same sense (both clockwise
10   6   or both counterclockwise).
11   7   See also *disrotatory*.
12
13   8   rev[3]
14
15   9
16   10   **conservation of orbital symmetry**
17
18   11   An approach to understanding *pericyclic reaction*s that focuses on a symmetry
19   12   element (e.g., a reflection plane) that is retained along a reaction pathway. If each of
20   13   the singly or doubly occupied orbitals of the reactant(s) is of the same symmetry as a
21
22   14   similarly occupied orbital of the product(s), that pathway is "allowed" by orbital
23   15   symmetry conservation. If instead a singly or doubly occupied orbital of the reactant(s)
24   16   is of the same symmetry as an unoccupied orbital of the product(s), and an unoccupied
25
26   17   orbital of the reactant(s) is of the same symmetry as a singly or doubly occupied orbital
27   18   of the product(s), that pathway is "forbidden" by orbital symmetry conservation.
28   19   *Note 1*: This principle permits the qualitative construction of correlation diagrams to
29
30   20   show how molecular orbitals transform and how their energies change during chemical
31   21   reactions.
32
33   22   *Note 2*: Considerations of orbital symmetry are frequently grossly simplified in that,
34   23   for example, the π and π^* orbitals of a carbonyl group in an asymmetric molecule are
35   24   treated as having the same topology (pattern of local nodal planes) as those of a
36
37   25   symmetric molecule (e.g., $CH_2=O$), despite the absence of formal symmetry elements.
38   26   See [107,123].
39   27   See also *orbital symmetry*.
40
41   28
42   29   **constitutional isomers**
43   30   Species (or *molecular entities*) with the same atomic composition (*molecular formula*)
44
45   31   but with different *connectivity*.
46   32   *Note:* The term structural isomers is discouraged, because all isomers differ in
47   33   structure and because isomers may be constitutional, configurational, or
48
49   34   conformational.
50   35   See [11].
51   36
52   37   **contributing structure**
53
54   38   resonance form
55   39   rev[3]
56   40
57
58
59
60

coordinate covalent bond

dative bond

coordination

Formation of a covalent *bond*, the two shared electrons of which come from only one of the two partners linked by the bond, as in the reaction of a *Lewis acid* and a *Lewis base* to form a *Lewis adduct*; alternatively, the bonding formed in this way.

Note: In the former sense, it is the reverse of *unimolecular heterolysis*.

See also *dative bond*, *π-adduct*.

rev[3]

coordination number

Number of other atoms directly linked to a specified atom in a *chemical species* regardless of the number of electrons in the bonds linking them [29, Rule IR-10.2.5]. For example, the coordination number of carbon in methane or of phosphorus in triphenylphosphane oxide (triphenylphosphine oxide) is four whereas the coordination number of phosphor is five in phosphorus pentafluoride.

Note: The term is used in a different sense in the crystallographic description of ionic crystals.

rev[3]

coronate

See *crown ether*.

rev[3]

correlation analysis

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

See [124,125,126,127,128].

See also *linear free-energy relation*, *quantitative structure-activity relationship (QSAR)*.

[3]

coupling constant (spin-spin coupling constant)

J

(Unit: Hz)

1 Quantitative measure of nuclear spin-spin coupling in nuclear magnetic resonance
2 spectroscopy.
3   *Note*: Spin-spin coupling constants have been correlated with atomic hybridization
4 and with molecular conformations.
5   See [129,130,131].
6   rev[3]

7

8 **covalent bond**
9 Stabilizing interaction associated with the sharing of electron pairs between two atomic
10 centres of a molecular entity, leading to a characteristic internuclear distance.
11   See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.
12   See [8].
13   rev[3]

14

15 **Cox–Yates equation**
16 Generalization of the *Bunnett-Olsen equation* of the form

17

18      $\lg([SH^+])/[S]) - \lg\{[H^+]\} = m^*X + pK_{SH^+}$

19

20 where $[H^+]$ is the amount concentration of acid, X is the activity-coefficient ratio
21 $\lg(\{\gamma_s\}\{\gamma_{H^+}\}/\{\gamma_{SH^+}\})$ for an arbitrary reference base, pK_{SH^+} is the thermodynamic
22 dissociation constant of SH^+, and m^* is an empirical parameter derived from linear
23 regression of the left-hand side vs. X. Arguments in the lg functions should be unitless.
24 Thus, the reduced quantities should be used: $\{[H^+]\}$ is $[H^+]$/units.
25   *Note*: The function X is called excess acidity because it gives a measure of the
26 difference between the acidity of a solution and that of an ideal solution of the same
27 concentration. In practice $X = - (H_o + \lg\{[H^+]\})$ and $m^* = 1 - \phi$, where H_o is the Hammett
28 *acidity function* and ϕ is the slope in the Bunnett-Olsen equation.
29   See [132,133,134].
30   See *Bunnett-Olsen equation*.
31   rev[3]

32

33 **critical micellisation concentration *(cmc)***
34 critical micelle concentration
35 Relatively small range of concentrations separating the limit below which virtually no
36 *micelle*s are detected and the limit above which virtually all additional surfactant
37 molecules form micelles.
38   *Note* 1: Many physical properties of surfactant solutions, such as conductivity or light
39 scattering, show an abrupt change at a particular concentration of the surfactant, which
40 can be taken as the *cmc*.

Note 2: As values obtained using different properties are not quite identical, the method by which the *cmc* is determined should be clearly stated.

See [135].

See also *inverted micelle*.

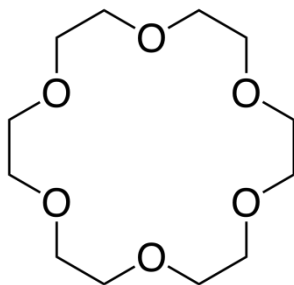rev[3]

cross-conjugation

Phenomenon of three conjugated groups, two pairs of which exhibit conjugation but without *through-conjugation* of all three, as in 2-phenylallyl, benzoate anion, divinyl ether, or *m*-xylylene [$1,3-C_6H_4(CH_2)_2$].

See [64].

rev[3]

crown ether

Molecular entity comprising a monocyclic *ligand* assembly that contains three or more *binding site*s held together by covalent bonds and capable of binding a *guest* in a central (or nearly central) position. The *adduct*s 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 $-CR_2-CR_2O-$ (where R is most commonly H).


"18-crown-6"

See [136,137].

See also *host*.

rev[3]

cryptand

Molecular entity comprising a cyclic or polycyclic assembly of *binding site*s that contains three or more binding sites held together by *covalent bond*s, 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).

Note 1: The *adduct* thus formed is called a "cryptate". The term is usually restricted to bicyclic or oligocyclic molecular entities.
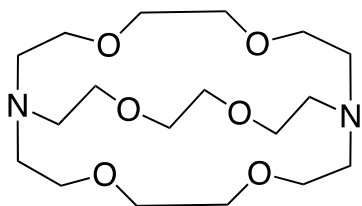
1   *Example*:

2

3   *Note 2*: Corresponding monocyclic *ligand* assemblies (*crown ether*) are sometimes
4   included in this group, if they can be considered to define a cavity in which a guest can
5   hide. The terms "podand" and "spherand" are used for certain specific ligand
6   assemblies. Coplanar cyclic polydentate ligands, such as porphyrins, are not normally
7   regarded as cryptands.
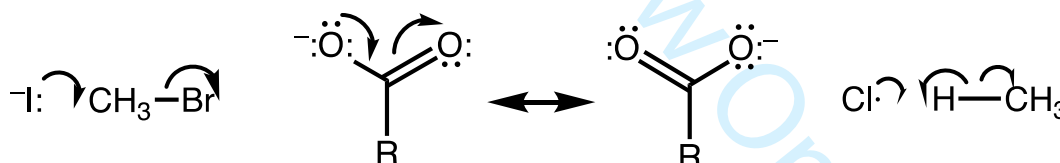8   See [138].
9   See also *host*. See also [139].
10   [3]
11

curly arrows
13   Symbols for depicting the flow of electrons in a chemical reaction or to generate
14   additional *resonance form*s.
15   *Note 1:* The tail of the curly arrow shows where an electron pair originates, and the
16   head of the curly arrow shows where the electron pair goes.
17   *Note 2:* Single-headed curly arrows are used to depict the flow of unpaired electrons.
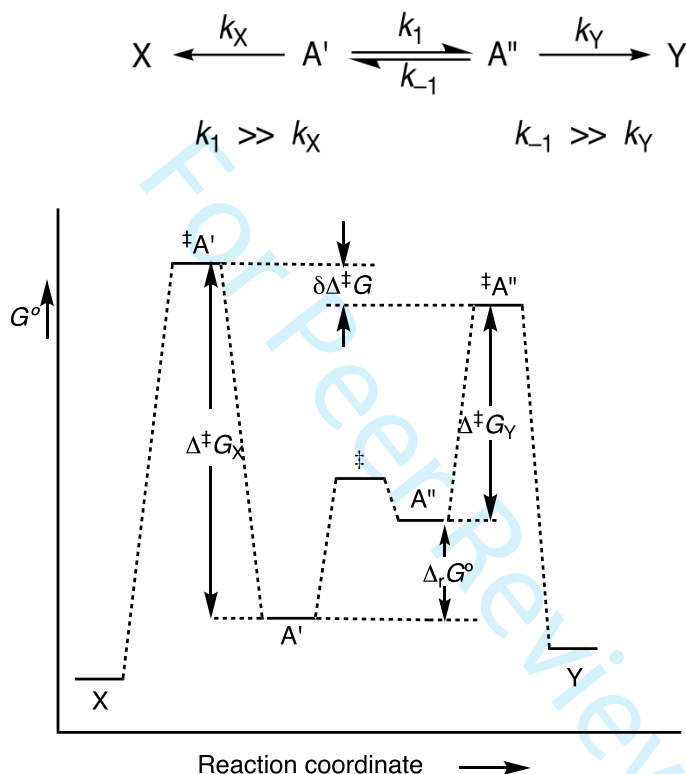18   *Examples:*
19

20
21
22   See *electron pushing*.
23

Curtin-Hammett principle
25   Statement that in a *chemical reaction* that yields one product (X) from one isomer (A')
26   and a different product (Y) from another isomer (A") (and provided these two isomers
27   are rapidly interconvertible relative to the rate of product formation, whereas the
28   products do not undergo interconversion) the product composition is not directly related
29   to the relative concentrations of the isomers in the *substrate*; it is controlled only by the
30   difference in standard Gibbs energies ($G^{\ddagger}_{A'} - G^{\ddagger}_{A''}$) of the respective *transition states*.

Note 1: The product composition is given by [Y]/[X] = $(k_Y k_1)/(k_{-1} k_X)$ or $K_c k_Y/k_X$, where K_c is the equilibrium constant, [A"]/[A'], and where k_Y and k_X are the respective *rate constant*s of their reactions; these parameters are usually unknown.

Note 2: The energy diagram below represents the transformation of rapidly interconverting isomers A' and A" into products X and Y.

$$X \xleftarrow{\ k_X\ } A' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A'' \xrightarrow{\ k_Y\ } Y$$

$$k_1 \gg k_X \qquad\qquad k_{-1} \gg k_Y$$

Note 3: A related concept is the Winstein-Holness equation for the overall rate of product formation in a system of rapidly interconverting isomers A' and A". The overall rate constant k is given by

$$k = x'k_X + x''k_Y$$

where x' and x'' are the respective mole fractions of the isomers at equilibrium [15]. However, since x' and x'' are simple functions of K_c, the apparent dependence of the overall rate on the relative concentrations of A' and A" disappears. The overall rate constant is the sum $k_X + K_c k_Y$, which is a function of the same quantities that determine the product ratio.

See [140]. See also [15,141,142].

rev[3]

cybotactic region

1

2

1   That part of a solution in the vicinity of a solute molecule in which the ordering of the

2   solvent molecules is modified by the presence of the solute molecule. The term solvent

3   "cosphere" of the solute has also been used.

4   See [143,144].

5   [3]

6

7   cyclization

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

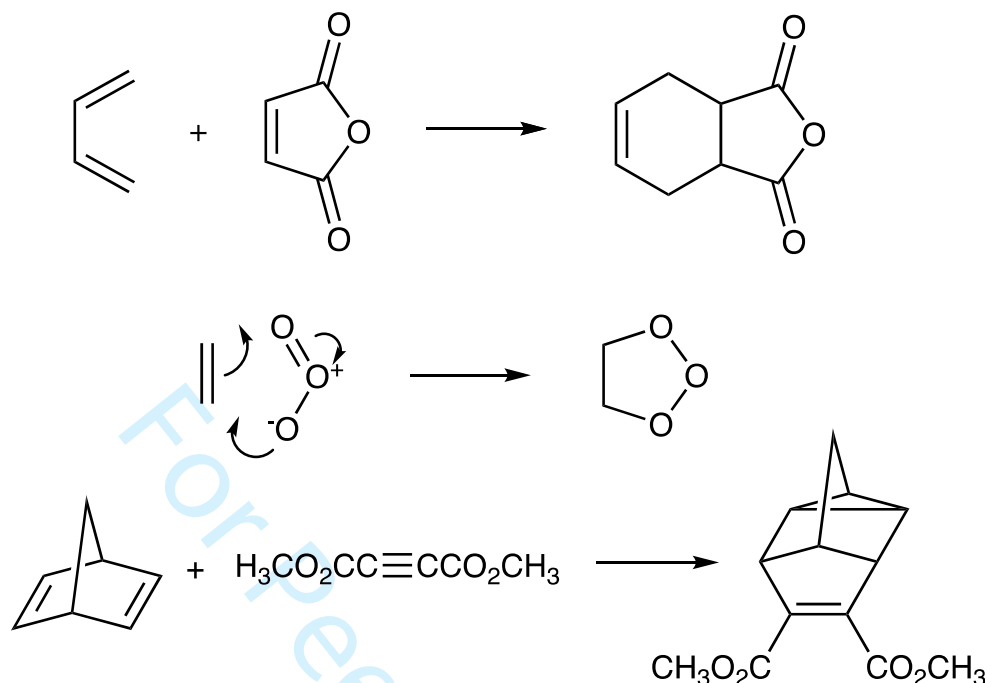9   See also *annulation*.

10   [3]

11
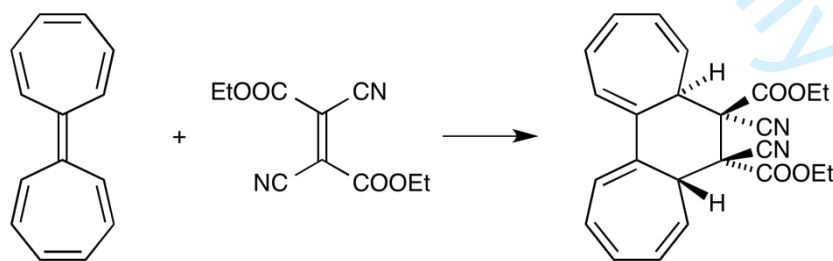
12   cycloaddition

13   Reaction in which two or more unsaturated molecules (or parts of the same molecule)

14   combine with the formation of a cyclic *adduct* in which there is a net reduction of the

15   bond multiplicity.

16   *Note 1*: The following two systems of notation have been used for the more detailed

17   specification of cycloadditions, of which the second, more recent system (described

18   under (2)) is preferred:

19   (1) An (i+j+...) cycloaddition is a reaction in which two or more molecules (or parts

20   of the same molecule), respectively, provide units of i, j,... linearly connected

21   atoms: these units become joined at their respective termini by new σ bonds so

22   as to form a cycle containing (i+j+...) atoms. In this notation, (a) a Diels-Alder

23   reaction is a (4+2) cycloaddition, (b) the initial reaction of ozone with an alkene is

24   a (3+2) cycloaddition, and (c) the reaction of norbornadiene below is a (2+2+2)

25   cycloaddition. (Parentheses are used to indicate the numbers of atoms, but

26   brackets are also used.)

1
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12
13

+

H₃CO₂CC≡CCO₂CH₃

CH₃O₂C   CO₂CH₃

1

2

3 (2) The symbolism [*i*+*j*+...] for a cycloaddition identifies the numbers *i*, *j*,... of
4 electrons in the interacting units that participate in the transformation of reactants
5 to products. In this notation the reaction (a) and (b) of the preceding paragraph
6 would both be described as [2+4] cycloadditions, and (c) as a [2+2+2]
7 cycloaddition. The symbol a or s (a = *antarafacial*, s = suprafacial) is often added
8 (usually as a subscript after the number to designate the stereochemistry of
9 addition to each fragment. A subscript specifying the orbitals, viz., σ, π (with their
10 usual significance) or n (for an orbital associated with a single atom), may be
11 added as a subscript before the number. Thus the normal Diels-Alder reaction is
12 a [4$_s$+2$_s$] or [$_\pi$4$_s$ + $_\pi$2$_s$] cycloaddition, whilst the reaction

13

EtOOC   CN   +   NC   COOEt

H   COOEt   CN   CN   COOEt   H

14

15 would be a [14$_a$+2$_s$] or [$_\pi$14$_a$ + $_\pi$2$_s$] cycloaddition, leading to the stereoisomer shown,
16 with hydrogens *anti*. (Brackets are used to indicate the numbers of electrons, and
17 they are also used instead of parentheses to denote the numbers of atoms.)

1   *Note 2*: Cycloadditions may be *pericyclic reaction*s or (non-*concerted*) *stepwise*

2   *reaction*s. The term "dipolar cycloaddition" is used for cycloadditions of 1,3-dipolar

3   compounds.

4   See [107,145,146].

5   See also *cheletropic reaction*, *ene reaction*, *pericyclic reaction*.

6   rev[3]

7

cycloelimination

9   Reverse of *cycloaddition*. The term is preferred to the synonyms "cycloreversion",

10   "retro-addition", and "retrocycloaddition".

11   [3]

12

cycloreversion

14   obsolete

15   See *cycloelimination*.

16   [3]

17

dative bond

19   obsolescent

20   *Coordination bond* formed between two chemical species, one of which serves as a

21   donor and the other as an acceptor of the electron pair that is shared in the bond.

22   *Examples*: the N–B bond in $H_3N^+{-}B^-H_3$, the S–O bond in $(CH_3)_2S^+{-}O^-$.

23   *Note 1*: A distinctive feature of dative bonds is that their minimum-energy rupture in

24   the gas phase or in inert solvent follows the heterolytic bond-cleavage path.

25   *Note 2:* The term is obsolescent because the distinction between dative bonds and

26   ordinary covalent bonds is not useful, in that the precursors of the bond are irrelevant:

27   $H_3N^+{-}B^-H_3$ is the same molecule, with the same bonds, regardless of whether the

28   precursors are considered to have been $H_3N + BH_3$ or $H_3N^+ + {}^-BH_3$.

29   See [8].

30   See *coordination*.

31   rev[3]

32

degenerate chemical reaction

34   See *identity reaction*.

35   [3]

36

degenerate rearrangement

38   *Chemical reaction* in which the product is indistinguishable (in the absence of isotopic

39   labelling) from the reactant.

1   *Note 1*: The term includes both "degenerate *intramolecular* rearrangements" and
2   reactions that involve *intermolecular* transfer of atoms or groups ("degenerate
3   intermolecular reactions"): both are degenerate *isomerization*s.
4   *Note 2*: The occurrence of degenerate rearrangements may be detectable by isotopic
5   labelling or by dynamic NMR techniques. For example: the [3,3]*sigmatropic*
6   *rearrangement* of hexa-1,5-diene (Cope rearrangement),
7   *Note 3:* Synonymous but less preferable terms are "automerization", "permutational
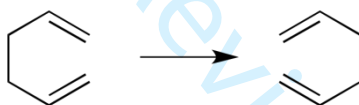8   isomerism", "isodynamic transformation", "topomerization".
9   See [147].
10   See also *fluxional*, *molecular rearrangement*, *narcissistic reaction*, *valence isomer*.
11   [3]
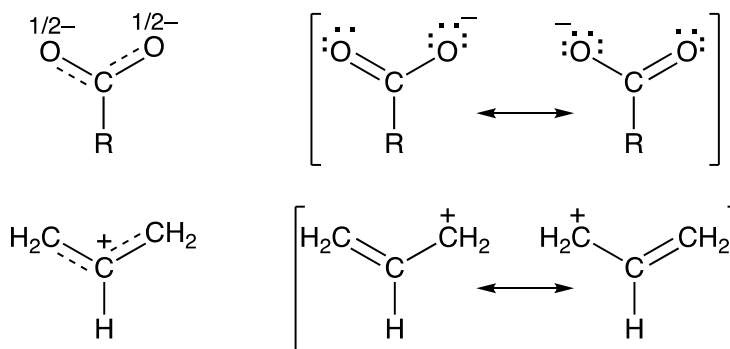12

delocalization

14   Quantum-mechanical concept most usually applied in organic chemistry to describe the
15   redistribution of π electrons in a *conjugated system*, where each link has a fractional
16   double-bond character, or a non-integer *bond order*, rather than π electrons that are
17   localized in double or triple bonds.
18   *Note 1*: There is a corresponding "delocalization energy", identifiable with the
19   stabilization of the system relative to a hypothetical alternative in which formal

20   (localized) single and double *bond*s are present. Some degree of delocalization is
21   always present and can be estimated by quantum mechanical calculations. The effects
22   are particularly evident in *aromatic* systems and in symmetrical *molecular entities* in
23   which a lone pair of electrons or a vacant p-orbital is conjugated with a double bond
24   (e.g., carboxylate ions, nitro compounds, enamines, the allyl cation).
25   *Note 2*: Delocalization in such species may be represented by partial bonds or by
26   *resonance* (here symbolized by a two-headed arrow) between *resonance form*s.
27

28

1 These examples also illustrate the concomitant delocalization of charge in ionic
2 conjugated systems. Analogously, delocalization of the spin of an unpaired electron
3 occurs in conjugated *radical*s.
4   *Note 3*: Delocalization is not limited to π electrons. *Hyperconjugation* is the
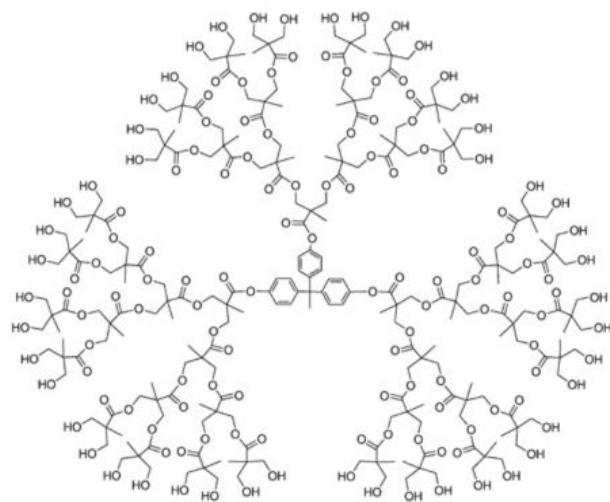5 delocalization of electrons of σ bonds.
6   [3]
7

dendrimer
9 Large molecule constructed from a central core with repetitive branching and multiple
10 functional groups at the periphery.
11   See [148].
12   *Example:* (with 48 CH_2OH at the periphery)
13

14
15
16   *Note*: The name comes from the Greek δενδρον (dendron), which translates to "tree".
17 Synonymous terms include arborols and cascade molecules.
18   See [148,149,150,151,152].
19

deshielding
21   See *shielding*.
22   [3]
23

detachment
25 Reverse of *attachment*.
26   [3]
27
28
29

1 **detailed balancing**

2 Principle that when equilibrium is reached in a reaction system (containing an arbitrary

3 number of components and reaction paths), as many atoms, in their respective

4 *molecular entities*, will pass forward in a given finite time interval as will pass backward

5 along each individual path.

6   *Note 1*: It then follows that the reaction path in the reverse direction must in every

7 detail be the reverse of the reaction path in the forward direction (provided that the

8 system is at equilibrium).

9   *Note 2*: The principle of detailed balancing is a consequence for macroscopic

10 systems of the principle of *microscopic reversibility*.

11   [3]

12

13 **diamagnetism**

14 Property of substances having a negative magnetic susceptibility (χ), whereby they are

15 repelled out of a magnetic field.

16   See also *paramagnetism*.

17   [3]

18

19 **diastereoisomerism**

20 Stereoisomerism other than *enantiomerism*.

21   See *diastereoisomers* [11].

22   [3]

23

24 **diastereomeric excess** (diastereoisomeric excess)

25 $x_1 - x_2$, where x_1 and x_2 (with $x_1 + x_2 = 1$) are the mole fractions of two *diastereoisomers*

26 in a mixture, or the fractional yields of two *diastereoisomers* formed in a reaction.

27   *Note:* Frequently this term is abbreviated to d.e.

28   See *stereoselectivity*, *diastereoisomers*.

29   See [11].

30

31 **diastereomeric ratio**

32 x_1/x_2, where x_1 and x_2 are the mole fractions of two *diastereoisomers* in a mixture formed

33 in a reaction.

34   *Note:* Frequently this term is abbreviated to d.r.

35   See *stereoselectivity*, *diastereoisomers*.

36   See [11].

37

38 **diastereoisomers (diastereomers)**

39 Stereoisomers not related as mirror images of each other.

1   *Note*: Diastereoisomers are characterized by differences in physical properties, and
2   by differences in chemical behaviour toward chiral as well as achiral reagents.
3   See [11].
4

5   **diastereoselectivity**
6   Preferential formation in a chemical reaction of one *diastereoisomer* over another.
7   *Note*: This can be expressed quantitatively by the *diastereoisomeric excess* or by the
8   *diastereomeric ratio*, which is preferable because it is more closely related to a Gibbs-
9   energy difference.
10   See [11].
11   See *selectivity*.
12

13   **dielectric constant**
14   obsolete
15   See [12].
16   See *permittivity (relative)*.
17   rev[3]
18

19   **dienophile**
20   Ene or yne component of a Diels-Alder reaction, including compounds with hetero-
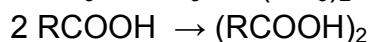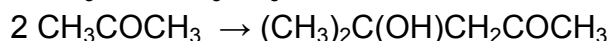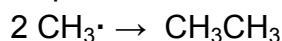21   double bonds and hetero-triple bonds.
22   See *cycloaddition*.
23   rev[3]
24

25   **diffusion-controlled rate**
26   See *encounter-controlled rate*, *microscopic diffusion control*. Contrast *mixing control*.
27   [3]
28

29   **dimerization**
30   *Transformation* of a *molecular entity* A to give a molecular entity A_2.
31   *Examples*:
32        $2\ CH_3\cdot\ \rightarrow\ CH_3CH_3$
33        $2\ CH_3COCH_3\ \rightarrow\ (CH_3)_2C(OH)CH_2COCH_3$
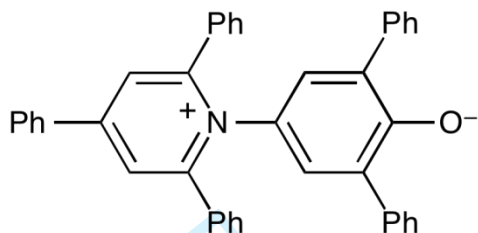34 $2\ RCOOH\ \rightarrow\ (RCOOH)_2$
35   See also *association*.
36   [3]
37

38   **Dimroth-Reichardt E_T parameter**

1 Quantitative measure of solvent polarity, based on the wavelength, λ_{max}, of the longest-
2 wavelength intramolecular charge-transfer absorption band of the *solvatochromic*
3 betaine dye 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-ium-1-yl)phenolate.
4

5
6 See [17,153,154,155].
7 See *solvent parameter*.
8 rev[3]
9

10 **dipolar aprotic solvent**
11 See *dipolar non-HBD solvent*.
12 rev[3]
13

14 **dipolar non-HBD solvent (**Non-hydrogen-bond donating solvent)
15 Solvent with a comparatively high relative *permittivity* ("dielectric constant"), greater
16 than ca. 15, and composed of molecules that have a sizable permanent dipole moment
17 and that, although it may contain hydrogen atoms, cannot donate suitably labile
18 hydrogen atoms to form strong solvent-solute hydrogen bonds.
19 *Examples*: dimethyl sulfoxide, acetonitrile, acetone, as contrasted with methanol and
20 *N*-methylformamide.
21 *Note 1*: The term "dipolar" refers to solvents whose molecules have a permanent
22 dipole moment, in contrast to solvents whose molecules have no permanent dipole
23 moment and should be termed "apolar" or "nonpolar".
24 *Note 2*: Non-HBD solvents are often called aprotic, but this term is misleading
25 because a proton can be removed by a sufficiently strong base. The aprotic nature of
26 a solvent molecule means that its hydrogens are in only covalent C–H bonds and not
27 in polar O–H$^{\delta+}$ or N–H$^{\delta+}$ bonds that can serve as hydrogen-bond donors. Use of
28 "aprotic" is therefore discouraged, unless the context makes the term unambiguous.
29 *Note 3*: It is recommended to classify solvents according to their capability to donate
30 or not donate, as well as to accept or not accept, hydrogen bonds to or from the solute,
31 as follows:
32 Hydrogen-bond donating solvents (short: HBD solvents), formerly protic solvents
33 Non-hydrogen-bond donating solvents (short: non-HBD solvents), formerly aprotic
34 solvents
35 Hydrogen-bond accepting solvents (short: HBA solvents)

1　　　　Non-hydrogen-bond accepting solvents (short: non-HBA solvents)

2　　See [156,157].

3

4　**dipole-dipole excitation transfer**

5　　*Förster resonance-energy transfer (FRET)*

6　　See [9].

7

8　**dipole-dipole interaction**

9　Intermolecular or intramolecular interaction between molecules or groups having a

10　permanent electric dipole moment. The strength of the interaction depends on the

11　distance and relative orientation of the dipoles.

12　　*Note*: A dipole/dipole interaction is a simplification of the electrostatic interactions

13　between molecules that originate from asymmetries in the electron densities. Such

14　interactions can be described more correctly by the use of higher-order multipole
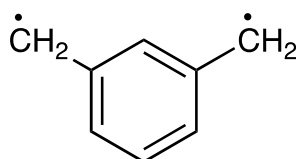
15　moments.

16　　See also *van der Waals forces*.

17　　rev[3]

18

19　**dipole-induced dipole forces**

20　　See *van der Waals forces*.

21　　[3]

22

23　**diradical**

24　biradical

25　Even-electron *molecular entity* with two (possibly delocalized) radical centres that act

26　nearly independently of each other, e.g.,

27

28　　*Note 1*: Species in which the two radical centres interact significantly are often

29　referred to as "diradicaloids". If the two radical centres are located on the same atom,

30　the species is more properly referred to by its generic name: carbene, nitrene, etc.

31　　*Note 2*: The lowest-energy triplet state of a diradical lies below or at most only a little

32　above its lowest singlet state (usually judged relative to $k_B T$, the product of the

33　Boltzmann constant k_B and the absolute temperature T). If the two radical centres

34　interact significantly, the singlet state may be more stable. The states of those diradicals

35　whose radical centres interact particularly weakly are most easily understood in terms

36　of a pair of local doublets.

Note 3: Theoretical descriptions of low-energy states of diradicals display two unsaturated valences: the dominant valence-bond structures have two dots, the low-energy molecular orbital *configuration*s have only two electrons in two approximately nonbonding molecular orbitals, and two of the natural orbitals have occupancies close to one.

See [9,158,159,160,161,162,163].

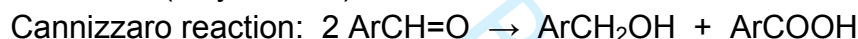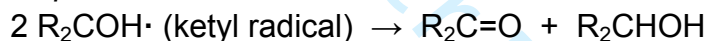See also *carbene*, *nitrene*.

[3]

dispersion forces

See *London forces, van der Waals forces*.

[3]

disproportionation

Any *chemical reaction* of the type A + A ⇋ A' + A", where A, A' and A" are different chemical species.

Examples:

2 $R_2COH\cdot$ (ketyl radical) → $R_2C=O$ + R_2CHOH

Cannizzaro reaction: 2 ArCH=O → $ArCH_2OH$ + ArCOOH

Note 1: The reverse of disproportionation is called *comproportionation*.

Note 2: A special case of disproportionation (or "dismutation") is "radical disproportionation", exemplified by

$\cdot CH_2CH_3$ + $\cdot CH_2CH_3$ → $CH_2=CH_2$ + CH_3CH_3
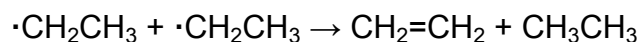
Note 3: A somewhat more restricted usage of the term prevails in inorganic chemistry, where A, A' and A" are of different oxidation states.
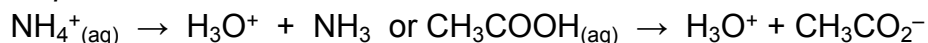
[3]

disrotatory

Stereochemical feature of an *electrocyclic reaction* in which the substituents at the interacting termini of the conjugated system rotate in opposite senses (one clockwise and the other counterclockwise).

See also *conrotatory*.

rev[3]

dissociation

Separation of a *molecular entity* into two or more molecular entities (or any similar separation within a polyatomic molecular entity).

1   *Example*:

2    $NH_4^{+}{}_{(aq)} \rightarrow H_3O^+ + NH_3$ or $CH_3COOH_{(aq)} \rightarrow H_3O^+ + CH_3CO_2^-$

3   *Note 1:* Although the separation of the constituents of an *ion pair* into free ions is a

4   dissociation, the *ionization* that produces the ion pair is not a dissociation, because the

5   ion pair is a single *molecular entity*.

6   *Note 2*: The reverse of dissociation is *association*.

7   rev[3]

8

distonic ion

10   Radical ion in which charge and radical sites are separated.

11   *Example:* $\cdot CH_2CH_2OCH_2^+$

12   See [164,165].

13   rev[3]

14

distortion interaction model (Activation Strain Model)

16   Method for analyzing activation energy as the sum of the energies to distort the

17   reactants into the geometries they have in transition states plus the energy of interaction

18   between the two distorted reactants.

19   See [166].

20

distribution ratio

22   partition ratio

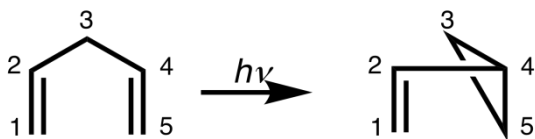23   Ratio of concentrations of a solute in a mixture of two immiscible phases at equilibrium.

24   See also *Hansch constant*.

25   See [167].

26

di-π-methane rearrangement

28   *Photochemical reaction* of a molecular entity with two π-systems separated by a

29   saturated carbon, to form an ene-substituted cyclopropane.

30   *Pattern*:

31

32   See [9,168].

33

donicity (also called donor number, DN, which is a misnomer)

35   Quantitative experimental measure of the Lewis basicity of a molecule B, expressed as

36   the negative enthalpy of the formation of the 1:1 complex $B \cdot SbCl_5$.

37   *Note*: donicity is often used as a measure of a solvent's basicity.

1 See also *acceptor parameter*, *Lewis basicity*.

2 See [63,169,170].

3

4 **downfield**

5 superseded but still widely used in NMR to mean deshielded.

6 See *chemical shift*, *shielding*.

7 rev[3]

8

9 **driving force**

10 (1) Negative of the Gibbs energy change ($\Delta_r G^0$) on going from the reactants to the

11 products of a *chemical reaction* under standard conditions. Also called affinity.

12 (2) Qualitative term that relates the favorable thermodynamics of a reaction to a specific

13 feature of molecular structure, such as the conversion of weaker bonds into stronger

14 (CH_3–H + Br–Br → CH_3–Br + H–Br), neutralization of an acid (Claisen *condensation* of

15 2 CH_3COOEt + EtO^- to CH_3COCH^-COOEt + EtOH), or increase of entropy

16 (*cycloelimination* of cyclohexene to butadiene + ethylene).

17 *Note 1*: This term is a misnomer, because favorable thermodynamics is due to

18 energy, not force.

19 *Note 2*: This term has also been used in connection with photoinduced electron

20 transfer reactions, to indicate the negative of the estimated standard Gibbs energy

21 change for the outer sphere electron transfer ($\Delta_{ET} G^0$) [9].

22 rev[3]

23

24 **dual substituent-parameter equation**

25 Any equation that expresses substituent effects in terms of two parameters.

26 *Note*: In practice the term is used specifically for an equation for modeling the effects

27 of *meta-* and *para*-substituents X on chemical reactivity, spectroscopic properties, etc.

28 of a probe site in benzene or other aromatic system.

29 $P_X = \rho_I \sigma_I + \rho_R \sigma_R$

30 where P_X is the magnitude of the property for substituent X, expressed relative to the

31 property for X = H; σ_I and σ_R are inductive (or polar) and resonance substituent

32 constants, respectively, there being various scales for σ_R; ρ_I and ρ_R are the

33 corresponding regression coefficients.

34 See [171,172,173].

35 See also *extended Hammett equation, Yukawa-Tsuno equation.*

36 [3]

37

38 **dynamic NMR**

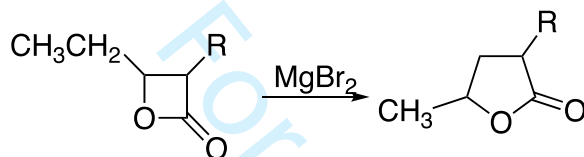39 NMR spectroscopy of samples undergoing chemical reactions.

1   *Note*: Customarily this does not apply to samples where the composition of the
2 sample, and thus its NMR spectrum, changes with time, but rather to samples at
3 equilibrium, without any net reaction. The occurrence of chemical reactions is
4 manifested by features of the NMR line-shape or by *magnetization transfer*.
5   See *chemical flux*.

6

dyotropic rearrangement

8 Process in which two σ bonds simultaneously migrate intramolecularly.

9   *Example*

10

11   See [174,175,176].

12   rev[3]

13

educt

15 deprecated: usage strongly discouraged

16 starting material, reactant

17   *Note*: This term should be avoided and replaced by reactant, because it means

18 "something that comes out", not "something that goes in".

19   rev[3]

20

effective charge, Z_{eff}

22 Net positive charge experienced by an electron in a polyelectronic atom, which is less

23 than the full nuclear charge because of *shielding* by the other electrons.

24   rev[3]

25

effective molarity (effective concentration)

27 Ratio of the first-order rate constant or equilibrium constant of an *intramolecular*

28 reaction involving two functional groups within the same *molecular entity* to the second-

29 order *rate constant* or equilibrium constant of an analogous *intermolecular* elementary

30 reaction.

31   *Note*: This ratio has unit of concentration, mol dm^{-3} or mol L^{-1}, sometimes denoted

32 by M.

33   See [177].

34   See also *intramolecular catalysis*.

35   [3]

36

37

1 **eighteen-electron rule**
2 Electron-counting rule that the number of nonbonding electrons at a metal plus the
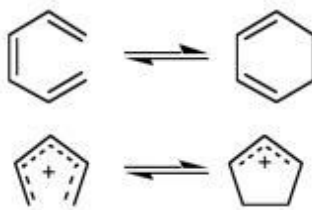3 number of electrons in the metal-*ligand* bonds should be 18.
4 *Note*: The 18-electron rule in transition-metal chemistry is an analogue of the Lewis
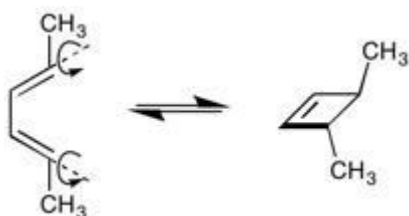5 *octet rule*.
6 [3]
7

8 **electrocyclic reaction (electrocyclization)**
9 *Molecular rearrangement* that involves the formation of a σ bond between the termini
10 of a fully *conjugated* linear π-electron system (or a linear fragment of a π-electron
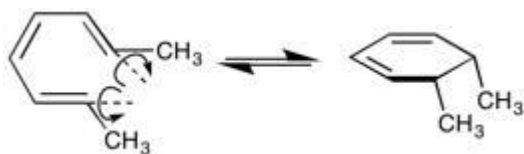11 system) and a decrease by one in the number of π bonds, or the reverse of that process.
12 *Examples*:

13

14 *Note*: The stereochemistry of such a process is termed "*conrotatory*" if the
15 substituents at the interacting termini of the conjugated system both rotate in the same
16 sense, as in

17

18 or "*disrotatory*" if one terminus rotates in a clockwise and the other in a
19 counterclockwise sense, as in

20

21 See also *pericyclic reaction*.
22 [3]
23

24 **electrofuge**
25 *Leaving group* that does not carry away the bonding electron pair.

1   *Examples*: In the nitration of benzene by NO_2^+, H^+ is the electrofuge, and in an S_N1
2   reaction the carbocation is the electrofuge.
3   *Note 1*: Electrofugality characterizes the relative rates of atoms or groups to depart
4   without the bonding electron pair. Electrofugality depends on the nature of the reference
5   reaction and is not the reverse of *electrophilicity* [178].
6   *Note 2*: For electrofuges in S_N1 reactions see [179].
7   See also *electrophile*, *nucleofuge*.
8   rev[3]
9

electromeric effect
11 obsolete
12 rev[3]
13

electron acceptor
15 *Molecular entity* to which an electron may be transferred.
16 *Examples*: 1,4-dinitrobenzene,1,1'-dimethyl-4,4'-bipyridinium dication,
17 benzophenone.
18 *Note 1*: A group that accepts electron density from another group is not called an
19 electron acceptor but an electron-withdrawing group.
20 Note *2*: A *Lewis acid* is not called an electron acceptor but an *electron-pair acceptor*.
21 rev[3]
22

electron affinity
24 Energy released when an additional electron (without excess energy) attaches itself to
25 a *molecular entity* (often electrically neutral but not necessarily).
26 *Note 1*: Equivalent to the minimum energy required to detach an electron from a
27 singly charged negative ion.
28 *Note 2*: Measurement of electron affinities is possible only in the gas phase, but there
29 are indirect methods for evaluating them from solution data, such as polarographic half-
30 wave potentials or charge-transfer spectra.
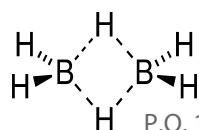31 See [8,180,181].
32 rev[3]
33

electron capture
35 Transfer of an electron to a *molecular entity*, resulting in a molecular entity of
36 (algebraically) increased negative charge.
37

electron-deficient bond
39 Bond between adjacent atoms that is formed by fewer than two electrons.
40 *Example*:

Note: The B–H–B bonds are also called "two-electron three-centre bonds".

[3]

electron density

The electron density at a point with coordinates x,y,z in an atom or *molecular entity* is the product of the probability $P(x,y,z)$ (units: m^{-3}) of finding an electron at that point with the volume element $dx\, dy\, dz$ (units: m^3).

Note: For many purposes (e.g., X-ray scattering, forces on atoms) the system behaves as if the electrons were spread out into a continuous distribution, which is a manifestation of the wave-particle duality.

See also *atomic charge*, *charge density*.

rev[3]

electron donor

Molecular entity that can transfer an electron to another molecular entity, or to the corresponding *chemical species*.

Note 1: After the electron transfer the two entities may separate or remain associated.

Note 2: A group that donates electron density to another group is an electron-donating group, regardless of whether the donation is of σ or π electrons.

Note 3: A *Lewis base* is not called an electron donor, but an *electron-pair donor*.

See also *electron acceptor*.

rev[3]

electron-donor-acceptor complex

obsolete

charge-transfer complex.

See also *adduct*, *coordination*.

electron-pair acceptor
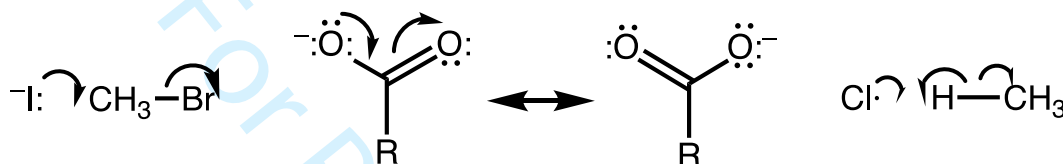
Lewis acid.

[3]

electron-pair donor

Lewis base.

[3]

1   **electron pushing**
2   Method using *curly arrows* for showing the formal movement of an electron pair (from
3   a lone pair or a σ or π bond) or of an unpaired electron, in order to generate additional
4   *resonance form*s or to denote a *chemical reaction*.
5   *Note 1*: The electron movement may be *intramolecular* or *intermolecular*.
6   *Note 2*: When a single electron is transferred, a single-headed curly arrow or "fish-
7   hook" is used, but the electron movement in the opposite direction is redundant and
8   sometimes omitted.
9   *Examples*:

10

11

12   **electron transfer**
13   Transfer of an electron from one *molecular entity* to another, or between two localized
14   sites in the same molecular entity.
15   See also *inner sphere (electron transfer)*, *Marcus equation*, *outer sphere (electron*
16   *transfer)*.
17   [3]

18

19   **electron-transfer catalysis**
20   Process describing a sequence of reactions such as shown in equations (1)-(3), leading
21   from A to B, via species $A^{\cdot-}$ and $B^{\cdot-}$ that have an extra electron:
22      $A + e^- \rightarrow A^{\cdot-}$ (1)
23      $A^{\cdot-} \rightarrow B^{\cdot-}$ (2)
24      $B^{\cdot-} + A \rightarrow B + A^{\cdot-}$ (3)
25   *Note 1*: An analogous sequence involving radical cations ($A^{\cdot+}$, $B^{\cdot+}$) also occurs.
26   *Note 2*: The most notable example of electron-transfer catalysis is the $S_{RN}1$ (or
27   $T+D_N+A_N$) reaction of haloarenes with nucleophiles.
28   *Note 3*: The term has its origin in an analogy to acid-base catalysis, with the electron
29   instead of the proton. However, there is a difference between the two catalytic
30   mechanisms, since the electron is not a true catalyst, but rather behaves as the initiator
31   of a *chain reaction*. "Electron-transfer induced chain reaction" is a more appropriate
32   term for the mechanism described by equations (1)-(3).
33   See [182,183].
34   [3]

35

36   **electronation**

1 obsolete
2   See *reduction*.
3   rev[3]
4

5 **electronegativity**
6 Measure of the power of an atom to attract electrons to itself.
7   *Note 1*: The concept has been quantified by a number of authors. The first, due to
8 Pauling, is based on *bond-dissociation energies*, E_d (units: eV), and is anchored by
9 assigning the electronegativity of hydrogen as $\chi_{r,H}$ = 2.1. For atoms A and B
10

11 $$\chi_{r,A} - \chi_{r,B} = \sqrt{\{E_d(A–B)/eV - \tfrac{1}{2}\,[E_d(A–A) + E_d(B–B)]/eV\}}$$

12
13 where χ_r denotes the Pauling relative electronegativity; it is relative in the senses that
14 the values are of dimension 1 and that only electronegativity differences are defined on
15 this empirical scale. See [12] section 2.5.
16   *Note* 2: Alternatively, the electronegativity of an element, according to the Mulliken
17 scale, is the average of its atomic *ionization* energy and electron affinity. Other scales
18 have been developed by Allred and Rochow, by Sanderson, and by Allen.
19   *Note 3*: Absolute electronegativity is property derived from density functional theory
20 [8].
21   See [75,184,185,186,187,188,189,190].
22   rev[3]
23

24 **electronic effects (of substituents)**
25 Changes exerted by a substituent on a molecular property or molecular reactivity, often
26 distinguished as *inductive* (through-bond polarization), through-space electrostatics
27 (*field effect*), or *resonance*, but excluding *steric*.
28   *Note 1*: The obsolete terms mesomeric and electromeric are discouraged.
29   *Note 2*: Quantitative scales of substituent effects are available.
30   See [126,173,191].
31   See also *polar effect*.
32   rev[3]
33

34 **electrophile (n.), electrophilic (adj.)**
35 Reagent that forms a *bond* to its reaction partner (the *nucleophile*) by accepting both
36 bonding electrons from that partner.
37   *Note 1*: Electrophilic reagents are *Lewis acid*s.
38   *Note 2*: "Electrophilic catalysis" is catalysis by Lewis acids.

Note 3: The term "electrophilic" is also used to designate the apparent polar character of certain *radical*s, as inferred from their higher relative reactivities with reaction sites of higher electron density.

See also *electrophilicity*.

[3]

electrophilic substitution

Heterolytic reaction in which the entering group adds to a nucleophile and in which the leaving group, or *electrofuge*, relinquishes both electrons to its reaction partner, whereupon it becomes another potential electrophile.

Example (azo coupling)*:*

RN_2^+ (electrophile) + $H_2NC_6H_5$ (nucleophile) $\rightarrow$ p-$H_2NC_6H_4N=NR$ + H^+ (electrofuge)

Note: It is arbitrary to emphasize the electrophile and ignore the feature that this is also a nucleophilic substitution, but the distinction depends on the electrophilic nature of the reactant that is considered to react with the *substrate*.

See also *substitution*.

electrophilicity

Relative reactivity of an electrophile toward a common *nucleophile*.

Note: The concept is related to *Lewis acid*ity. However, whereas Lewis acidity is measured by relative equilibrium constants toward a common Lewis base, electrophilicity is measured by relative *rate constant*s for reactions of different electrophilic reagents towards a common nucleophilic *substrate*.

See [192,193,194].

See also *nucleophilicity*.

rev[3]

element effect

Ratio of the *rate constant*s of two reactions that differ only in the identity of the element in the *leaving group*.

Example: k_{Br}/k_{Cl} for the reaction of N_3^- (azide) with CH_3Br or CH_3Cl.

rev[3]

elementary reaction

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 only one *transition state* or none.

See [13].

See also *composite reaction, stepwise reaction*.

1   rev[3]

2

3 **elimination**

4 Reverse of an *addition reaction*.

5   *Note 1*: In an elimination two groups (called eliminands) are lost, most often from two

6 different centres (1,2-elimination (*β-elimination*) or 1,3-elimination, etc.) with

7 concomitant formation of an unsaturation (double bond, triple bond) in the molecule, or

8 formation of a ring.

9   *Note 2*: If the groups are lost from a single carbon or nitrogen centre (1,1-elimination,

10 *α-elimination*), the resulting product is a *carbene* or *nitrene*, respectively.

11   rev[3]

12

13 **empirical formula**

14 List of the elements in a *chemical species*, with integer subscripts indicating the simplest

15 possible ratios of all elements.

16   *Note 1:* In organic chemistry C and H are listed first, then the other elements in

17 alphabetical order.

18   *Note 2:* This differs from the *molecular formula*, in which the subscripts indicate how

19 many of each element is included and which is an integer multiple of the empirical

20 formula. For example, the empirical formula of glucose is CH_2O while its molecular

21 formula is $C_6H_{12}O_6$.

22   *Note 3:* The empirical formula is the information provided by combustion analysis,

23 which has been largely superseded by mass spectrometry, which provides the

24 *molecular formula*.

25

26 **enantiomer**

27 One of a pair of stereoisomeric *molecular entities* that are non-superimposable mirror

28 images of each other.

29   See [11].

30   [3]

31

32 **enantiomeric excess**

33 Absolute value of the difference between the mole fractions of two enantiomers:

34

35      $\Delta x(\text{e.e.}) = |x_+ - x_-|$

36

37 where $x_+ + x_- = 1$.

38   *Note*: Enantiomeric excess can be evaluated experimentally from the observed

39 specific optical rotatory power $[\alpha]_{obs}$, relative to $[\alpha]_{max}$, the (maximum) specific optical

40 rotatory power of a pure enantiomer:

1
2
3   1
4
5   2 Δx(e.e.) = | $[\alpha]_{obs}/[\alpha]_{max}$ |
6
7   3
8
9   4   and also by chiral chromatography, NMR, and MS methods.
10   5   See [11].
11   6   rev[3]
12
13   7
14   8   **enantiomeric ratio**
15   9   mole fraction of one *enantiomer* in a mixture divided by the mole fraction of the other.
16
17   10
18   11 r(e.r.) = x_+/x_- or x_-/x_+
19
20   12
21   13   where $x_+ + x_- = 1$
22   14   See [11].
23   15   rev[3]
24
25   16
26   17   **enantioselectivity**
27   18   See *stereoselectivity*.
28   19   [3]
29
30   20
31   21   **encounter complex**
32   22   *Complex* of *molecular entities* produced at an *encounter-controlled rate*, and which
33   23   occurs as an intermediate in a reaction.
34   24   *Note 1*: When the complex is formed from two molecular entities it is called an
35   25   "encounter pair". A distinction between encounter pairs and (larger) encounter
36   26   complexes may be relevant for mechanisms involving *pre-association*.
37   27   *Note 2*: The separation between the entities is small compared to the diameter of a
38   28   solvent molecule.
39   29   See also [9].
40   30   rev[3]
41
42   31
43   32   **encounter-controlled rate**
44   33   *Rate of reaction* corresponding to the rate at which the reacting *molecular entities*
45   34   encounter each other. This is also known as the "diffusion-controlled rate", since rates
46   35   of encounter are themselves controlled by diffusion rates (which in turn depend on the
47   36   viscosity of the *medium* and the dimensions of the reacting molecular entities).
48   37   *Note*: At 25 °C in most solvents, including water, a *bimolecular* reaction that proceeds
49   38   at an encounter-controlled rate has a second-order *rate constant* of 10^9 to 10^{10} dm^3
50   39   mol^{-1} s^{-1}.
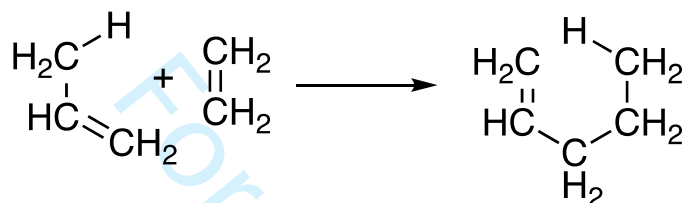51   40   See also *microscopic diffusion control*.
52
53

1   [3]

2

3   **ene reaction**

4   Addition of a compound with a double bond and an allylic hydrogen (the "ene") to a

5   compound with a multiple bond (the "enophile") with transfer of the allylic hydrogen and

6   a concomitant reorganization of the bonding.

7   *Example*, with propene as the ene and ethene as the enophile.

8

9   *Note*: The reverse is a "retro-ene" reaction.

10   [3]

11

12   **energy of activation**

13   E_a or E_A

14   *Arrhenius energy of activation*

15   activation energy

16   (SI unit: kJ mol^{-1})

17   Operationally defined quantity expressing the dependence of a <u>rate constant</u> on

18   temperature according to

19

20
$$E_a(T) = -R \frac{d\ln\{\frac{k(T)}{[k]}\}}{d(\frac{1}{T})}$$

21

22   as derived from the *Arrhenius equation*, $k(T) = A \exp(-E_A/RT)$, where A is the pre-

23   exponential factor and R the gas constant. As the argument of the ln function, k should

24   be divided by its units, i.e., by $[k]$.

25   *Note 1:* According to collision theory, the pre-exponential factor A is the frequency of

26   collisions with the correct orientation for reaction and E_a (or E_0) is the threshold energy

27   that collisions must have for the reaction to occur.

28   *Note 2*: The term Arrhenius activation energy is to be used only for the empirical

29   quantity as defined above. There are other empirical equations with different activation

30   energies, see [12].

31   See [13].

32   See also <u>enthalpy of activation</u>.

1
2
3 1   rev[3]
4
5 2
6 3   **energy profile**
7 4   See *Gibbs energy diagram*, *potential-energy profile*.
8
9 5   [3]
10
11 6
12 7   **enforced concerted mechanism**
13 8   Situation where a putative intermediate possesses a lifetime shorter than a bond
14 9   vibration, so that the steps become concerted.
15 10   See [195,196,197].
16 11   rev[3]
17
18 12
19 13   **enthalpy of activation (standard enthalpy of activation)**
20
21 14 $\Delta^{\ddagger}H^{\circ}$
22 15   (SI unit: kJ mol^{-1})
23 16   Standard enthalpy difference between the *transition state* and the ground state of the
24 17   reactants at the same temperature and pressure. It is related experimentally to the
25 18   temperature dependence of the *rate coefficient* k according to equation (1) for first-order
26 19   *rate constant*s:
27 20

21
$$\Delta^{\ddagger}H^{\circ} = -R \left\{ \frac{\partial \ln \left(\frac{k/s^{-1}}{T/K} \right)}{\partial \left(\frac{1}{T} \right)} \right\}_{P} \tag{1}$$

22

23   and to equation (2) for second order rate coefficients

24

25
$$\Delta^{\ddagger}H^{\circ} = -R \left\{ \frac{\partial \ln \left(\frac{k/(\text{mol dm}^3 \text{ s}^{-1})}{T/K} \right)}{\partial \left(\frac{1}{T} \right)} \right\}_{P} \tag{2}$$

26

27   This quantity can be obtained, along with the *entropy of activation* $\Delta^{\ddagger}S^{\circ}$, from the slope

28   and intercept of the linear least-squares fit of rate coefficients k to the equation

1

$$\ln\left(\frac{k/_{\mathrm{s}^{-1}}}{T/\mathrm{K}}\right) = \Delta^{\ddagger}S^{\mathrm{o}}/R - \Delta^{\ddagger}H^{\mathrm{o}}/RT + \ln[\ (k_{\mathrm{B}}/\mathrm{J\ K^{-1}})/(h/\mathrm{J\ s})\ ]$$

3   for a first-order rate coefficient

4   and

$$\ln\left(\frac{k/(\mathrm{mol\ dm^3\ s^{-1}})}{T/\mathrm{K}}\right) = \Delta^{\ddagger}S^{\mathrm{o}}/R - \Delta^{\ddagger}H^{\mathrm{o}}/R\ (1/T) + \ln[\ (k_{\mathrm{B}}/\mathrm{J\ K^{-1}})/(h/\mathrm{J\ s})\ ]$$

6

7   for a second-order rate coefficient where k_{B} is Boltzmann constant, h is Planck constant,

8   and $k_{\mathrm{B}}/h = 2.08366\ldots \times 10^{10}\ \mathrm{K^{-1}\ s^{-1}}$.

9   *Note 1*: An advantage of the least-squares fit is that it can also give error estimates

10 for $\Delta^{\ddagger}H^{\mathrm{o}}$ and $\Delta^{\ddagger}S^{\mathrm{o}}$.

11   *Note 2*: It is also given by

12

13     $\Delta^{\ddagger}H^{\mathrm{o}} = RT^2(\partial\ln k/[k]/\partial T)_{\mathrm{P}} - RT = E_{\mathrm{a}} - RT$

14

15     $\Delta^{\ddagger}H^{\mathrm{o}} = RT^2(\partial\ln\{k\}/\partial T)_{\mathrm{P}} - RT$

16

17 where E_{a} is the *energy of activation*, provided that the *rate coefficient*s for reactions

18 other than first-order are expressed in temperature-independent concentration units

19 (e.g., mol kg^{-1}, measured at a fixed temperature and pressure*)*. The argument in a

20 logarithmic function should be of dimension 1. Thus k is divided by its units, i.e., by [k],

21 as in the alternative form, in terms of reduced variables.

22   See also *entropy of activation*, *Gibbs energy of activation*.

23   See [12,13].

24   rev[3]

25

26 **entropy of activation**, **(standard entropy of activation)**

27 $\Delta^{\ddagger}S^{\mathrm{o}}$

28 (SI unit: J mol^{-1} K^{-1})

29 Standard entropy difference between the *transition state* and the *ground state* of the

30 reactants, at the same temperature and pressure. It is related to the *Gibbs energy of*

31 *activation* and *enthalpy of activation* by the equations

32

33     $\Delta^{\ddagger}S^{\mathrm{o}} = (\Delta^{\ddagger}H^{\mathrm{o}} - \Delta^{\ddagger}G^{\mathrm{o}})/T$

34

provided that *rate coefficient*s for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3}, measured at fixed temperature and pressure). The numerical value of S depends on the standard state (and therefore on the concentration units selected).

Note 1: It can also be obtained from the intercept of the linear least-squares fit of rate coefficients k to the equation

$$\ln(k/[k]/T[T]) = \Delta^{\ddagger}S^{o}/R - \Delta^{\ddagger}H^{o}/R \,(1/T) + \ln(k_B/h),$$

$$\ln(\{k\}/\{T\}) = \Delta^{\ddagger}S^{o}/R - \Delta^{\ddagger}H^{o}/R \,(1/T) + \ln(k_B/h),$$

where $k_B/h = 2.08366\ldots \times 10^{10}$ K^{-1} s^{-1}. k should be divided by its units, i.e., by $[k] = $ s^{-1} for first-order, and by $[k] = $ (s^{-1} mol^{-1} dm^{3}) for second-order rate coefficients and T should be divided by its units $[T] = $ K, as in the second equation, in terms of reduced variables..

Note 2: The information represented by the entropy of activation may alternatively be conveyed by the pre-exponential factor A, which reflects the fraction of collisions with the correct orientation for reaction (see *energy of activation*).

See [12,13].

rev[3]

epimer

Diastereoisomer that has the opposite *configuration* at only one of two or more tetrahedral *stereogenic centre*s in the respective *molecular entity*.

See [11].

[3]

epimerization

Interconversion of *epimer*s by reversal of the configuration at one of the *stereogenic centre*s.

See [11].

[3]

equilibrium, chemical

Situation in which reversible processes (processes that may be made to proceed in either the forward or reverse direction by the infinitesimal change of one variable) have reached a point where the rates in both directions are identical, so that the amount of each species no longer changes.

Note 1: In this situation the Gibbs energy, G, is a minimum. Also, the sum of the chemical potentials of the reactants equals that of the products, so that

$$\Delta_r G^{o} = -RT \ln K$$

1 where the thermodynamic equilibrium constant, K (of dimension 1), is the product of
2 product activities divided by the product of reactant activities.
3   *Note 2*: In dilute solutions the numerical values of the thermodynamic activities may
4 be approximated by the respective concentrations.
5   rev[3]
6

equilibrium control
7
8   See *thermodynamic control*.
9   [3]
10

11 **E_T-value**
12 See *Dimroth-Reichardt E_T parameter*, *Z-value*.
13   [3]
14

15 **excess acidity**
16 See *Bunnett-Olsen equations*, *Cox-Yates equation*.
17   [3]
18

19 **excimer** ("excited dimer")
20 *Complex* formed by the interaction of an *excited* molecular entity with another identical
21 molecular entity in its ground state.
22   *Note*: The complex is not stable in the ground state.
23   See [9].
24   See also *exciplex*.
25   [3]
26

27 **exciplex**
28 Electronically excited *complex* of definite stoichiometry that is non-bonding in the
29 ground state.
30   *Note*: An exciplex is a complex formed by the noncovalent interaction of an excited
31 *molecular entity* with the ground state of a different molecular entity, but an *excimer*,
32 formed from two identical components, is often also considered to be an exciplex.
33   See [9].
34   See also *excimer*.
35   [3]
36

37 **excited state**
38 Condition of a system with energy higher than that of the ground state. This term is
39 most commonly used to characterize a *molecular entity* in one of its electronically

1 excited states, but may also refer to vibrational and/or rotational excitation in the
2 electronic ground state.
3   See [9].
4   [3]
5

6 **EXSY** (NMR exchange spectroscopy)
7 Two-dimensional NMR technique producing cross peaks corresponding to site-to site
8 chemical exchange. The cross-peak amplitudes carry information about exchange
9 rates.
10   See [198].
11

12 **extended Hammett equation**
13 Multiparameter extension of the *Hammett equation* for the description of substituent
14 effects.
15   *Note 1*: The major extensions using two parameters (*dual substituent-parameter*
16 *equation*s) were devised for the separation of inductive and steric effects (*Taft equation*)
17 or of inductive (or field) and resonance effects.
18   *Note 2*: Other parameters may be added (polarizability, hydrophobicity…) when
19 additional substituent effects are operative.
20   See [191].
21   See also *Yukawa-Tsuno equation*.
22   [3]
23

24 **external return (external ion-pair recombination)**
25 Recombination of free ions formed in an S_N1 reaction (as distinguished from ion-pair
26 collapse).
27   See *ion-pair recombination*.
28   rev[3]
29

30 **extrusion**
31 *Transformation* in which an atom or *group* Y connected to two other atoms or groups X
32 and Z is lost from a molecule, leading to a product in which X is bonded to Z, i.e.,
33   X–Y–Z → X–Z + Y
34   *Example*

Note 1: When Y is a metal, this process is called a reductive elimination.

Note 2: The reverse of an extrusion is called an *insertion*.

See also *cheletropic reaction*.

[3]

field effect

Experimentally observable substituent effect (on reaction rates, etc.) of *intramolecular* electrostatic interaction between the centre of interest and a monopole or dipole, by direct electric-field action through space rather than through bonds.

Note 1: The magnitude of the field effect depends on the monopole charge or dipole moment, on the orientation of the dipole, on the distance between the centre of interest and the monopole or dipole, and on the effective dielectric constant that reflects how the intervening bonds are polarized.

Note 2: Although a theoretical distinction may be made between the field effect and the *inductive effect* as models for the Coulomb interaction between a given site and a remote monopole or dipole within the same entity, the experimental distinction between the two effects has proved difficult, because the field effect and the inductive effect are ordinarily influenced in the same direction by structural changes.

Note 3: The substituent acts through the electric field that it generates, and it is an oversimplification to reduce that interaction to that of a monopole or dipole.

See also *electronic effect*, *inductive effect*, *polar effect*.

See [172,191,199,200].

rev[3]

flash photolysis

Spectroscopic or kinetic technique in which an *ultraviolet*, *visible*, or *infrared* radiation pulse is used to produce transient species.

Note 1: Commonly, an intense pulse of short duration is used to produce a sufficient concentration of transient species, suitable for spectroscopic observation. The most common observation is of the absorption of the transient species (transient absorption spectroscopy).
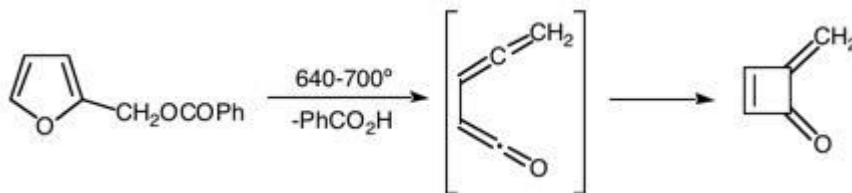
Note 2: If only photophysical processes are involved, a more appropriate term would be "pulsed photoactivation". The term "flash photolysis" would be correct only if chemical bonds are broken (the Greek "lysis" means dissolution or decomposition and in general lysis is used to indicate breaking). However, historically, the name has been used to describe the technique of pulsed excitation, independently of the process that follows the excitation.

See [9].

1　　**flash vacuum pyrolysis (FVP)**

2　　Thermal reaction of a molecule by exposure to a short thermal shock at high
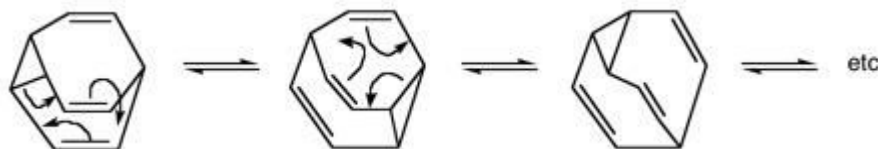
3　　temperature, usually in the gas phase.

4　　　*Example:*

5　　　See [201,202,203,204].

6　　　rev[3]

7

8　　**fluxionality**

9　　Property of a *chemical species* that undergoes rapid *degenerate rearrangement*s

10　　(generally detectable by methods that allow the observation of the behaviour of

11　　individual nuclei in a rearranged chemical species, e.g., NMR, X-ray).

12　　　*Example*: tricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (bullvalene), which has 1 209 600 (=

13　　10!/3) interconvertible arrangements of the ten CH groups.

14

15

16　　　*Note 1*: Fluxionality differs from *resonance*, where no rearrangement of nuclear

17　　positions occurs.

18　　　*Note 2*: The term is also used to designate positional change among *ligand*s of

19　　complex compounds and organometallics. In these cases the change is not necessarily

20　　degenerate.

21　　　See also *valence tautomerization*.

22　　　rev[3]

23

24　　**force-field calculations**

25　　　See *molecular mechanics calculation*.

26　　　GB

27

28　　**formal charge**

29　　Quantity (omitted if zero) attached to each atom in a *Lewis structure* according to

30

31　　　　$Z_{formal} = N_{valence} - N_{lonepairs} - \frac{1}{2} N_{bonds}$

32

1   *Examples*: $CH_2=N^+=N^-$, H_3O^+, $(CH_3)_2C=N-O^-$

2

3   *Note:* This formalism assumes that electrons in bonds are shared equally, regardless

4 of *electronegativity*.

5

6 Förster resonance-energy transfer (FRET)

7 dipole-dipole excitation transfer

8 Nonradiative mechanism for transfer of electronic excitation energy from one molecular

9 entity to another, distant one. It arises from the interaction between the *transition dipole*

10 *moment*s of the two entities.

11   See [9].

12

13 fractionation factor, isotopic

14 Ratio $[x_1(A)/x_2(A)]/[x_1(B)/x_2(B)]$, where x is the mole fraction of the isotope designated

15 by the subscript, when the two isotopes are equilibrated between two different *chemical*

16 *species* A and B (or between specific sites A and B in the same chemical species).

17   *Note 1*: The term is most commonly met in connection with deuterium solvent *isotope*

18 *effect*s, where the fractionation factor, symbolized by ϕ, expresses the ratio

19      $\phi = [x_D(solute)/x_H(solute)]/[x_D(solvent)/x_H(solvent)]$

20 for the exchangeable hydrogen atoms in the chemical species (or sites) concerned.

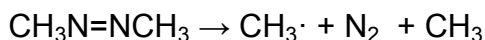21   *Note 2*: The concept is also applicable to *transition states*.
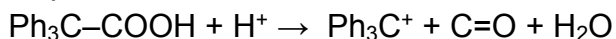
22   See [2].

23   [3]

24

25 fragmentation

26 (1) *Heterolytic* or *homolytic* cleavage of a molecule into more than two fragments,

27 according to the general reaction (where a, b, c, d, and X are atoms or groups of atoms)
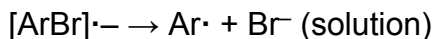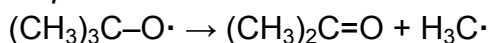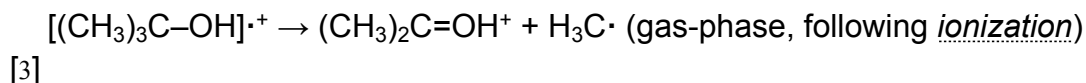
28

29      $a–b–c–d–X \rightarrow (a–b)^+ + c=d + X^-$

30 or $a–b–c–d–X \rightarrow (a–b)\cdot + c=d + X$

31   *Examples*:

32      $Ph_3C–COOH + H^+ \rightarrow Ph_3C^+ + C=O + H_2O$

33      $CH_3N=NCH_3 \rightarrow CH_3\cdot + N_2 + CH_3$

34   See [205].

35

36 (2) Breakdown of a radical or radical ion into a closed-shell molecule or ion and a

37 smaller radical

38   *Examples*:

39      $(CH_3)_3C–O\cdot \rightarrow (CH_3)_2C=O + H_3C\cdot$

40      $[ArBr]\cdot^- \rightarrow Ar\cdot + Br^-$ (solution)

1     $[(CH_3)_3C{-}OH]^{\cdot+} \rightarrow (CH_3)_2C{=}OH^+ + H_3C\cdot$ (gas-phase, following *ionization*)

2   [3]

3

Franck-Condon Principle

5   Approximation that an electronic transition is most likely to occur without change in

6   nuclear positions.

7   *Note 1*: The resulting state is called a Franck–Condon state, and the transition

8   involved is called a vertical transition.

9   *Note 2*: As a consequence, the intensity of a vibronic transition is proportional to the

10   square of the overlap integral between the vibrational wavefunctions of the two states

11   that are involved in the transition.

12   See [9].

13

free energy

15   The thermodynamic function Gibbs energy (symbol G) or Helmholtz energy (symbol A)

16   specifically defined as

17

18              $G = G(P,T) = H - TS$

19   and $A = A(V,T) = U - TS$

20

21   where H is enthalpy, U is internal energy, and S is entropy. The possibility of

22   spontaneous motion for a statistical distribution of an assembly of atoms (at absolute

23   temperature T above 0 K) is governed by free energy and not by potential energy.

24   *Note 1*: The IUPAC recommendation is to use the specific terms Gibbs energy or

25   Helmholtz energy whenever possible. However, it is useful to retain the generic term

26   "free energy" for use in contexts where the distinction between (on the one hand) either

27   Gibbs energy or Helmholtz energy and (on the other hand) potential energy is more

28   important than the distinction between conditions either of constant pressure or of

29   constant volume; e.g., in computational modelling to distinguish between results of

30   simulations performed for ensembles under conditions of either constant P or constant

31   V at finite T and calculations based purely on potential energy.

32   *Note 2*: Whereas motion of a single *molecular entity* is determined by the force acting

33   upon it, which is obtained as the negative gradient of the potential energy, motion for

34   an assembly of many molecular entities is determined by the mean force acting upon

35   the statistical distribution, which is obtained as the negative gradient of the *potential of*

36   *mean force*.

37

free radical

39   See *radical*.

40   [3]

1

frontier orbitals

Highest-energy Occupied Molecular Orbital (HOMO) and Lowest-energy Unoccupied Molecular Orbital (LUMO) of a *molecular entity*.

Note 1: These terms should be limited to doubly occupied orbitals, and not to a singly occupied molecular orbital (sometimes designated as a *SOMO*), because HOMO and LUMO are ambiguous for molecular orbitals that are half filled and thus only partly occupied or unoccupied.

Note 2: 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 theory of chemical behaviour.

Note 3: In some cases a *subjacent orbital* (*N*ext-to-*H*ighest *O*ccupied *M*olecular *O*rbital (NHOMO) or a *S*econd *L*owest *U*noccupied *M*olecular *O*rbital (SLUMO)) may affect reactivity.
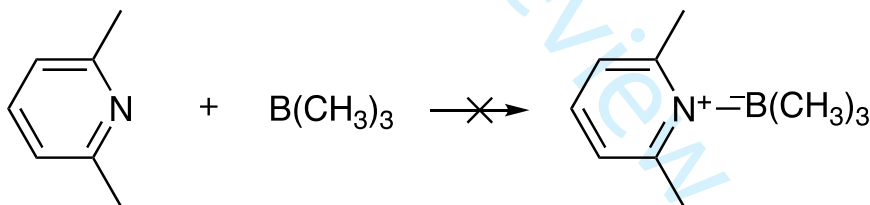
See [8,206,207].

See also *SOMO*, *subjacent orbital*.

rev[3]

frustrated Lewis acid-base pair

Acid and base for which *adduct* formation is prevented by *steric hindrance.*

See [208,209].

fullerene

Molecular entity composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube.

Note: Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes.

See [40,210].

functional group

Atom or group of atoms within *molecular entities* that are responsible for the characteristic *chemical reaction*s of those *molecular entities*. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the

molecule it is a part of. However, its relative reactivity can be modified by nearby *substituent*s.

rev[3]

gas-phase acidity

Standard reaction Gibbs energy ($\Delta_rG°$) change for the gas-phase reaction.
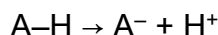
$$A–H \rightarrow A^- + H^+$$

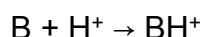*Note 1*: The symbol often found in the literature is $\Delta_{acid}G$ or GA.

Note 2: The corresponding enthalpy Δ_rH^o is often symbolized by $\Delta_{acid}H$ and called "enthalpy of acidity" or deprotonation enthalpy, abbreviated DPE.

See [211,212].

rev[3]

gas-phase basicity

Negative of the standard reaction Gibbs energy (Δ_rG^o) change for the gas-phase reaction

$$B + H^+ \rightarrow BH^+$$

Note: An acronym commonly used in the literature is GB. The corresponding enthalpy Δ_rH^o is called *proton affinity*, PA, even though affinity properly refers to Gibbs energy. Moreover, such acronyms are not accepted by IUPAC.

See [213,214].

rev[3]

Gaussian orbital

Function centred on an atom of the form $\phi(r) \propto x^i y^j z^k \exp(-\zeta r^2)$, used to approximate atomic orbitals in the LCAO-MO method.

See [8].

geminate pair

Pair of *molecular entities* in close proximity within a solvent cage and resulting from reaction (e.g., bond scission, electron transfer, group transfer) of a precursor.

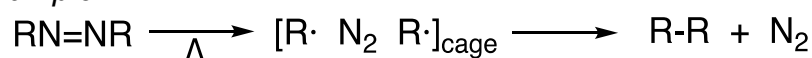*Note*: Because of the proximity the pair constitutes only a single kinetic entity.

See also *ion pair*, *radical pair*.

rev[3]

geminate recombination

Recombination reaction of a *geminate pair*.

Example:

$$RN=NR \xrightarrow{\Delta} [R\cdot \ N_2 \ R\cdot]_{cage} \longrightarrow R\text{-}R \ + \ N_2$$

1   rev[3]

2

3

4   **general acid catalysis**

5   *Catalysis* of a chemical reaction by *Brønsted acid*s (which may include the solvated

6   hydrogen ion), where the rate of the catalysed part of the reaction is given by $\Sigma_{HA}k_{HA}[HA]$

7   multiplied by some function of *substrate* concentrations.

8   *Note 1*: General acid catalysis can be experimentally distinguished from *specific*

9   *catalysis* by hydrogen cations (*hydron*s) if the *rate of reaction* increases with buffer

10   concentration at constant pH and ionic strength.

11   *Note 2*: The acid catalysts HA are unchanged by the overall reaction. This

12   requirement is sometimes relaxed, but the phenomenon is then properly called *pseudo-*

13   *catalysis*.

14   See also *catalysis*, *catalytic coefficient*, *intramolecular catalysis*, *pseudo-catalysis*,

15   *specific catalysis*.

16   rev[3]

17

18   **general base catalysis**

19   Catalysis of a *chemical reaction* by *Brønsted base*s (which may include the *lyate ion*),

20   where the rate of the catalysed part of the reaction is given by $\Sigma_{B}k_{B}[B]$ multiplied by

21   some function of *substrate* concentrations.

22   See also *general acid catalysis*.

23   [3]

24

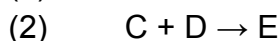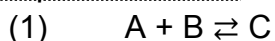25   **Gibbs energy diagram**

26   Diagram showing the relative standard Gibbs energies of reactants, *transition state*s,

27   reaction *intermediate*s, and products, in the same sequence as they occur in a *chemical*

28   *reaction*.

29   *Note 1*: The abscissa expresses the sequence of reactants, products, reaction

30   intermediates, and transition states and is often an undefined "reaction coordinate" or

31   only vaguely defined as a measure of progress along a reaction path. In some

32   adaptations the abscissas are however explicitly defined as *bond order*s, Brønsted
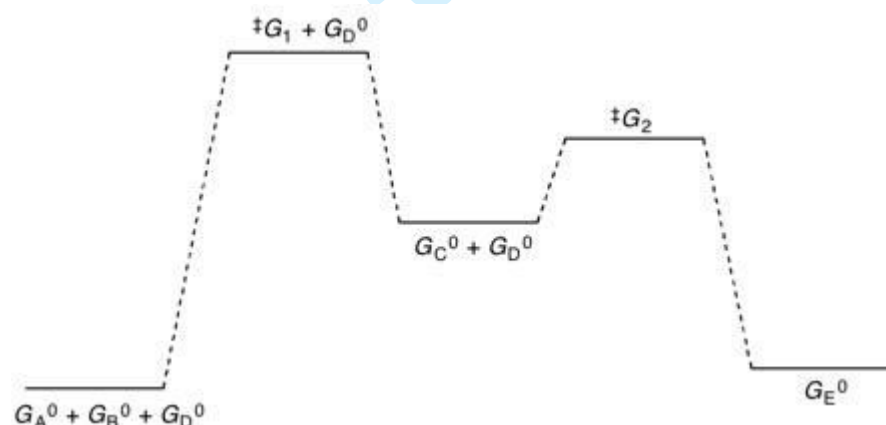
33   exponents, etc.

34   *Note 2*: These points are often connected by a smooth curve (a "Gibbs energy

35   profile", commonly referred to as a "free-energy profile", a terminology that is

36   discouraged), but experimental observation can provide information on relative

37   standard Gibbs energies only at the maxima and minima and not at the configurations

38   between them.

39   *Note 3*: It should be noted that the use of standard Gibbs energies implies a common

40   standard state for all chemical species (usually 1 M for reactions in solution). Contrary

1 to statements in many textbooks, the highest point on a Gibbs energy diagram does not
2 automatically correspond to the transition state of the *rate-limiting step*. For example,
3 in a stepwise reaction consisting of two elementary reaction steps
4   (1) $A + B \rightleftarrows C$
5   (2) $C + D \rightarrow E$
6 one of the two transition states must (in general) have a higher standard Gibbs energy
7 than the other. Under experimental conditions where all species have the standard-
8 state concentration, then the *rate-limiting step* is that whose transition state is of highest
9 standard Gibbs energy. However, under (more usual) experimental conditions where
10 all species do not have the standard-state concentration, then the value of the
11 concentration of D determines which reaction step is rate-limiting. However, if the
12 particular concentrations of interest, which may vary, are chosen as the standard state,
13 then the rate-limiting step is indeed the one of highest Gibbs energy.
14

15 $G_A^0 + G_B^0 + G_D^0$
16
17   See also *potential energy profile*, *potential-energy surface*, *reaction coordinate*.
18   rev[3]
19
20 **Gibbs energy of activation (standard free energy of activation)**
21 $\Delta^{\ddagger}G^{\circ}$
22 (SI unit: kJ mol^{-1})
23 Standard Gibbs energy difference between the *transition state* of an *elementary*
24 *reaction* and the ground state of the reactants for that step. It is calculated from the *rate*
25 *constant k* via the absolute rate equation:
26

27     $\Delta^{\ddagger}G^{\circ} = RT [\ln((k_B/\text{J K}^{-1})/(h/\text{J s})) - \ln(k/[k]/T/\text{K})]$

28

29     $\Delta^{\ddagger}G^{\circ} = RT [\ln(\{k_B\}/\{h\}) - \ln(\{k\}/\{T\})]$

30

where k_B is Boltzmann's constant, $[k]$ are the units of k, and h Planck's constant. The values of the rate constants, and hence the Gibbs energies of activation, depend upon the choice of concentration units (or of the thermodynamic standard state).

Note 1: For a complex *stepwise reaction*, composed of many elementary reactions, $\Delta^{\ddagger}G^{\circ}$, the observed Gibbs energy of activation (activation free energy), can be calculated as $RT\,[\ln(k_B/\mathrm{J\ K^{-1}})/(h/\mathrm{J\ s}) - \ln(k'/[k']/T/\mathrm{K})]$, where k' is the observed rate constant, k' should be divided by its units, and T/K is the absolute temperature, of dimension 1, since the argument of a logarithmic function should be of dimension 1, as expressed by the reduced variables in the second form of the equation.

Note 2: Both $\Delta^{\ddagger}G^{\circ}$ and k' are non-trivial functions of the rate constants and activation energies of the elementary steps.

See also *enthalpy of activation*, *entropy of activation*.

rev[3]

graphene

Allotrope of carbon, whose structure is a one-atom-thick planar sheet of sp^2-bonded carbon atoms in a honeycomb (hexagonal) crystal lattice.

ground state

State of lowest Gibbs energy of a system [2].

Note: In *photochemistry* and quantum chemistry the lowest-energy state of a chemical entity (ground electronic state) is usually meant.

See [9].

See also *excited state*.

rev[3]

group

See *functional group*, *substituent*.

rev[3]

Grunwald-Winstein equation

Linear Gibbs-energy relation (*Linear free-energy relation*)

$$\lg(k_S/k_0) = mY$$

expressing the dependence of the rate of solvolysis of a substrate on the ionizing power of the solvent, where the *rate constant* k_0 applies to the reference solvent (80:20 ethanol-water by volume) and k_S to the solvent S.

1 *Note 1*: The parameter *m* is characteristic of the substrate and is assigned the value
2 unity for *tert*-butyl chloride (2-chloro-2-methylpropane). The value *Y* is intended to be a
3 quantitative measure of the *ionizing power* of the solvent S.
4   *Note 2*: The equation was later extended [215] to the form
5
6     $\lg(k_S/k_0) = mY + lN$
7
8 where *N* is the *nucleophilicity* of the solvent and *l* a susceptibility parameter
9   *Note 3*: The equation has also been applied to reactions other than solvolysis.
10   *Note 4*: For the definition of other *Y*-scales, see [216,217,218,219].
11   See also *Dimroth-Reichardt E$_T$ parameter*, *polarity*.
12   rev[3]
13

14 **guest**
15 Organic or inorganic ion or molecule that occupies a cavity, cleft, or pocket within the
16 molecular structure of a *host molecular entity* and forms a *complex* with it or that is
17 trapped in a cavity within the crystal structure of a host, but with no covalent bond being
18 formed.
19   See also *crown ether*, *cryptand*, *inclusion compound*.
20   [3]
21

22 **half-life**
23 $t_{1/2}$
24 (SI unit: s)
25 Time required for the concentration of a particular reacting *chemical species* to fall to
26 one-half of its initial value.
27   *Note 1*: Half-life is independent of initial concentration only for a first-order process.
28   *Note 2*: For first-order reactions $t_{1/2} = \tau \ln 2$, where τ is the *lifetime*.
29   See also *lifetime*.
30   rev[3]
31

32 **halochromism**
33 Colour change that occurs on addition of *acid* or *base* to a solution of a compound as a
34 result of chemical reaction, or on addition of a salt as a result of changing the solvent
35 polarity.
36   See [220,221].
37   [3]
38

39 **halogen bond**

1 *Association* between a Lewis-acidic halogen atom in a *molecular entity* and a Lewis-
2 basic region in another, or the same, molecular entity, which acts as an electron-pair
3 donor, such that the balance of forces of attraction and repulsion results in net
4 stabilization.
5   *Note 1*: Typical halogen-bond donors are I_2, Br_2, ICN, and $IC\equiv CH$.
6   *Note 2*: This is analogous to a *hydrogen bond*, in which the H is the acidic atom.
7   *Note 3:* The interaction provides a stabilization of a few kJ mol^{-1}.
8   See [222,223,224,225].

9

10

11 **Hammett equation (Hammett relation)**
12 Equation of the form

13

14     $\lg \{k_X\} = \rho\, \sigma_X + \lg \{k_0\}$
15 or $\lg \{K_X\} = \rho\, \sigma_X + \lg \{K_0\}$

16

17 expressing the influence of *meta* and *para* substituents X on the reactivity of the
18 functional group Y in the benzene derivatives *m*- and *p*-XC_6H_4Y, where $\{k_X\}$ and $\{K_X\}$
19 are the numerical values of the rate or equilibrium constant, respectively, for the
20 reactions of *m*- and *p*-XC_6H_4Y, σ_X is the substituent constant characteristic of *m*- or *p*-
21 X, and ρ is the reaction constant characteristic of the given reaction of Y. The values $\lg$
22 $\{k_0\}$ and $\lg \{K_0\}$ are intercepts for graphical plots of $\lg \{k_X\}$ or $\lg \{K_X\}$, respectively, against
23 σ_X for all substituents X (including X = H, if present).
24   *Note* 1: It is very common in the literature to find either of these equations written
25 without the curly brackets denoting a reduced rate or equilibrium constant, i.e., *k* or *K*
26 divided by its unit, [*k*] or [*K*], respectively.
27   *Note* 2: The Hammett equation is most frequently used to obtain the value of ρ which,
28 as the slope of a graph or least-squares fit, is independent of the choice of units for k_X
29 or K_X. If the equation is used to estimate the unknown value of a rate or equilibrium
30 constant for an X-substituted compound based upon the known value of σ_X, the ordinate
31 must be multiplied by [k_X] or [K_X] in order to obtain the value with its appropriate units.
32   *Note 3:* The equation is often encountered in a form with k_H or K_H incorporated into
33 the logarithm on the left-hand side, where k_H or K_H corresponds to the reaction of parent
34 C_6H_5Y, with X = H;

35

36     $\lg(k_X/k_H) = \rho\, \sigma_X$
37 or $\lg(K_X/K_H) = \rho\, \sigma_X$

38

39 This form satisfies the requirement that arguments of the lg function must be of
40 dimension 1, but it would suggest a one-parameter linear least-squares fit, whereas lg

1   k_0, lg K_0, lg $k_0/[k_0]$ and lg $K_0/[K_0]$, in the other forms correctly represent the intercept in

2   a two-parameter linear least-squares fit of lg k, lg K, lg $k/[k]$, or lg $K/[K]$ vs. σ_X.

3   See [21,22,126,191,226].

4   See also *extended Hammett equation*, *Taft equation*, *Yukawa-Tsuno equation*, *σ-*

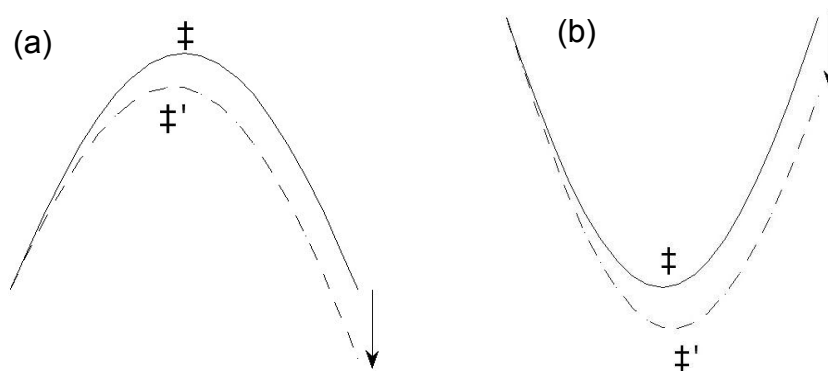5   *constant*, *ρ-value*.

6   rev[3]

7

8

9

10

11   **Hammond postulate (Hammond-Leffler principle)**

12   Hypothesis that, when a *transition state* leading to a high-energy reaction *intermediate*

13   (or product) has nearly the same energy as that intermediate (or product), the two are

14   interconverted with only a small reorganization of molecular structure.

15   *Note 1:* Essentially the same idea is sometimes referred to as "Leffler's assumption",

16   namely, that the *transition state* bears a greater resemblance to the less stable species

17   (reactant or reaction intermediate/product). Many textbooks and physical organic

18   chemists, however, express the idea in Leffler's form (couched in terms of Gibbs

19   energies) but attribute it to Hammond (whose original conjecture concerns structure).

20   *Note 2:* As a corollary, it follows that a factor stabilizing a reaction *intermediate* will

21   also stabilize the *transition state* leading to that *intermediate*.

22   *Note 3*: If a factor stabilizes a reaction intermediate (or reactant or product), then the

23   position of the transition state along the *minimum-energy reaction path* (MERP) for that

24   elementary step moves away from that intermediate, as shown in the energy diagram

25   (a) below left, where the transition state moves from ‡ to ‡' when the species to the

26   right is stabilized. This behaviour is often called a Hammond effect and is simply a

27   consequence of adding a linear perturbation to the parabola.

28

(a)   ‡   (b)

‡'

‡

‡'

29

30   *Note 4:* If a structure lying off the MERP is stabilized, then the position of the

31   *transition state* moves toward that structure, as shown in the energy diagram (b) above

right, where the transition state moves from ‡ to ‡'. This behaviour is often called anti-Hammond and arises because the transition state is a maximum along the MERP but a minimum perpendicular to it.

See [227,228,229,230].

See *Leffler's relation*, *More O'Ferrall – Jencks diagram*, *parallel effect*, *perpendicular effect*.

rev[3]

Hansch constant

Measure of the contribution of a substituent to the *partition ratio* of a solute, defined as

$$\pi_X = \lg(P_X/P_H)$$

where P_X is the partition ratio for the compound with substituent X and P_H is the partition constant for the parent.

See [231,232].

rev[3]

hapticity

Topological description for the number of contiguous atoms of a *ligand* that are bonded to a central metal atom.

Note: The hapticity is indicated as a superscript following the Greek letter η.

Example: $(C_5H_5)_2Fe$ (ferrocene) = bis(η^5-cyclopentadienyl)iron, where η^5 can be read as eta-five or pentahapto.

See [29].

hard acid, base

Lewis acid with an acceptor centre or *Lewis base* with a donor centre (e.g., an oxygen atom) of low *polarizability*.

Note 1: A high polarizability characterizes a soft acid or base.

Note 2: Whereas the definition above is qualitative, a theoretically consistent definition of hardness η, in eV, is as half the second derivative of the calculated energy E with respect to N, the number of electrons, at constant potential v due to the nuclei.

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v$$

1
2
3   1   *Note 3*: Other things being equal, complexes of hard acids with hard bases or of soft
4
5   2   acids with soft bases have an added stabilization (sometimes called the HSAB rule).
6   3   For limitations of the HSAB rule, see [36,233].
7
8   4   See [234,235,236].
9   5   rev[3]
10
11   6
12
13   7   **HBA solvent**
14   8   Strongly or weakly basic solvent capable of acting as a *hydrogen-bond* acceptor (HBA)
15   9   and forming strong intermolecular solute-solvent hydrogen bonds.
16
17   10   *Note:* A solvent that is not capable of acting as a hydrogen-bond acceptor is called
18   11   a non-HBA solvent.
19
20   12   See [17].
21   13
22
23   14   **HBD solvent** (*Hydrogen-Bond* Donating solvent, also *dipolar HBD solvent* and *protic*
24   15   *solvent*)
25
26   16   Solvent with a sizable permanent dipole moment that bears suitably acidic hydrogen
27   17   atoms to form strong intermolecular solvent-solute hydrogen bonds.
28
29   18   *Note:* A solvent that is not capable of acting as hydrogen-bond donor is called a *non-*
30   19   *HBD solvent* (formerly aprotic solvent).
31   20   See [17,155].
32
33   21
34   22   **heat capacity of activation**
35   23 $C_P^{\ddagger}$
36
37   24   (SI unit: J mol^{-1} K^{-1})
38   25   Temperature coefficient of $\Delta^{\ddagger}H$ (*enthalpy of activation*) or $\Delta^{\ddagger}S$ (*entropy of activation*) at
39   26   constant pressure according to the equations:
40   27
41   28 $C_P^{\ddagger} = (\partial\Delta^{\ddagger}H/\partial T)_P = T(\partial\Delta^{\ddagger}S/\partial T)_P$
42   29
43   30   See [237].
44   31   rev[3]
45   32
46
47   33   **Henderson-Hasselbalch equation**
48   34   Equation of the form
49   35
50   36 $\mathrm{pH} = \mathrm{p}K_a - \lg([HA]/[A^-])$
51   37
52   38   relating the pH of a buffer solution to the ratio [HA]/[A$^-$] and the dissociation constant of
53   39   the acid K_a.
54   40   See [238].
55
56
57
58
59
60

1 rev[3]

2

heterobimetallic complex

Metal complex having two different metal atoms or ions.
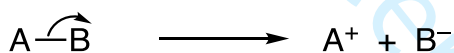
rev[3]

heteroleptic

Characteristic of a transition metal or Main Group compound having more than one type of *ligand*.

See also *homoleptic*.

[3]

heterolysis, heterolytic bond fission

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.,

$$A \overset{\frown}{-} B \longrightarrow A^+ + B^-$$

See also *heterolytic bond-dissociation energy*, *homolysis*.

[3]

heterolytic bond-dissociation energy

Energy required to break a given *bond* of a specific compound by *heterolysis*.

Note: For the *dissociation* of a neutral molecule AB in the gas phase into A^+ and B^- the heterolytic *bond-dissociation energy* $D(A^+B^-)$ is the sum of the homolytic bond-dissociation energy, $D(A–B)$, and the adiabatic *ionization* energy of the radical A· minus the electron affinity of the radical B·.

[3]

high-throughput screening

Automated method to quickly assay large libraries of *chemical species* for the affinity of small organic molecules toward a target of interest.

Note: Currently more than 10^5 different compounds can be tested per day.

See [239].

highest occupied molecular orbital (HOMO)

Doubly filled molecular orbital of highest energy.

Note: Examination of the HOMO can predict whether an *electrocyclic reaction* is *conrotatory* or *disrotatory*.

See also *frontier orbitals*.

1 **Hildebrand solubility parameter** [symbol δ, derived unit: $Pa^{1/2} = (kg\ m^{-1}\ s^{-2})^{1/2}$]

2 Ability of a solvent to dissolve a non-electrolyte, defined as the square root of the

3 solvent's cohesive energy density (also called cohesive pressure, equal to the energy

4 of vaporization divided by the solvent's molar volume and corresponding to the energy

5 necessary to create a cavity in the solvent).

6   See [240].

7 rev[3]

8

9 **Hofmann rule**

10 Observation that when two or more alkenes can be produced in a *β-elimination* reaction,

11 the alkene having the smallest number of alkyl groups attached to the double bond

12 carbon atoms is the predominant product.

13   *Note:* This orientation is observed in elimination reactions of quaternary ammonium

14 salts and tertiary sulfonium (sulfanium) salts, and in certain other cases where there is

15 steric hindrance.

16   See [241].

17   See also *Saytzeff rule*.

18 rev[3]

19

20 **HOMO**

21 (1) Acronym for **H**ighest **O**ccupied **M**olecular **O**rbital.

22   See also *frontier orbitals*.

23 (2) Prefix (in lower case) used to indicate a higher homologue of a compound, as

24 homocysteine for $HSCH_2CH_2CH(NH_2)COOH$, the homologue of cysteine,

25 $HSCH_2CH(NH_2)COOH$.

26   rev[3]

27

28 **homoaromatic**

29 Showing features of *aromaticity* despite a formal discontinuity in the overlap of a cyclic

30 array of p orbitals resulting from the presence of an sp^3-hybridized atom at one or

31 several positions within the cycle, in contrast to an *aromatic* molecule, where there is a

32 continuous overlap of p orbitals over a cyclic array.

33   *Note 1:* Homoaromaticity arises because p-orbital overlap can bridge an sp^3 centre.

34   *Note 2:* Pronounced homoaromaticity is not normally associated with neutral

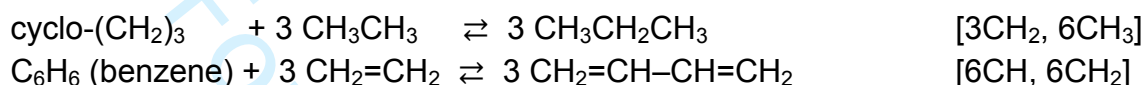35 molecules, but mainly with ionic species, e.g., the "homotropylium" cation, $C_8H_9^+$,

36

1   *Note 3:* In bis-, tris-, (etc.) homoaromatic species, two, three, (etc.) single sp^3 centres
2 separately interrupt the π-electron system.
3   [3]
4

homodesmotic reaction
6 Subclass of *isodesmic* reactions in which reactants and products contain not only the
7 same number of carbon atoms in each state of hybridization but also the same number
8 of each CH_n group joined to *n* hydrogen atoms.
9   *Examples:*
10

11   cyclo-$(CH_2)_3$ + 3 CH_3CH_3 ⇌   3 $CH_3CH_2CH_3$ [3CH_2, 6CH_3]
12   C_6H_6 (benzene) + 3 CH_2=CH_2 ⇌ 3 CH_2=CH–CH=CH_2 [6CH, 6CH_2]
13

14   *Note:* The definition may be extended to molecules with heteroatoms.
15   See [8].
16   rev[3]
17

homoleptic
19 Characteristic of a transition-metal or Main Group compound having only one type of
20 *ligand*, e.g., $Ta(CH_3)_5$
21   See also *heteroleptic*.
22   [3]
23

homolysis
25 Cleavage of a *bond* so that each of the molecular fragments between which the bond
26 is broken retains one of the bonding electrons.
27   *Note 1:* A *unimolecular* reaction involving homolysis of a bond not forming part of a
28 cyclic structure in a *molecular entity* containing an even number of (paired) electrons
29 results in the formation of two radicals:

$$A\text{—}B \longrightarrow A^\bullet + B^\bullet$$

30
31   *Note 2:* Homolysis is the reverse of *colligation*.
32   See also *bond dissociation energy*, *heterolysis*.
33   [3]
34

host
36 *Molecular entity* that forms *complex*es (*adduct*s) with organic or inorganic guests, or a
37 chemical species that can accommodate guests within cavities of its crystal structure.
38   Examples include *cryptands* and *crown ethers* (where there are ion/dipole attractions
39 between heteroatoms and cations), *hydrogen-bonded* molecules that form clathrates

1
2
3   1   (e.g., hydroquinone or water), and host molecules of *inclusion compounds* (e.g., urea
4   2   or thiourea), where *intermolecular* forces and *hydrophobic interaction*s bind the guest
5   3   to the host molecule.
6   4   rev[3]
7
8   5
9
10   6   **Hückel molecular orbital (HMO) theory**
11   7   Simplest molecular orbital theory of π-conjugated molecular systems. It uses the
12   8   following approximations: π-electron approximation; LCAO representation of the π
13   9   molecular orbitals; neglect of electron-electron and nuclear-nuclear repulsions. The
14   10   diagonal elements of the effective Hamiltonian (Coulomb integrals) and the off-diagonal
15   11   elements for directly bonded atoms (resonance integrals) are taken as empirical
16   12   parameters, all overlap integrals being neglected.
17   13   See [8].
18   14   rev[3]
19
20   15
21
22   16   **Hückel ($4n + 2$) rule**
23   17   Principle that monocyclic planar (or almost planar) systems of trigonally (or sometimes
24   18   digonally) hybridized atoms that contain ($4n + 2$) π electrons (where n is an integer,
25   19   generally 0 to 5) exhibit *aromatic* character.
26   20   *Note 1:* This rule is derived from *Hückel MO theory* calculations on planar monocyclic
27   21   conjugated hydrocarbons $(CH)_m$ where integer m is at least 3, according to which ($4n +$
28   22   2) electrons are contained in a closed-shell system.
29   23   *Examples:*
30
31

Cyclopropenyl cation   Cyclopentadienide anion   Benzene
($m = 3$, $n = 0$)   ($m = 5$, $n = 1$)   ($m = 6$, $n = 1$)

32   24

33   25   *Note 2:* Planar systems containing $4n$ π electrons (such as cyclobutadiene and
34   26   cyclopentadienyl cation) are antiaromatic.
35   27   *Note 3:* Cyclooctatetraene, with 8 π electrons, is nonplanar and therefore neither
36   28   aromatic nor antiaromatic but nonaromatic.
37   29   See [8].
38   30   See also *conjugation*, *Möbius aromaticity*.
39   31   rev[3]
40
41   32
42
43   33   **hybrid orbital**
44   34   Atomic orbital constructed as a linear combination of *atomic orbital*s on an atom.

Note 1: Hybrid orbitals are often used to describe the bonding in molecules containing tetrahedral (sp^3), trigonal (sp^2), and digonal (sp) atoms, whose σ bonds are constructed using 1:3, 1:2, or 1:1 combinations, respectively, of s and p atomic orbitals.

Note 2: Construction of hybrid orbitals can also include d orbitals, as on an octahedral atom, with d^2sp^3 hybridization.

Note 3: Integer ratios are not necessary, and the general hybrid orbital made from s and p orbitals can be designated as sp^{λ}.

hydration

Addition of water or of the elements of water (i.e., H and OH) to a *molecular entity* or to a *chemical species*.

Example: hydration of ethene:

$$CH_2=CH_2 + H_2O \rightarrow CH_3CH_2OH$$

Note: In contrast to *aquation*, hydration, as in the incorporation of waters of crystallization into a protein or in the formation of a layer of water on a nonpolar surface, does not necessarily require bond formation.

See [48].

See also *aquation*.

rev[3]

hydrogen bond

An attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.

Note 1: Both electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e., N, O, or F.

Note 2: A hydrogen bond is largely an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges.

Note 3: Hydrogen bonds may be *intermolecular* or *intramolecular*.

Note 4: With few exceptions, usually involving hydrogen fluoride and fluoride and other ions, the associated energies are less than 20-25 kJ mol^{-1}.

Note 5: Hydrogen bonds are important for many chemical structures, giving rise to the attraction between H_2O molecules in water and ice, between the strands of DNA, and between aminoacid residues in proteins.

See [242,243].

rev[3]

hydrolysis

Solvolysis by water, generally involving the rupture of one or more bonds in the reactant and involvement of water as *nucleophile* or base.

1   *Example:* $CH_3C(=O)OCH_2CH_3 + H_2O \rightarrow CH_3C(=O)OH + CH_3CH_2OH$

2   rev[3]

3

4   **hydron**

5   General name for the ion H^+ either in natural abundance or where it is not desired to

6   distinguish between the isotopes, as opposed to proton for $^1H^+$, deuteron for $^2H^+$ and

7   triton for $^3H^+$.

8   See [244].

9   [3]

10

11   **hydronation**

12   Attachment of the ion H^+ either in natural abundance or where it is not desired to

13   distinguish between the isotopes.

14

15   **hydrophilicity**

16   Capacity of a *molecular entity* or of a *substituent* to undergo stabilizing interactions with

17   polar solvents, in particular with water and aqueous mixtures, to an extent greater than

18   with a nonpolar solvent.

19   rev[3]

20

21   **hydrophobic interaction**

22   Tendency of *lipophilic* hydrocarbon-like groups in solutes to form *intermolecular*

23   aggregates in an aqueous *medium*.

24   *Note:* The name arises from the attribution of the phenomenon to the apparent

25   repulsion between water and hydrocarbons. However, the phenomenon is more

26   properly attributed to the effect of the hydrocarbon-like groups to avoid disrupting the
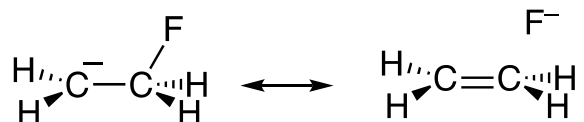
27   favorable water-water interactions.

28   [3]

29

30   **hyperconjugation**

31   *Delocalization* of electrons between σ bonds and a π network.

32   *Note 1:* The concept of hyperconjugation is often applied to *carbenium ion*s and

33   *radical*s, where the interaction is between σ bonds and an unfilled or partially filled p or

34   π orbital. *Resonance* illustrating this for the *tert*-butyl cation is:

35

Note 2: A distinction is made between positive hyperconjugation, as above, and negative hyperconjugation, where the interaction is between a filled σ or π orbital and adjacent antibonding σ^* orbitals, as for example in the fluoroethyl anion (2-fluoroethan-1-ide).

Note 3: Historically, conjugation involves only π bonds, and hyperconjugation is considered unusual in involving σ bonds.

See [245,246,247,248].

See also *σ, π, delocalization*.

rev[3]

hypercoordinated

Feature of a main-group atom with a *coordination number* greater than four.

Example: the pentacoordinate carbon in the *carbonium ion* CH_5^+, where three C–H bonds may be regarded as two-electron bonds and the two electrons in the remaining CH_2 fragment are delocalized over three atoms. Likewise, both hydrogens in the CH_2 fragment are hypercoordinated.

See [2,8].

See also *agostic.*

rev[3]

hypervalency

Ability of an atom in a *molecular entity* to expand its valence shell beyond the limits of the Lewis octet rule.

Examples: PF_5, SO_3, iodine(III) compounds, and pentacoordinate carbocations (*carbonium ion*s).

Note: Hypervalent compounds are more common for the second- and subsequent-row elements in groups 15-18 of the periodic table. A proper description of the hypervalent bonding implies a transfer of electrons from the central (hypervalent) atom to the nonbonding molecular orbitals of the attached *ligand*s, which are usually more electronegative.

See [8].

See also *valence*.

rev[3]

hypsochromic shift

1 Shift of a spectral band to higher frequency (shorter wavelength) upon substitution or
2 change in medium.
3   *Note:* This is informally referred to as a blue shift and is opposite to a *bathochromic*
4 *shift* ("red shift"), but these historical terms are discouraged because they apply only to
5 visible transitions.
6   See [9].
7   rev[3]

8

identity reaction
9

10 *Chemical reaction* whose products are chemically identical with the reactants
11   *Examples*:
12   (i)   bimolecular exchange reaction of CH_3I with I^-
13   (ii) proton transfer between NH_4^+ and NH_3
14   (iii) electron transfer between manganate(VI) MnO_4^{2-} and permanganate MnO_4^-.
15   See also *degenerate rearrangement*.
16   rev[3]

17

imbalance
18

19 Feature that reaction parameters characterizing different bond-forming or bond-
20 breaking processes in the same reaction change to different extents as the *transition*
21 *state* is approached (along some arbitrarily defined reaction path).
22   *Note*: Imbalance is common in reactions such as elimination, addition, and other
23 complex reactions that involve proton (*hydron*) transfer.
24   *Example*: the nitroalkane anomaly, where the Brønsted β exponent for hydron
25 removal is smaller than the Brønsted α for the nitroalkane as acid, because of
26 imbalance between the extent of bond breaking and the extent of resonance
27 delocalization in the transition state.
28   See [249].
29   See also *Brønsted relation*, *synchronization (principle of nonperfect*
30 *synchronization)*, *synchronous*.
31   rev[3]

32

inclusion compound (inclusion complex)
33

34 *Complex* in which one component (the *host*) forms a cavity or, in the case of a crystal,
35 a crystal lattice containing spaces in the shape of long tunnels or channels in which
36 molecular entities of a second *chemical species* (the *guest*) are located.
37   *Note*: There is no covalent bonding between guest and host, the attraction being
38 generally due to *van der Waals forces*. If the spaces in the host lattice are enclosed on
39 all sides so that the guest species is "trapped" as in a *cage*, such compounds are known
40 as clathrates or cage compounds".

1   See [40].

2   [3]

3

4 **induction period**

5 Initial slow phase of a *chemical reaction* whose rate later accelerates.

6   *Note*: Induction periods are often observed with radical reactions, but they may also

7 occur in other reactions, such as those where a steady-state concentration of the

8 reactants is not established immediately.

9   See [13].

10   [3]

11

12 **inductive effect**

13 Experimentally observable effect (on rates of reaction, etc.) of a *substituent* through

14 transmission of charge through a chain of atoms by electrostatics.

15   *Note*: Although a theoretical distinction may be made between the *field effect* and

16 the inductive effect as models for the Coulomb interaction between a given site within

17 a *molecular entity* and a remote monopole or dipole within the same entity, the

18 experimental distinction between the two effects has proved difficult (except for

19 molecules of peculiar geometry, which may exhibit "reversed field effects"), because

20 the inductive effect and the field effect are ordinarily influenced in the same direction by

21 structural changes.

22   See [171,172,250].

23   See also *field effect*, *polar effect*.

24   rev[3]

25

26 **inert**

27 *Stable* and *unreactive* under specified conditions.

28   [3]

29

30 **inhibition**

31 Decrease in *rate of reaction* brought about by the addition of a substance (inhibitor), by

32 virtue of its effect on the concentration of a reactant, *catalyst*, or reaction *intermediate*.

33   For example, molecular oxygen or 1,4-benzoquinone can act as an inhibitor in many

34 chain reactions involving *radical*s as intermediates by virtue of its ability to act as a

35 *scavenger* toward those radicals.

36   *Note*: If the rate of a reaction in the absence of inhibitor is v_o and that in the presence

37 of a certain amount of inhibitor is v, the degree of inhibition (i) is given by

38

39     $i = (v_o - v)/v_o$

40

1   See also *mechanism-based inhibition*.

2   [3]

3

initiation

5   Reaction or process generating *radical*s (or some other reactive reaction *intermediate*s)
6   which then induce a *chain reaction* or catalytic cycle.
7   *Example*: In the chlorination of alkanes by a radical mechanism the initiation step
8   may be the *dissociation* of molecular chlorine.
9   rev[3]

10

inner-sphere (electron transfer)
12 Feature of an electron transfer between two metal centres that in the transition state
13 share a *ligand* or atom in their coordination shells.
14   *Note*: The definition has been extended to any situation in which the interaction
15 between the electron-donor and electron-acceptor centres in the *transition state* is
16 significant (>20 kJ mol^{-1}).
17   See [9].
18   See also *outer-sphere electron transfer*.
19   [3]

20

insertion
22 *Chemical reaction* or *transformation* of the general type

23

24   X–Z + Y $\rightarrow$ X–Y–Z

25

26 in which the connecting atom or *group* Y replaces the bond joining the parts X and Z of
27 the reactant XZ.
28   *Example*: *carbene* insertion reaction

29

30      $R_3C–H + H_2C\colon \rightarrow R_3C–CH_3$

31

32   *Note*: The reverse of an insertion is called an *extrusion*.
33   [3]

34

intermediate (reactive intermediate)
36 *Molecular entity* in a stepwise chemical reaction with a *lifetime* appreciably longer than
37 a molecular vibration (corresponding to a local potential energy minimum of depth
38 greater than *RT*, and thus distinguished from a *transition state*) that is formed (directly
39 or indirectly) from the reactants and reacts further to give (directly or indirectly) the
40 products of a chemical reaction.

1   See also *elementary reaction*, *reaction step*, *stepwise reaction*.

2   [3]

3

4   **intermolecular**

5   (1) Descriptive of any process that involves a transfer (of atoms, *group*s, electrons, etc.)

6   or interactions between two or more *molecular entities*.

7   (2) Relating to a comparison between different molecular entities.

8   See also *intramolecular*.

9   [3]

10

11 **internal return**

12 See *ion-pair recombination*.

13 rev[3]

14

15 **intramolecular**

16 (1) Descriptive of any process that involves a transfer (of atoms, *group*s, electrons, etc.)

17 or interactions between different parts of the same *molecular entity*.

18 (2) Relating to a comparison between different groups within the same molecular entity.

19 See also *intermolecular*.

20 [3]

21

22 **intramolecular catalysis**

23 Acceleration of a chemical transformation at one site of a *molecular entity* through the

24 involvement of another *functional* ("catalytic") *group* in the same molecular entity,

25 without that group appearing to have undergone change in the reaction product.

26 *Note 1:* The use of the term should be restricted to cases for which analogous

27 intermolecular catalysis by a *chemical species* bearing that catalytic group is

28 observable.

29 *Note 2:* Intramolecular catalysis can be detected and expressed in quantitative form

30 by a comparison of the reaction rate with that of a comparable model compound in

31 which the catalytic group is absent, or by measurement of the *effective molarity* of the

32 catalytic group.

33 See also *effective molarity*, *neighbouring group participation*.

34 [3]

35

36 **intrinsic barrier, $\Delta^{\ddagger}G_0$**

37 *Gibbs energy of activation* in the limiting case where $\Delta_r G^o = 0$, i.e., when the effect of

38 thermodynamic driving force is eliminated, as in an identity reaction, $X^* + AX \rightarrow X^*A +$

39 X, where A may be an atom, ion, or group of atoms or ions, and where the *equilibrium*

40 constant K is equal to 1.

1　　　1　　*Note:* According to the *Marcus equation*, originally developed for outer-sphere
2　　　2　　electron transfer reactions, the intrinsic barrier is related to λ, the *reorganization energy*
3　　　3　　of the reaction, by the equation
4
5　　　4
6　　　5　　　　$\Delta^{\ddagger}G^{\circ} = \lambda/4$
7
8　　　6
9
10　　 7　　For a non-identity reaction, $Y + AX \rightarrow YA + X$, the intrinsic barrier $\Delta^{\ddagger}G^{\circ}(Y,X)$ is estimated
11
12　　 8　　as $\frac{1}{2}[\Delta^{\ddagger}G(X,X) + \Delta^{\ddagger}G(Y,Y)]$, where the latter two terms are the Gibbs energies of
13　　 9　　activation of the identity reactions $X^* + AX \rightarrow X^*A + X$ and $Y^* + AY \rightarrow Y^*A + Y$,
14　　10　　respectively.
15
16　　11　　　See [251,252,253,254].
17　　12　　　rev[3]
18
19　　13
20
21　　14　　**intrinsic reaction coordinate (IRC)**
22　　15　　Minimum-energy path leading from the saddle point (corresponding to the *transition*
23　　16　　*structure*) on the *potential-energy surface* for an *elementary reaction*, obtained by
24
25　　17　　tracing the steepest descent in mass-weighted coordinates in both directions.
26　　18　　　*Note*: The IRC is mathematically well defined, in contrast to the (generally) vague
27　　19　　*reaction coordinate*. Strictly, the IRC is a specific case of a *minimum-energy reaction*
28
29　　20　　*path*, and its numerical value at any point along this path is usually taken to be zero at
30　　21　　the saddle point, positive in the direction of the products, and negative in the direction
31　　22　　of the reactants.
32
33　　23　　　See [8,255].
34　　24　　　rev[3]
35　　25
36
37　　26　　**inverted micelle (reverse micelle)**
38　　27　　Association colloid formed reversibly from surfactants in non-polar solvents, leading to
39
40　　28　　aggregates in which the polar *group*s of the surfactants are concentrated in the interior
41　　29　　and the *lipophilic* groups extend toward and into the non-polar solvent.
42　　30　　　*Note:* Such association is often of the type
43　　31　　　　Monomer $\rightleftarrows$ Dimer $\rightleftarrows$ Trimer $\rightleftarrows$ $\cdots$ $\rightleftarrows$ *n*-mer
44
45　　32　　and a *critical micelle concentration* is consequently not observed.
46　　33　　　[3]
47　　34
48
49　　35　　**ion pair**
50　　36　　Pair of oppositely charged ions held together by coulomb attraction without formation
51　　37　　of a *covalent bond*.
52
53　　38　　　*Note 1:* Experimentally, an ion pair behaves as one unit in determining conductivity,
54　　39　　kinetic behaviour, osmotic properties, etc.
55
56
57
58
59
60

1   *Note 2:* Following Bjerrum, oppositely charged ions with their centres closer together
2   than a distance

3

4    $$d = \frac{Z_+ Z_- e^2}{4\pi\varepsilon_0\varepsilon_r k_B T}$$

5

6   are considered to constitute an ion pair. Here Z_+ and Z_- are the charge numbers of the
7   ions, e is the elementary charge, ε_0 is the vacuum permittivity, ε_r is the relative
8   *permittivity* ("dielectric constant") of the medium, k_B is Boltzmann's constant, and T is
9   the absolute temperature. This is the distance at which the Coulomb energy equals the
10   thermal energy, and $e^2/(4\pi\varepsilon_0 k_B)$ is approximately equal to 1.671×10^{-5} m K^{-1}.
11   *Note 3:* An ion pair, the constituent ions of which are in direct contact (and not
12   separated by intervening solvent or by other neutral molecule) is designated as a "tight
13   ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of R$^+$ and X$^-$ is symbolically
14   represented as R$^+$X$^-$.
15   *Note 4:* By contrast, an ion pair whose constituent ions are separated by one or
16   several solvent or other neutral molecules is described as a "loose ion pair",
17   symbolically represented as R$^+$||X$^-$. The components of a loose ion pair can readily
18   interchange with other free or loosely paired ions in the solution. This interchange may
19   be detectable (e.g., by isotopic labelling) and thus afford an experimental distinction
20   between tight and loose ion pairs.
21   *Note 5:* A further conceptual distinction has sometimes been made between two
22   types of loose ion pairs. In "solvent-shared ion pairs" for which the ionic constituents of
23   the pair are separated by only a single solvent molecule, whereas in "solvent-separated
24   ion pairs" more than one solvent molecule intervenes. However, the term "solvent-
25   separated ion pair" must be used and interpreted with care since it has also widely been
26   used as a less specific term for "loose" ion pair.
27   See [256].
28   See also *common-ion effect*, *dissociation*, *ion-pair return*, *special salt effect*.
29   [3]

30

31   **ion-pair recombination** (formerly **ion-pair return**)
32   Recombination of a pair of ions R$^+$ and X$^-$ formed from *ionization* of RX.
33   *Note:* Ion-pair recombination can be distinguished as external or internal, depending
34   on whether the ion pair did or did not undergo dissociation to free ions.
35   See *ion pair*.
36   rev[3]

37

38   **ionic liquid (ionic solvent, molten salt)**

1 Liquid that consists exclusively or almost exclusively of equivalent amounts of
2 oppositely charged ions.
3   *Note 1:* In practice the ions are monocations and monoanions.
4   *Note 2:* Ionic liquids that are liquid at or around room temperature are called room-
5 temperature ionic liquids (RTILs).
6   *Note 3:* The term *ionic liquid* has been often restricted to those water-free liquids that
7 have melting points (or glass-transition temperatures) below 100 °C, following a
8 definition given by Walden [257], who prepared the first ionic liquid, ethylammonium
9 nitrate, $CH_3CH_2NH_3^+\ NO_3^-$, mp. 13-14 °C, for conductivity measurements.
10   *Note 4:* The terminology for ionic liquids is not yet settled, as stated by Welton [258].
11 Room-temperature ionic liquid, non-aqueous ionic liquid, molten salt, liquid organic salt,
12 and fused salt are often synonymous.
13   See [259,260,261].
14

15 **ionic strength**
16 *I*
17 (In concentration basis, I_c, SI unit: mol m^{-3}, more commonly mol dm^{-3} or mol L^{-1}, in
18 molality basis, I_m, SI unit: mol kg^{-1})
19 In concentration basis: $I_c = 0.5\ \Sigma_i c_i Z_i^2$, in which c_i is the concentration of a fully
20 dissociated electrolyte in solution and Z_i the charge number of ionic species i.
21 In molality basis: $I_m = 0.5\ \Sigma_i m_i Z_i^2$, in which m_i is the molality of a fully dissociated
22 electrolyte in solution and Z_i the charge number of ionic species i.
23   rev[3]
24

25 **ionization**
26 Generation of one or more ions.
27   *Note 1:* This may occur, e.g., by loss or gain of an electron from a neutral *molecular*
28 *entity*, by the *unimolecular heterolysis* of that entity into two or more ions, or by a
29 heterolytic *substitution* reaction involving neutral molecules, such as
30       $M \rightarrow M^{+\bullet} + e^-$ (photoionization, electron ionization in mass spectrometry)
31       $SF_6 + e^- \rightarrow SF_6^{-\bullet}$ (electron capture)
32       $Ph_3CCl \rightarrow Ph_3C^+\ Cl^-$ (*ion pair*, which may dissociate to free ions)
33       $CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3CO_2^-$ (*dissociation*)
34   *Note 2:* In mass spectrometry ions may be generated by several methods, including
35 electron ionization, photoionization, laser desorption, chemical ionization, and
36 electrospray ionization.
37   *Note 3:* Loss of an electron from a singly, doubly, etc. charged cation is called
38 second, third, etc. ionization.
39   See also *dissociation*, *ionization energy*.
40   rev[3]

1

ionization energy

E_i

(SI unit J)

Minimum energy required to remove an electron from an isolated *molecular entity* (in its vibrational ground state) in the gaseous phase.

Note 1: If the resulting molecular entity is in its vibrational ground state, the energy is the "adiabatic ionization energy".

Note 2: 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 the "vertical ionization energy".

Note 3: The name ionization energy is preferred to the somewhat misleading earlier name "ionization potential".

See also *ionization*.

[3]

ionizing power

Tendency of a particular solvent to promote *ionization* of a solute.

Note: The term has been used in both kinetic and thermodynamic contexts.

See also *Dimroth-Reichardt E_T parameter*, *Grunwald-Winstein equation*, *Z-value*.

[3]

***ipso* attack**

Attachment of an entering group to a position in an aromatic compound already carrying a *substituent* group other than hydrogen.

Note: The entering group may displace that substituent group or may 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.

Example:
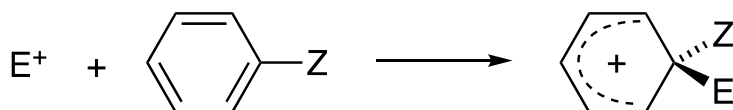
where E^+ is an *electrophile* and Z is a substituent other than hydrogen.

See [262].

See also *cine-substitution*, *tele-substitution*.

[3]

isentropic

See *isoentropic*.

1

isodesmic

Property of a reaction (actual or hypothetical) in which the types of bonds that are made in forming the products are the same as those that are broken in the reactants.

Examples:

(i) $PhCOOH + p\text{-}ClC_6H_4CO_2^- \rightleftarrows PhCO_2^- + p\text{-}ClC_6H_4COOH$ (1)

(ii) $2 CH_3F \rightleftarrows CH_2F_2 + CH_4$ (2)

Note 1: Such processes have advantages for theoretical treatment.

Note 2: The *Hammett equation* as applied to equilibria, as in (1), succeeds because it deals with isodesmic processes.

Note 3: For the use of isodesmic processes in quantum chemistry, see [263].

See [8].

See also *homodesmotic.*

rev[3]

isoelectronic

Having the same number of valence electrons and the same structure, i.e., number and *connectivity* of atoms, but differing in some or all of the elements involved.

Examples:

(i) CO, N_2, and NO^+

(ii) $CH_2=C=O$ and $CH_2=N^+=N^-$

[3]

isoentropic

Isentropic

Property of a reaction series in which the individual reactions have the same standard entropy or *entropy of activation*.

[3]

isoequilibrium relationship

Feature of a series of related substrates or of a single *substrate* under a series of reaction conditions whereby the enthalpies and entropies of reaction can be correlated by the equation

$$\Delta_r H - \beta \Delta_r S = \text{constant}$$

Note: The parameter β is called the isoequilibrium temperature.

See [264,265].

See also *compensation effect*, *isokinetic relationship.*

1   [3]

2

3   **isokinetic relationship**

4   Feature of a series of related substrates or of a single *substrate* under a series of

5   reaction conditions whereby the *enthalpies of activation* and *entropies of activation* can

6   be correlated by the equation

7        $\Delta^{\ddagger}H - \beta \Delta^{\ddagger}S$ = constant

8   *Note 1:* The parameter β is called the isokinetic temperature. At this temperature all

9   members of the series react at the same rate.

10   *Note 2:* Isokinetic relationships as established by direct correlation of $\Delta^{\ddagger}H$ with $\Delta^{\ddagger}S$

11   are often spurious, and the calculated value of β is meaningless, because errors in $\Delta^{\ddagger}H$

12   lead to compensating errors in $\Delta^{\ddagger}S$. Satisfactory methods of establishing such

13   relationships have been devised.

14   See [264,265].

15   See also *compensation effect*, *isoequilibrium relationship*, *isoselective relationship*.

16   [3]

17

18   **isolobal**

19   Feature of two molecular fragments for which the number, symmetry properties,

20   approximate energy, shape of the *frontier orbitals*, and number of electrons in them are

21   similar.

22   *Example:*

23

24   See also *isoelectronic*.

25   rev[3]

26

27   **isomer**

28   One of several species (or *molecular entities*) all of which have the same atomic

29   composition (molecular formula) but differ in their connectivity or stereochemistry and

30   hence have different physical and/or chemical properties.

31   *Note:* Conformational isomers that interconvert by rapid rotation about single bonds

32   and configurations that interconvert by rapid pyramidal inversion are often not

33   considered as separate isomers.

34   rev[3]

35

36   **isomerization**

37   *Chemical reaction* in which the product is an *isomer* of the reactant.

1   See also *molecular rearrangement*.

2   rev[3]

3

4   **isosbestic point**

5   Wavelength (or frequency) at which two or more components in a mixture have the

6   same molar absorption coefficients.

7   *Note 1:* Isosbestic points are commonly met when electronic spectra are taken (a)

8   on a solution in which a *chemical reaction* is in progress (in which case the two

9   absorbing components concerned are a reactant and a product, A → B), or (b) on a

10   solution in which the two absorbing components are in *equilibrium* and their relative

11   proportions are controlled by the concentration of some other component, typically the

12   concentration of hydrogen ions, as in an acid-base indicator equilibrium.

13   *Note 2:* The effect may also appear (c) in the spectra of a set of solutions of two or

14   more non-interacting components having the same total concentration.

15   *Note 3:* In all these examples, A (and/or B) may be either a single *chemical species*

16   or a mixture of chemical species present in invariant proportion.

17   *Note 4:* If absorption spectra of the types considered above intersect not at one or

18   more isosbestic points but over a progressively changing range of wavelengths, this is

19   prima facie evidence (a) for the formation of a reaction *intermediate* in substantial

20   concentration (A → C → B) or (b) for the involvement of a third absorbing species in

21   the equilibrium, e.g.,

22       $A \rightleftarrows B + H^+_{aq} \rightleftarrows C + 2\ H^+_{aq}$

23   or (c) for some interaction of A and B, e.g.,

24       $A + B \rightleftarrows C$

25   *Note 5:* Isobestic is a misspelling and is discouraged.

26   rev[3]

27

28   **isoselective relationship**

29   Relationship analogous to the *isokinetic relationship*, but applied to *selectivity* data of

30   reactions.

31   *Note:* At the isoselective temperature, the selectivities of the series of reactions

32   following the relationship are identical, within experimental error.

33   See [266].

34   See also *isoequilibrium relationship*, *isokinetic relationship*.

35   [3]

36

37   **isotope effect**

38   Relative difference between, or the ratio of, the *rate coefficients* or *equilibrium* constants

39   of two reactions that differ only in the isotopic composition of one or more of their

40   otherwise chemically identical components.

1   *Note:* The ratio k_l/k_h of rate constants (or K_l/K_h of equilibrium constants) for "light" and
2 "heavy" reactions is most often used in studies of chemical reaction mechanisms.
3 However, the opposite ratios are frequently used in environmental chemistry and
4 geochemistry; i.e., k_h/k_l or K_h/K_l. Furthermore the relative difference $k_h/k_l - 1$ or $K_h/K_l -$
5 1 (often expressed as the percentage deviation of the ratio from unity) is commonly
6 used to quantify isotopic fractionation.
7   See *kinetic isotope effect*, *equilibrium isotope effect*.
8   rev[3]
9

10 **isotope effect, equilibrium**
11 isotope effect, thermodynamic
12 Effect of isotopic substitution on an *equilibrium* constant
13   *Note 1:* For example, the effect of isotopic substitution in reactant A that participates
14 in the equilibrium:
15   A + B ⇄ C
16 is the ratio K_l/K_h of the equilibrium constant for the reaction in which A contains the light
17 isotope to that in which it contains the heavy isotope. The ratio can also be expressed
18 as the equilibrium constant for the isotopic exchange reaction:
19     $A_l + C_h ⇄ A_h + C_l$
20 in which reactants such as B that are not isotopically substituted do not appear.
21   *Note 2:* The *potential-energy surface*s of isotopic molecules are identical to a high
22 degree of approximation, so thermodynamic isotope effects can arise only from the
23 effect of isotopic mass on the nuclear motions of the reactants and products, and can
24 be expressed quantitatively in terms of nuclear partition functions:
25

26     $K_l/K_h = [Q^l(C)/Q^h(C)]/ [Q^l(A)/Q^h(A)]$
27

28   *Note 3:* Although the nuclear partition function is a product of the translational,
29 rotational, and vibrational partition functions, the isotope effect is usually determined
30 almost entirely by the last named, specifically by vibrational modes involving motion of
31 isotopically different atoms. In the case of light atoms (i.e., protium vs. deuterium or
32 tritium) at moderate temperatures, the isotope effect is dominated by zero-point energy
33 differences.
34   See [267].
35   See also *fractionation factor*.
36   rev[3]
37

38 **isotope effect, heavy-atom**
39   *Isotope effect* due to isotopes other than those of hydrogen.
40   [3]

isotope effect, intramolecular

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.

    Example: $PhCH_2D$ + Br· → BrH + PhCHD· vs. BrD + $PhCH_2$·

The intramolecular isotope effect k_H/k_D can be measured from the D content of product ($PhCH_2Br$ + PhCHDBr), which is experimentally much easier than measuring the intermolecular isotope effect k_H/k_D from the separate rates of reaction of $PhCH_3$ and $PhCD_3$.
    rev[3]

isotope effect, inverse

Kinetic isotope effect in 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.
    Note: The isotope effect will be "normal" when the vibrational frequency differences between the isotopic *transition state*s are smaller than in the reactants. Conversely, an inverse isotope effect can be taken as evidence for an increase in the force constants on passing from the reactant to the *transition state*.
    [3]

isotope effect, kinetic

Effect of isotopic substitution on a *rate constant*.
    For example in the reaction
        A + B → C
    the effect of isotopic substitution in reactant A is expressed as the ratio of *rate constant*s k_l/k_h, where the superscripts l and h represent reactions in which the molecules A contain the light and heavy isotopes, respectively.
    Note 1: Within the framework of transition-state theory, where the reaction is rewritten as
        A + B $\rightleftarrows$ [TS]‡ → C
k_l/k_h can be regarded as if it were the *equilibrium* constant for an isotope exchange reaction between the *transition state* [TS]‡ and the isotopically substituted reactant A, and calculated from their vibrational frequencies as in the case of a thermodynamic isotope effect (see *thermodynamic (equilibrium) isotope effect*).
    Note 2: Isotope effects like the above, involving a direct or indirect comparison of the rates of reaction of *isotopologue*s, are called "intermolecular", in contrast to

intramolecular isotope effects (see *intramolecular isotope effect*), in which a single substrate reacts to produce a non-statistical distribution of isotopologue product molecules.

See [267,268].

[3]

isotope effect, primary

Kinetic isotope effect attributable to isotopic substitution of an atom to which a bond is made or broken in the *rate-limiting step* or in a *pre-equilibrium* step of a reaction.

Note: 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*.

See also *secondary isotope effect*.

[3]

isotope effect, secondary

Kinetic isotope effect that is attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the *rate-limiting step* or in a *pre-equilibrium* step of a specified reaction.

Note 1: The corresponding isotope effect on the equilibrium constant of such a reaction is called a secondary *equilibrium isotope effect*.

Note 2: Secondary isotope effects can be classified as α, β, etc., where the label denotes the position of isotopic substitution relative to the reaction centre.

Note 3: Although secondary isotope effects have been discussed in terms of conventional electronic effects, e.g., induction, *hyperconjugation*, *hybridization*, such an effect is not electronic but vibrational in origin.

See [269].

See also *steric isotope effect*.

rev[3]

isotope effect, solvent

Kinetic or equilibrium isotope effect resulting from change in the isotopic composition of the solvent.

See also *kinetic isotope effect*, *equilibrium isotope effect*.

[3]

isotope effect, steric

Secondary isotope effect attributed to the different vibrational amplitudes of *isotopologue*s.

Note 1: 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.

Note 2: Ultimately the steric isotope effect arises from changes in vibrational frequencies and zero-point energies, as normally do other isotope effects.
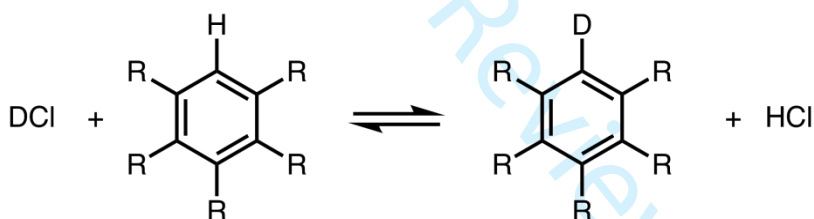
rev[3]

isotope effect, thermodynamic

See isotope effect, equilibrium.

[3]

isotope exchange

Chemical reaction in which the reactant and product *chemical species* are chemically identical but have different isotopic composition.

Note: 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,

[3]

isotopic perturbation, method of

Measurement of the NMR shift difference due to the *isotope effect* on a fast (degenerate) *equilibrium* between two species that are equivalent except for isotopic substitution.

Note: This method can distinguish a rapidly equilibrating mixture with time-averaged symmetry from a single structure with higher symmetry.

See [270,271,272,273].

[3]

isotopic scrambling

Achievement of, or the process of achieving, a redistribution of isotopes within a specified set of atoms in a *chemical species* or group of chemical species.

1 *Examples*

(a) (b) reaction schemes

2

3 (where * denotes the position of an isotopically different atom.)

4 See also *fractionation factor*.

5 [3]

6

7 **isotopologues**

8 *Molecular entities* that differ only in isotopic composition (number of isotopic

9 substitutions), e.g., CH_4, CH_3D, CH_2D_2,

10 *Note:* These are isotopic homologues. It is a misnomer to call them *isotopomers*,

11 because they are not isomers with the same atoms.

12 rev[3]

13

14 **isotopomers**

15 *Isomers* having the same number of each isotopic atom but differing in their positions.

16 The term is a contraction of "isotopic isomer".

17 *Note:* Isotopomers can be either constitutional isomers (e.g., $CH_2DCH=O$ and

18 $CH_3CD=O$) or isotopic stereoisomers (e.g., (*R*)- and (*S*)-CH_3CHDOH or (*Z*)- and (*E*)-

19 $CH_3CH=CHD$).

20 See [11].

21 [3]

22

23 **Kamlet-Taft solvent parameters**

24 Quantitative measure of solvent *polarity*, based on the solvent's hydrogen-bond donor,

25 hydrogen-bond acceptor, dipolarity/*polarizability*, and cohesive-pressure properties.

26 See [274,275,276,277,278,279].

27 See *solvent parameter*.

28 rev[3]

29

30 **Kaptein-Closs rules**

31 Rules used to predict the sign of *chemically induced dynamic nuclear polarization*

32 (CIDNP) effects.

33 See [280,281,282].

Kekulé structure

Representation of a *molecular entity* (usually *aromatic*) with fixed alternating single and double bonds, in which interactions between multiple bonds are ignored.

Example: For benzene the Kekulé structures are

and

Note: The distinction among *Lewis structure*, *Kekulé structure*, and *line formula* is now not generally observed, nor is the restriction to aromatic molecular entities.
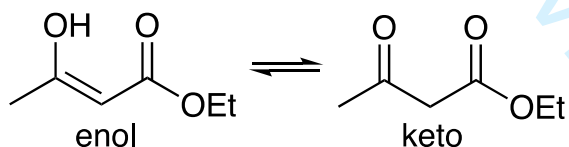
See also *non-Kekulé structure*.

rev[3]

keto-enol tautomerization

Interconversion of ketone and enol *tautomers* by hydron migration, accelerated by acid or base catalysis.

Example:

enol   keto

See also *tautomerization*.

kinetic ambiguity

deprecated

See *kinetic equivalence*.

kinetic control (of product composition)

Conditions (including reaction times) that lead to reaction products in a proportion governed by the relative rates of the parallel (forward) reactions by which those products are formed, rather than by the *equilibrium* constants.

See also *thermodynamic control*.

[3]

kinetic electrolyte effect

kinetic ionic-strength effect

1   General effect of an added electrolyte (i.e., other than, or in addition to, that due to its

2   possible involvement as a reactant or catalyst) on the *rate constant* of a reaction in

3   solution.

4   *Note 1:* At low concentrations (when only long-range coulombic forces need to be

5   considered) the effect on a given reaction is determined only by the *ionic strength* of

6   the solution and not by the chemical identity of the ions. This concentration range is

7   roughly the same as the region of validity of the Debye-Hückel limiting law for activity

8   coefficients. At higher concentrations the effect of an added electrolyte depends also

9   on the chemical identity of the ions. Such specific actions can sometimes be interpreted

10 as the incursion of a *reaction path* involving an ion of the electrolyte as reactant or

11 catalyst, in which case the action is not properly to be regarded just as a kinetic

12 electrolyte effect. At higher concentrations the effect of an added electrolyte does not

13 necessarily involve a new reaction path, but merely the breakdown of the Debye-Hückel

14 law, whereby ionic activity coefficients vary with the ion.

15 *Note 2:* Kinetic electrolyte effects are also called kinetic salt effects.

16 *Note 3:* A kinetic electrolyte effect ascribable solely to the influence of the *ionic*

17 *strength* on activity coefficients of ionic reactants and transition states is called a primary

18 kinetic electrolyte effect. A kinetic electrolyte effect arising from the influence of the

19 ionic strength of the solution upon the *pre-equilibrium* concentration of an ionic species

20 that is involved in a subsequent *rate-limiting step* of a reaction is called a secondary

21 kinetic electrolyte effect. A common case is the secondary electrolyte effect on the

22 concentration of hydrogen ion (acting as catalyst) produced from the *ionization* of a

23 weak acid in a buffer solution. To eliminate the complication of kinetic electrolyte effects

24 in buffer solutions, it is advisable to maintain constant ionic strength.
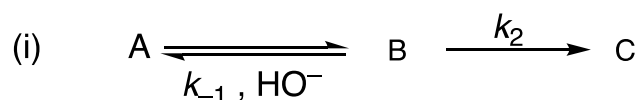
25 See [283].

26 See also *common-ion effect*, *order of reaction.*
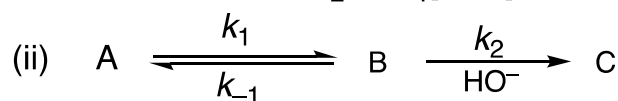
27 [3]

28

29 **kinetic equivalence**

30 Property of two reaction schemes that imply the same *rate law*.

31 *Example*: Schemes (i) and (ii) for the formation of C from A under conditions that B

32 does not accumulate as a reaction *intermediate*:

$$(i) \quad A \underset{k_{-1},\ HO^-}{\overset{}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][HO^-]}{k_2 + k_{-1}[HO^-]}$$

$$(ii) \quad A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow[HO^-]{k_2} C$$

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][HO^-]}{k_{-1} + k_2[HO^-]}$$

1
2
3   1
4   2
5   3
6   4
7
8
9   5   Both equations for d[C]/dt are of the form

$$\frac{d[C]}{dt} = \frac{r\,[A][HO^-]}{1 + s[HO^-]}$$

6

7   where r and s are constants (sometimes called *rate coefficients*). The equations are
8   identical in their dependence on concentrations and do not distinguish whether HO^-
9   catalyses the formation of B and its reversion to A, or is involved only in its further
10   transformation to C. The two schemes are therefore kinetically equivalent.
11   [3]
12
13

14   **Koppel-Palm solvent parameters**
15   Quantitative measure of solvent *polarity*, based on the solvent's *permittivity*, refractive
16   index, *basicity* or *nucleophilicity*, and *acidity* or *electrophilicity*.
17   See [284].
18   See *solvent parameter*.
19   rev[3]
20

21   **Kosower Z value**
22   See *Z-value*.
23   [3]
24

25   **labile**
26   Property of a *chemical species* that is relatively *unstable* and *transient* or reactive.
27   *Note:* This term must not be used without explanation of the intended meaning.
28   See also *inert*, *persistent*, *reactivity*, *unreactive*.
29   [3]
30

31   **Laurence solvent parameters**
32   Quantitative measures of solvent *polarity*, based on the solvent's dispersion/induction
33   interactions, electrostatic interactions between permanent multipoles, solute Lewis
34   base/solvent Lewis acid interactions, and solute HBD/solvent HBA interactions.
35   See [285].
36

37   **least nuclear motion, principle of** (hypothesis of least motion)

Hypothesis that, for given reactants, the reactions involving the smallest change in nuclear positions will have the lowest *energy of activation*.

Note: The basis for this hypothesis is that the energy of a structural deformation leading toward reaction is proportional to the sum of the squares of the changes in nuclear positions, which holds only for small deformations and is therefore not always valid.
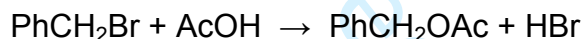
See [8,286].

rev[3]

leaving group

Species (charged or uncharged) that carries away the bonding electron pair when it becomes detached from another fragment in the residual part of the *substrate*.

Example 1: In the heterolytic *solvolysis* of (bromomethyl)benzene (benzyl bromide) in acetic acid

$$PhCH_2Br + AcOH \rightarrow PhCH_2OAc + HBr$$

the leaving group is Br^-.

Example 2: In the reaction

$$MeS^- + PhCH_2N^+Me_3 \rightarrow MeSCH_2Ph + NMe_3$$
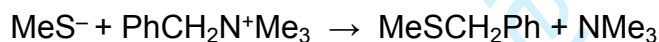
the leaving group is NMe_3.

Note: The historical term "leaving group" is ambiguous, because in the heterolysis of R–X, both R^+ and X^- are fragments that leave from each other. For that reason, X^- (as well as Br^- and NMe_3 in examples 1 and 2) can unambiguously be called nucleofuges, whereas R^+ is an electrofuge.

See also *electrofuge*, *entering group*, *nucleofuge*.

rev[3]

Leffler's relation

Leffler's assumption

In a series of elementary reactions the changes in Gibbs activation energies are often found to be proportional to the changes in Gibbs energies for the overall reaction.

$$\delta \Delta^{\ddagger}G = \alpha \, \Delta_r G^0$$

This relation was interpreted in terms of the simple assumption that a small change in any transition-state property $P_{\ddagger}$ is a linear combination of changes in reactant- and product-state properties, P_R and P_P.

1    $\delta P_{\ddagger} = \alpha \, \delta P_{P} + (1 - \alpha) \, \delta P_{R}$

2

3   Within the limits of this assumption, the parameter α is an approximate measure of the
4   fractional displacement of the transition state along the *minimum-energy reaction path*
5   from reactants to products.
6   See [109].
7   *Note:* There are many exceptions to the validity of Leffler's assumption that α is a
8   measure of the position of the transition state.
9   See [287].
10   See *Hammond postulate*.
11   rev[3]

12

13   **left-to-right convention**
14   Arrangement of the structural formulae of the reactants so that the bonds to be made
15   or broken form a linear array in which the *electron pushing* proceeds from left to right.
16   See [288].
17   [3]

18

19   **levelling effect**
20   Tendency of a solvent to make all *Brønsted acid*s whose *acidity* exceeds a certain value
21   appear equally acidic.
22   *Note 1:* This phenomenon is due to the complete transfer of a hydron to a Brønsted-
23   basic solvent from a dissolved acid stronger than the *conjugate acid* of the solvent. The
24   only acid present to any significant extent in all such solutions is the *lyonium ion.*
25   *Note 2:* For example, the solvent water has a levelling effect on the acidities of $HClO_4$,
26   HCl, and HI. Aqueous solutions of these acids at the same (moderately low)
27   concentrations have the same acidities.
28   *Note 3:* A corresponding levelling effect applies to strong bases in *protogenic*
29   solvents.
30   [3]

31

32   **Lewis acid**
33   *Molecular entity* (and the corresponding *chemical species*) that is an electron–pair
34   acceptor and therefore able to react with a *Lewis base* to form a *Lewis adduct* by
35   sharing the electron pair furnished by the Lewis base.
36   *Example:*

37

38   Me_3B (Lewis acid) + $:NH_3$ (Lewis base) $\rightarrow$ $Me_3B^- - N^+H_3$ (Lewis adduct)

39

40   See also *coordination*.

1   [3]

2

3   **Lewis acidity**

4   Thermodynamic tendency of a substrate to act as a *Lewis acid*.

5   *Note 1*: This property is defined quantitatively by the *equilibrium* constant or Gibbs

6   energy for *Lewis adduct* formation of a series of Lewis acids with a common reference

7   *Lewis base*.

8   *Note 2.* An alternative measure of Lewis acidity in the gas phase is the enthalpy of

9   *Lewis adduct* formation for that Lewis acid with a common reference *Lewis base*.

10   See also *electrophilicity, Lewis basicity*.

11   rev[3]

12

13   **Lewis adduct**

14   *Adduct* formed between a *Lewis acid* and a *Lewis base*.

15   [3]

16

17   **Lewis base**

18   *Molecular entity* (and the corresponding *chemical species*) able to provide a pair of

19   electrons and thus capable of *coordination* to a *Lewis acid*, thereby producing a *Lewis*

20   *adduct*.

21   [3]

22

23   **Lewis basicity**

24   Thermodynamic tendency of a substance to act as a *Lewis base*.

25   *Note 1:* This property is defined quantitatively by the equilibrium constant or Gibbs

26   energy of *Lewis adduct* formation for that Lewis base with a common reference *Lewis*

27   *acid*.

28   *Note 2:* An alternative measure of Lewis *basicity* in the gas phase is the enthalpy of

29   *Lewis adduct* formation for that Lewis base with a common reference *Lewis acid*.

30   See also *donicity, Lewis acidity, nucleophilicity, proton affinity*.

31   rev[3]

32

33   **Lewis structure**

34   electron-dot structure, Lewis formula

35   Representation of molecular structure in which (a) nonbonded valence electrons are

36   shown as dots placed adjacent to the atoms with which they are associated and in

37   which (b) a pair of bonding valence electrons in a *covalent bond* is shown as two dots

38   between the bonded atoms, and in which (c) formal charges (e.g., +, −, 2+) are attached

39   to atoms to indicate the difference between the nuclear charge (atomic number) and

the total number of electrons associated with that atom, on the formal basis that bonding electrons are shared equally between atoms they join.

Examples:

$$H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \qquad :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:^{-} \qquad H:C:::C:H$$
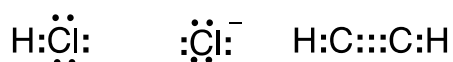
Note 1: A double bond is represented by two pairs of dots, and a triple bond by three pairs, as in the last example above.

Note 2: Bonding pairs of electrons are usually denoted by lines, representing covalent bonds, as in *line formula*s, rather than as a pair of dots, and the lone pairs are sometimes omitted.

Examples:

$$H–Cl \qquad Cl^{-} \qquad H-C{\equiv}C-H$$

Note 3: The distinction among Lewis structure, *Kekulé structure*, and *line formula* is now not generally observed.

rev[3]

lifetime (mean lifetime)

τ

Time needed for the concentration of a *chemical species* that decays in a first-order process to decrease to 1/e of its original value. i.e., $c(t = \tau) = c(t = 0)/e$.

Note 1: Statistically, it represents the mean life expectancy of the species.

Note 2: Mathematically: $\tau = 1/k = 1/(\Sigma_i k_i)$ where k_i is the first-order *rate constant* for the *i*-th decay process of the species.

Note 3: Lifetime is sometimes applied to processes that are not first-order. However, in such cases the lifetime depends on the initial concentration of the entity or of a *quencher* and, therefore, only an initial lifetime can be defined. In this case, it should be called *decay time*.

See [9].

See also *chemical relaxation*, *half-life*, *rate of reaction*.

[3]

ligand

Atom or *group* bound to a central atom in a polyatomic *molecular entity* (if it is possible to indicate such a central atom).

See [29].

*Note 1:*The term is generally used in connection with metallic central atoms.

Note 2: 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.
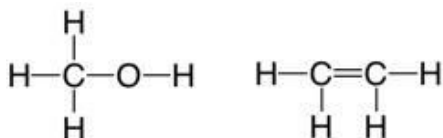
1   See [289], p. 335.

2   [3]

3

line formula

Two-dimensional representation of *molecular entities* in which atoms are shown joined by lines representing single bonds (or multiple lines for multiple bonds), without any indication or implication concerning the spatial direction of bonds.

    Examples: methanol, ethene

    See also *condensed formula, Kekulé formula, Lewis formula, skeletal formula.*

rev[3]

linear free-energy relation

linear Gibbs-energy relation

    [3]

linear Gibbs-energy relation

linear free-energy relation (LFER)

Linear correlation between the logarithm of a *rate constant* or *equilibrium* constant for a series of reactions and the logarithm of the rate constant or equilibrium constant for a related series of reactions.

    Typical examples of such relations are the *Brønsted relation* and the *Hammett equation* (see also *σ-value*).

    Note: The name arises because the logarithm of the value of an equilibrium constant (at constant temperature and pressure) is proportional to a standard Gibbs energy (free energy) change, and the logarithm of the value of a rate constant is a linear function of the Gibbs energy (free energy) of activation.

    [3]

linear solvation-energy relationship (LSER)

Application of *solvent parameter*s in the form of a single- or multi-parameter equation expressing the solvent effect on a given property: e.g., *rate of reaction*, *equilibrium* constant, spectroscopic shift.

    Note: The solvent effect may be estimated as a linear combination of elementary effects on a given property P, relative to the property P_0 in the reference solvent:

$$P - P_0 = a\,A + b\,B + p\,DP\ldots$$

where *A*, *B*, *DP*, etc. are acidity, basicity, dipolarity, etc. parameters, and *a, b, p*… are the sensitivity of the property to each effect.

See *Catalán solvent parameters*, *Dimroth-Reichardt E_T parameter*, *Kamlet-Taft solvent parameters*, *Koppel-Palm solvent parameters*, *Laurence solvent parameters*, *Z-value*.

rev[3]

line-shape analysis

Method for determination of *rate constant*s for dynamic chemical exchange from the shapes of spectroscopic signals, most often used in nuclear magnetic resonance spectroscopy.

[3]

Lineweaver-Burk plot

See *Michaelis-Menten kinetics*.

[3]

lipophilic

Feature of *molecular entities* (or parts of molecular entities) that have a tendency to dissolve in fat-like solvents (e.g., hydrocarbons).

See also *hydrophilic*, *hydrophobic interaction*.

rev[3]

London forces

dispersion forces

Attractive forces between molecules due to their mutual *polarizability*.

Note: London forces are the principal components of the forces between nonpolar molecules.

See [290].

See also *van der Waals forces*.

[3]

lone (electron) pair (nonbonding electron pair)

Two spin-paired electrons localized in the valence shell on a single atom.

Note: In structural formulas lone pairs should be designated as two dots.

See also *Lewis structure*.

rev[3]

LUMO

1 Acronym for Lowest Unoccupied Molecular Orbital

2   See *frontier orbitals*.

3   rev[3]

4

5 **lyate ion**

6 Anion produced by *hydron* (proton, deuteron, triton) removal from a solvent molecule.

7   *Example*: the hydroxide ion is the lyate ion of water.

8   [3]

9

10 **lyonium ion**

11 Cation produced by *hydronation* (protonation, deuteronation, tritonation) of a solvent

12 molecule.

13   *Example:* $CH_3OH_2^+$ is the lyonium ion of methanol.

14   See also *onium ion*.

15   [3]

16

17

18

19 **macroscopic diffusion control**

20   See *mixing control*.

21   [3]

22

23 **magnetic equivalence**

24 Property of nuclei that have the same resonance frequency in nuclear magnetic

25 resonance spectroscopy and also identical spin-spin interactions with each nucleus of

26 a neighbouring group.

27   *Note 1:* The spin-spin interaction between magnetically equivalent nuclei is not

28 manifested in the spectrum, and has no effect on the multiplicity of the respective NMR

29 signals.

30   *Note 2:* Magnetically equivalent nuclei are necessarily chemically equivalent, but the

31 reverse is not necessarily true.

32   [3]

33

34 **magnetization transfer**

35 NMR method for determining kinetics of chemical exchange by perturbing the

36 magnetization of nuclei in a particular site or sites and following the rate at which

37 magnetic equilibrium is restored.

38   *Note:* The most common perturbations are saturation and inversion, and the

39 corresponding techniques are often called "saturation transfer" and "selective inversion-

40 recovery".

1   See also *saturation transfer*.

2   [3]

3

4   **Marcus equation**

5   General expression that correlates the *Gibbs energy of activation* ($\Delta^{\ddagger}G$) with the Gibbs

6   energy of the reaction ($\Delta_r G^o$)

7

8    $$\Delta^{\ddagger}G = (\lambda/4)(1 + \Delta_r G^o/\lambda)^2 = \Delta^{\ddagger}G_o + \tfrac{1}{2}\Delta_r G^o + (\Delta_r G^o)^2/(16\,\Delta^{\ddagger}G_o)$$

9

10   where λ is the *reorganization energy* and $\Delta^{\ddagger}G_o$ is the *intrinsic barrier*, with $\lambda = 4\Delta^{\ddagger}G_o$.

11   *Note:* Originally developed for outer-sphere electron transfer reactions, the Marcus

12   equation applies to many atom- and group-transfer reactions. The Marcus equation

13   captures earlier ideas that reaction thermodynamics can influence reaction barriers:

14   e.g., the *Brønsted relation* (1926), the *Bell-Evans-Polanyi principle* (1936-38), *Leffler's*

15   *relation* (1953), and the *Hammond postulate* (1955) [227]. It also implies that changes

16   in intrinsic barriers may dominate over changes of reaction Gibbs energies and thus

17   account for the fact that reaction rates may not be controlled by the relative

18   thermodynamic stabilities of the products.

19   See [291,292,293,294,295,296].

20   rev[3]

21

22   **Markovnikov (Markownikoff) rule**

23   Statement of the common mechanistic observation that in electrophilic addition

24   reactions the more electropositive atom (or part) of a polar molecule becomes attached

25   to the carbon bearing more hydrogens.

26   *Note 1:* This rule was originally formulated by Markownikoff (Markovnikov) as "In the

27   addition of hydrogen halides to [unsaturated] hydrocarbons, the halogen atom becomes

28   attached to the carbon bearing the lesser number of hydrogen atoms".

29   *Note 2:* This rule can be rationalized as the addition of the more electropositive atom

30   (or part) of the polar molecule to the end of the multiple bond that would result in the

31   more stable *carbenium* ion (regardless of whether the carbenium ion is a stable

32   *intermediate* or a transient structure along the *minimum-energy reaction path*).

33   *Note 3:* Addition in the opposite sense, as in radical addition reactions, is commonly

34   called anti-Markovnikov addition.

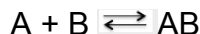35   See [297].

36   [3]

37

38   **mass action, law of**

39   Statement that the velocity of a reaction depends on the active mass, i.e., the

40   concentrations of the reactants.

1   *Example:* for an association reaction (1) and its reverse (2)

2

3   A + B $\rightarrow$ AB   (1)

4   AB $\rightarrow$ A + B   (2)

5

6 the forward velocity is $v_1 = k_1$ [A][B], with k_1 the _rate constant_ for the association reaction.

7 For the dissociation reaction 2 the velocity is $v_2 = k_2$ [AB]. This is valid only for

8 _elementary reactions_. Furthermore, the law of mass action states that, when a

9 reversible chemical reaction reaches _equilibrium_ at a given temperature, the forward

10 rate is the same as the backward rate. Therefore, the concentrations of the chemicals

11 involved bear a constant relation to each other, described by the equilibrium constant,

12 i.e_.,_ for

13

14   A + B $\rightleftarrows$ AB

15

16 in equilibrium, $v_1 = k_1$ [A][B] $= v_2 = k_2$ [AB] and one form of the equilibrium constant for

17 the above chemical reaction is the ratio

18

19       $$K_c = \frac{[AB]}{[A][B]} = \frac{k_1}{k_2}$$

20

21   *Note*: First recognized in 1864 as the kinetic law of mass action by Guldberg and

22 Waage, who first introduced the concept of dynamic equilibrium, but incorrectly

23 assumed that the rates could be deduced from the stoichiometric equation [298]. Only

24 after the work of Horstmann [299] and van't Hoff [300] a mathematical derivation of the

25 reaction rates considering the _order of the reaction_ involved was correctly made.

26   See also [301,302,303].

27   rev[3]

28

matrix isolation

29

30 Technique for preparation of a reactive or unstable species by dilution in an inert solid

31 matrix (argon, nitrogen, etc.), usually condensed on a window or in an optical cell at low

32 temperature, to preserve its structure for identification by spectroscopic or other means.

33   See [304].

34   [3]

35

Mayr-Patz equation

36

37 _Rate constant_s for the reactions of sp^2-hybridized _electrophile_s with _nucleophile_s can

38 be expressed by the correlation

39

1
2
3   1   lg [k/ (dm^3 mol^{-1} s^{-1})] = $s_N(E + N)$,
4
5   2
6   3   where E is the nucleophile-independent *electrophilicity* parameter, N is the electrophile-
7   4   independent *nucleophilicity* parameter, and s_N is the electrophile-independent
8   5   nucleophile-specific susceptibility parameter.
9   6   *Note 1:* This equation is equivalent to the conventional *linear Gibbs energy*
10   7   *relationship* lg $k = Nu + s_N E$, where $Nu = s_N N$. The use of N is preferred, because it
11   8   provides an approximate ranking of relative reactivities of nucleophiles.
12   9   *Note 2:* The correlation should not be applied to reactions with bulky electrophiles,
13   10   where steric effects cannot be neglected. Because of the way of parametrization, the
14   11   correlation is applicable only if one or both reaction centres are carbon.
15   12   *Note 3:* As the E parameters of the reference electrophiles are defined as solvent-
16   13   independent, all solvent effects are shifted into the parameters N and s_N.
17   14   *Note 4:* The equation transforms into the *Ritchie equation* for $s_N = 1$.
18   15   *Note 5:* Applications to S$_N$2-type reactions are possible if an electrophile-specific
19   16   susceptibility parameter is introduced.
20   17   See [305,306,307,308].
21   18   See also *Ritchie equation, Swain-Scott equation*.
22   19   The Mayr scale is available at http://www.cup.lmu.de/oc/mayr/DBintro.htm
23   20

24   21   **mechanism**
25   22   Detailed description of the process leading from the reactants to the products of a
26   23   reaction, including a characterization as complete as possible of the composition,
27   24   structure, energy and other properties of reaction *intermediate*s, products, and
28   25   *transition state*s.
29   26   *Note 1:* An acceptable mechanism of a specified reaction (and there may be a
30   27   number of such alternative mechanisms not excluded by the evidence) must be
31   28   consistent with the reaction stoichiometry, the *rate law*, and with all other available
32   29   experimental data, such as the stereochemical course of the reaction.
33   30   *Note 2*: Inferences concerning the electronic motions that dynamically interconvert
34   31   successive species along the *reaction path* (as represented by curved arrows, for
35   32   example) are often included in the description of a mechanism.
36   33   rev[3]

37   34

38   35   **mechanism-based inhibition** (suicide inhibition)
39   36   Irreversible *inhibition* of an enzyme by formation of covalent bond(s) between the
40   37   enzyme and the inhibitor, which is a substrate analogue that is converted by the enzyme
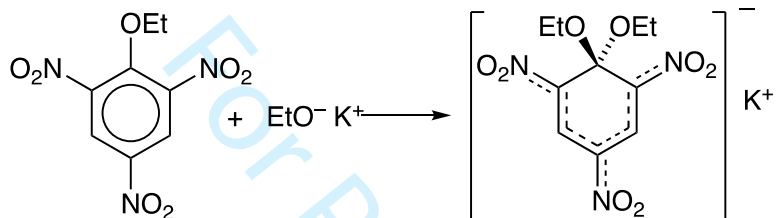41   38   into a species that reacts with the enzyme.
42   39   rev[3]

43   40

1 **medium**
2 Phase (and composition of the phase) in which _chemical species_ and their reactions
3 are studied.
4 [3]
5

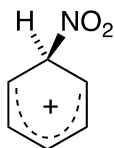6 **Meisenheimer adduct** (Jackson-Meisenheimer adduct)
7 _Lewis adduct_ formed in nucleophilic aromatic substitution from a _nucleophile_ (_Lewis_
8 _base_) and an _aromatic_ or heteroaromatic compound,

9

10   _Note 1:_ In cases where the substrate lacks electron-withdrawing groups, and
11 depending also on the nucleophile, the Meisenheimer adduct is not a minimum on the
12 _potential-energy surface_ but a _transition state_.
13   See [309,310,311,312].
14   _Note 2:_ Analogous cationic adducts, such as
15

16
17
18 which are _intermediate_s in _electrophilic_ aromatic _substitution_ reactions, are instead
19 called Wheland intermediates or σ-_adduct_s (or the discouraged term σ-complexes).
20   See [313,314].
21   rev[3]
22

23 **melting point (corrected/uncorrected)**
24 Temperature at which liquid and solid phases coexist in equilibrium, as measured with
25 a thermometer whose reading was corrected (or not) for the emergent stem that is in
26 ambient air.
27   _Note:_ In current usage the qualification often means that the thermometer was/(was
28 not) calibrated or that its accuracy was/(was not) verified. This usage is inappropriate
29 and should be abandoned.
30   [3]
31

32 **mesolytic cleavage**

1   Cleavage of a bond in a *radical ion* whereby a *radical* and an ion are formed. The term

2   reflects the mechanistic duality of the process, which can be viewed as homolytic or

3   heterolytic depending on how the electrons are assigned to the fragments.

4   See [315,316].

5   [3]

6

7   mesomerism, mesomeric structure

8   obsolete

9   *Resonance*, *resonance form*

10   rev[3]

11

12   mesophase

13   Phase of a liquid crystalline compound between the crystalline and the isotropic liquid

14   phase.

15   See [317].

16   [3]

17

18   metastable (chemical species)

19   deprecated

20   *Transient (chemical species)*.

21   [3]

22

23   metathesis

24   Process formally involving the redistribution of fragments between similar *chemical*

25   *species* so that the bonds to those fragments in the products are identical (or closely

26   similar) to those in the reactants.

27   *Example*:

$$RCH{=}CHR \quad \xrightleftharpoons{\text{catalyst}} \quad RCH \quad\ RCH$$
$$\qquad\qquad\qquad\qquad\qquad\ \, \| \qquad\ \|$$
$$RCH{=}CHR \qquad\qquad\qquad RCH \quad\ RCH$$

28

29   *Note:* The term has its origin in inorganic chemistry, with a different meaning, but that

30   older usage is not applicable in physical organic chemistry.

31   [3]

32

33   micellar catalysis

34   Acceleration of a *chemical reaction* in solution by the addition of a surfactant at a

35   concentration higher than its *critical micelle concentration* so that the reaction can

36   proceed in the environment of surfactant aggregates (*micelles*).

1   *Note 1:* Rate enhancements may be due to a higher concentration of the reactants
2 in that environment, or to a more favourable orientation and solvation of the species, or
3 to enhanced *rate constant*s in the micellar pseudophase of the surfactant aggregate.
4   *Note 2:* Micelle formation can also lead to a decreased reaction rate.
5   See [318].
6   See also *catalyst*.
7   [3]
8

micelle

9
10 Aggregate of 1- to 1000-nm diameter formed by surfactants in solution, which exists in
11 equilibrium with the molecules or ions from which it is formed.
12   See [135].
13   See also *inverted micelle*.
14   rev[3]
15

Michaelis-Menten kinetics

16
17 Appearance of saturation behavior in the dependence of the initial *rate of reaction* v_0
18 on the initial concentration $[S]_0$ of a *substrate* when it is present in large excess over
19 the concentration of an enzyme or other *catalyst* (or reagent) E, following the equation,
20

21     $v_0 = V_{max} [S]_0 /(K_M + [S]_0),$

22
23 where v_0 is the observed initial rate, V_{max} is its limiting value at substrate saturation (i.e.,
24 when $[S]_0 >> K_M$, so that all enzyme is bound to substrate), and K_M is the substrate
25 concentration at which $v_0 = V_{max}/2$.
26   *Note 1:* Empirical definition, applying to any reaction that follows an equation of this
27 general form.
28   *Note 2:* Often only initial rates are measured, at low conversion, so that $[S]_0$ can be
29 considered as time-independent but varied from run to run.
30   *Note* 3: The parameters V_{max} and K_M (the Michaelis constant) can be evaluated from
31 slope and intercept of a linear plot of $1/v_0$ against $1/[S]_0$ (Lineweaver-Burk plot) or from
32 slope and intercept of a linear plot of $[S]_0/v_0$ against $[S]_0$ (Eadie-Hofstee plot), but a
33 nonlinear fit, which is readily performed with modern software, is preferable.
34   *Note 4:* This equation is also applicable to the condition where E is present in large
35 excess, in which case [E] appears in the equation instead of $[S]_0$.
36   *Note 5:* The term has been used to describe reactions that proceed according to the
37 scheme

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_{cat}} Products + E$$

38
39

1 in which case $K_M = (k_{-1} + k_{cat})/k_1$ (Briggs-Haldane conditions). It has more usually been
2 applied only to the special case in which $k_{-1} \gg k_{cat}$ and $K_M = k_{-1}/k_1$; in this case K_M is a
3 true dissociation constant (Michaelis-Menten conditions).
4   See [319,320].
5   [3]
6

7 **microscopic diffusion control (encounter control)**
8 Observable consequence of the limitation that the rate of a bimolecular *chemical*
9 *reaction* in a homogeneous medium cannot exceed the rate of encounter of the reacting
10 *molecular entities*.
11   *Note:* The maximum *rate constant* is usually in the range 10^9 to 10^{10} dm^3 mol^{-1} s^{-1} in
12 common solvents at room temperature.
13   See also *mixing control*.
14   rev[3]
15

16 **microscopic reversibility, principle of**
17 In a reversible reaction the *mechanism* in one direction is exactly the reverse of the
18 mechanism in the other direction.
19   See also *chemical reaction*, *detailed balancing*.
20   [3]
21

22 **migration**
23 Transfer (usually *intramolecular*) of an atom or *group* during the course of a *molecular*
24 *rearrangement*.
25   *Example* (of a hydrogen migration):
26

27        $RCH_2CH{=}CH_2 \rightarrow RCH{=}CHCH_3$
28   rev[3]
29

30 **migratory aptitude**
31 Tendency of a *group* to participate in a *molecular rearrangement*, relative to that of
32 another group, often in the same molecule.
33   *Example:* In the Baeyer-Villiger rearrangement of $PhCOCH_3$, via *intermediate*
34 $PhC(OH)(OOCOAr)CH_3$, the major product is CH_3COOPh, by phenyl migration, rather
35 than $PhCOOCH_3$.
36   *Note:* In *nucleophilic* rearrangements (migration to an electron-deficient centre) the
37 migratory aptitude of a group is loosely related to its capacity to stabilize a partial
38 positive charge, but exceptions are known, and the position of hydrogen in the series is
39 often unpredictable.
40   rev[3]

1

migratory insertion

Reaction that involves the *migration* of a *group* to another position on a metal centre, with insertion of that group into the bond between the metal and the group that is in that other position.

*Example*s:

CO insertion

Ziegler-Natta reaction

Note: On repetition of the reaction the substituent alternates between the two positions.

rev[3]

minimum structural change, principle of

Principle that a *chemical reaction* is expected to occur with a minimum of bond changes or with a minimum redistribution of electrons (although more complex reaction cascades are also possible).

Example:
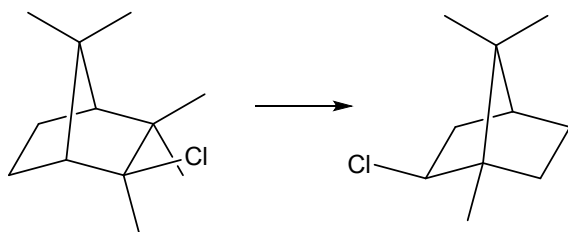
where the transfer of Cl is accompanied by migration of only one carbon, rather than a more extensive *molecular rearrangement* involving *migration* of three methyls.

See [286].

See also *least nuclear motion, principle of*.

rev[3]

1   **minimum-energy reaction path (MERP)**
2   Path of steepest-descent from a saddle point on a *potential-energy surface* in each
3   direction towards adjacent energy minima; equivalent to the energetically easiest route
4   from reactants to products.
5   See *intrinsic reaction coordinate.*
6   See [8].
7
8   **mixing control**
9   Experimental limitation of the rate of reaction in solution by the rate of mixing of
10   solutions of the two reactants.
11   *Note 1:* Mixing control can occur even when the reaction *rate constant* is several
12   orders of magnitude less than that for an encounter-controlled reaction.
13   *Note 2:* Analogous (and more important) effects of the limitation of reaction rates by
14   the rate of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas)
15   systems.
16   See [321].
17   See also *microscopic diffusion control*, *stopped flow*.
18   [3]
19
20
21
22   **Möbius aromaticity**
23   Feature of a monocyclic array of π orbitals in which there is a single out-of-phase
24   overlap (or, more generally, an odd number of out-of-phase overlaps), whereby the
25   pattern of aromatic character is opposite to Hückel systems; with $4n$ π electrons it is
26   stabilized (aromatic), whereas with $4n + 2$ it is destabilized (antiaromatic).
27   *Note 1:* The name is derived from the topological analogy of such an arrangement of
28   orbitals to a Möbius strip.
29   *Note 2:* The concept has been applied to transition states of pericyclic reactions.*Note
30   3:* In the electronically excited state $4n + 2$ Möbius π-electron systems are stabilized,
31   and 4n systems are destabilized.
32   *Note 4:* A few examples of ground-state Möbius π systems are known [322,323].
33   See [324,325].
34   See also *aromatic*, *Hückel (4n + 2) rule*.
35   rev[3]
36
37   **molecular entity**
38   Any constitutionally or isotopically distinct atom, *molecule*, ion, *ion pair*, *radical*, *radical
39   ion*, *complex*, *conformer*, etc., identifiable as a separately distinguishable entity.

1   *Note 1:* Molecular entity is used in this glossary as a general term for singular entities,
2   irrespective of their nature, while *chemical species* stands for sets or ensembles of
3   molecular entities. Note that the name of a substance may refer to the molecular entity
4   or to the chemical species, e.g., methane, may mean either a single molecule of CH_4
5   (molecular entity) or an ensemble of such species, specified or not (chemical species),
6   participating in a reaction.
7   *Note 2:* The degree of precision necessary to describe a molecular entity depends
8   on the context. For example "hydrogen molecule" is an adequate definition of a certain
9   molecular entity for some purposes, whereas for others it may be necessary to
10   distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the
11   molecule.
12   [3]
13

14   **molecular formula**
15   List of the elements in a *chemical species* or *molecular entity*, with subscripts indicating
16   how many atoms of each element are included.
17   *Note:* In organic chemistry C and H are listed first, then the other elements in
18   alphabetical order.
19   See [29].
20   See also *empirical formula*.
21
22

23   **molecular mechanics (**MM**) (empirical force-field calculation)**
24   Computational method intended to give estimates of structures and energies for
25   molecules.
26   *Note:* Even though such calculations can be made with either classical or quantum
27   mechanics (or both), the term molecular mechanics is widely understood as a classical
28   mechanics method that does not explicitly describe the electronic structure of the
29   molecular entities. It is based on the assumption of preferred bond lengths and angles,
30   deviations from which lead to strain, and the existence of torsional interactions and
31   attractive and repulsive *van der Waals* and Coulombic forces between non-bonded
32   atoms, all of which are parametrized to fit experimental properties such as energies or
33   structures. In contrast, in the quantum mechanical implementation no such
34   assumptions/parameters are needed.
35   See [8,326].
36   rev[3]
37

38   **molecular metal**
39   Non-metallic material whose properties, such as conductivity, resemble those of metals,
40   usually following oxidative doping.

1   *Example:* polyacetylene following oxidative doping with iodine.

2   [3]

3

4   **molecular orbital**

5   One-electron *wavefunction* describing a single electron moving in the field provided by

6   the nuclei and all other electrons of a *molecular entity* of more than one atom.

7   *Note 1:* Molecular orbitals describing valence electrons are often delocalized over

8   several atoms of a molecule. They are conveniently expressed as linear combinations

9   of *atomic orbital*s. They can be described as two-centre, multi-centre, etc. in terms of

10   the number of nuclei (or "centres") encompassed.

11   *Note 2:* For molecules with a plane of symmetry, a molecular orbital can be classed

12   as sigma (σ) or pi (π), depending on whether the orbital is symmetric or antisymmetric

13   with respect to reflection in that plane.

14   See *atomic orbital*, *orbital*.

15   See [8].

16   rev[3]

17

18   **molecular rearrangement**

19   Reaction of a *molecular entity* that involves a change of *connectivity*.

20   *Note 1*: The simplest type of rearrangement is an *intramolecular* reaction in which

21   the product is isomeric with the reactant (intramolecular *isomerization*). An example is

22   the first step of the Claisen rearrangement.

23

24

25   *Note 2*: The definition of molecular rearrangements includes reactions in which there

26   is a *migration* of an atom or bond (unexpected on the basis of the principle of *minimum*

27   *structural change*), as in the reaction

28

29       $CH_3CH_2CH_2Br + AgOAc \rightarrow (CH_3)_2CHOAc + AgBr$

30

31   where the rearrangement step can formally be represented as the "1,2-shift" of hydride

32   between adjacent carbon atoms in a carbocation

33

34       $CH_3CH_2CH_2^+ \rightarrow (CH_3)_2CH^+$

35

36   *Note 3*: Such migrations also occur in *radical*s, e.g.,

1

2   PhC(CH$_3$)$_2$–CH$_2$· → ·C(CH$_3$)$_2$CH$_2$Ph (neophyl rearrangement)

3

4   *Note 4*: The definition also includes reactions in which an entering group takes up a
5   different position from the *leaving group*, with accompanying *bond* migration, such as
6   in the "allylic rearrangement":

7

8   (CH$_3$)$_2$C=CHCH$_2$Br + HO$^-$ → (CH$_3$)$_2$C(OH)CH=CH$_2$ + Br$^-$

9

10   *Note 5*: A distinction can be made between intramolecular rearrangements (or "true"
11   molecular rearrangements) and *intermolecular* rearrangements (or apparent
12   rearrangements). In the former case the atoms and groups that are common to a
13   reactant and a product never separate into independent fragments during the
14   rearrangement stage, whereas in an intermolecular rearrangement a migrating *group*
15   becomes completely free from the parent molecule and is re-attached to a different
16   position in a subsequent step, as in the Orton reaction:

17

18   C$_6$H$_5$N(Cl)COCH$_3$ + HCl → C$_6$H$_5$NHCOCH$_3$ + Cl$_2$
19   → *o*- and *p*-ClC$_6$H$_4$NHCOCH$_3$ + HCl
20   See [327].
21   rev[3]

22

23   **molecular recognition**
24   Attraction between specific molecules through noncovalent interactions that often
25   exhibit electrostatic and stereochemical complementarity between the partners
26   *Note:* The partners are usually designated as *host* and *guest*, where the host
27   recognizes and binds the guest with high selectivity over other molecules of similar size
28   and shape.

29

30   **molecularity**
31   Number of reactant *molecular entities* that are involved in the "microscopic chemical
32   event" constituting an *elementary reaction*.
33   *Note 1:* For reactions in solution this number is always taken to exclude molecular
34   entities that form part of the *medium* and which are involved solely by virtue of their
35   solvation of solutes.
36   *Note 2:* A reaction with a molecularity of one is called "*unimolecular*", one with a
37   molecularity of two "bimolecular", and of three "termolecular".
38   See also *chemical reaction*, *order of reaction*.
39   [3]

40

1   **molecule**
2   An electrically neutral entity consisting of more than one atom.
3   *Note:* Rigorously, a molecule must correspond to a depression on the *potential-*
4   *energy surface* that is deep enough to confine at least one vibrational state.
5   See also *molecular entity*.
6   [3]

7

8   **More O'Ferrall - Jencks diagram**
9   Conceptual visualization of the *potential-energy surface* for a reacting system, as a
10   function of two coordinates, usually bond lengths or bond orders.
11   *Note 1:* The diagram is useful for analyzing structural effects on transition-state
12   geometry and energy.
13   *Note 2:* According to the *Hammond postulate*, stabilization of the products relative to
14   the reactants (an effect parallel to the *minimum-energy reaction path*, MERP) shifts the
15   transition state away from the product geometry, whereas destabilization of the
16   products shifts the *transition state* towards the product geometry. As first noted by
17   Thornton, stabilization of a structure located off the assumed MERP in a direction
18   perpendicular to it shifts the transition state toward that more stabilized geometry (a
19   *perpendicular effect*); destabilization shifts the transition state in the opposite direction.
20

23   *Figure*. More O'Ferrall-Jencks diagram for *β-elimination* reaction, with reactants,
24   products, and possible *intermediate*s at the four corners.

1

2   *Case 1*: In a concerted *elimination* the transition state ($\ddagger_1$) is a saddle point near the

3   centre of the diagram, and the assumed MERP follows close to the diagonal.

4   *Case 2*: If the *carbanion* intermediate is stabilized, the transition state shifts toward

5   that *intermediate*, to a transition state ($\ddagger_2$) in which the C–H bond is more extensively

6   broken and the C–X bond is more intact. Conversely, if the *carbocation* intermediate is

7   stabilized, the transition state shifts towards the top-left corner of the Figure, with less

8   C–H bond breaking and more C–X bond making

9   *Case 3*: If leaving group X^- is stabilised, energy decreases along the dotted vertical

10   arrow. It follows that in the resulting transition state ($\ddagger_3$) the C–H bond is more intact but

11   there is little change in the C–X bond, the shift of the transition state is the resultant of

12   a parallel (Hammond) component away from the top-right corner and a perpendicular

13   (anti-Hammond) component towards the top-left corner, yielding a transition state ($\ddagger_3$)

14   with less C–H bond breaking but approximately no change in the extent of C–X bond

15   making.

16   See [229,328,329,330,331].

17   See also *Hammond Postulate*, *anti-Hammond effect*.

18   rev[3]

19

20   **Morse potential**

21   $V(r)$

22   (unit J)

23   Empirical function relating the potential energy of a molecule to the interatomic distance

24   r accounting for the anharmonicity of bond stretching:

25

26   $$V(r) = D_e\{1 - \exp[-a(r-r_e)]\}^2$$

27

28   where D_e is the *bond-dissociation energy*, r_e is the equilibrium bond length, and a is a

29   parameter characteristic of a given molecule.

30   See [8].

31

32   **mu**

33   μ

34   (1) Symbol used to designate (as a prefix) a ligand that bridges two or more atoms.

35   *Note*: If there are more than two atoms being bridged, μ carries a subscript to denote

36   the number of atoms bridged.

37   (2) Symbol used to designate dipole moment as well as many other terms in physics

38   and physical chemistry.

39

40   **multi-centre bond**

1   *Bond* in which an electron pair is shared among three or more atomic centres.

2   *Note 1:* This may be needed when the representation of a *molecular entity* solely by

3   localized two-electron two-centre *bonds* is unsatisfactory, or when there are not enough

4   electrons to allow one electron pair shared between two adjacent atoms.

5   *Note 2:* This is restricted to σ bonds and does not apply to species with delocalized

6   π electrons.

7   Examples include the three-centre bonds in diborane B_2H_6 and in *bridged*

8   *carbocation*s.

9   rev[3]

10

11   **multident**

12   multidentate

13   See *ambident*.

14   [3]

15

16   **nanomaterial**

17   Substance whose particles are in the size range of 1 to 100 nm.

18   *Note:* This may have chemical properties different from those of the corresponding

19   bulk material.

20

21   **narcissistic reaction**

22   *Chemical reaction* that can be described as the *automerization or* enantiomerization of

23   a reactant into its mirror image (regardless of whether the reactant is *chiral*).

24   Examples are cited under *degenerate rearrangement* and *fluxional*.

25   See [332].

26   rev[3]

27

28   **neighbouring-group participation**

29   Direct interaction of the reaction centre (usually, but not necessarily, an incipient

30   *carbenium-ion* centre) with a lone pair of electrons of an atom or with the electrons of a

31   σ or π bond contained within the parent molecule but not *conjugated* with the reaction

32   centre.

33   *Example:*

34

35

36   *Note 1:* A distinction is sometimes made between *n*, σ, and π participation.

37   *Note 2:* The neighbouring group serves as a *nucleophile*, as in S_N2 reactions, except

38   that the nucleophile is *intramolecular*, so that this step is *unimolecular*.

Note 3: A rate increase due to neighbouring-group participation is known as anchimeric assistance.

Note 4: Synartetic acceleration is the name given to the special case of participation by electrons on a substituent attached to a β-carbon, relative to the *leaving group* attached to the α-carbon, as in the example above. This term is deprecated.

See also *intramolecular catalysis*, *multi-centre bond*.

rev[3]

NHOMO

Next-to-highest occupied *molecular orbital*.

See *subjacent orbital*.

rev[3]

NIH shift

Intramolecular hydrogen *migration* that can be observed in enzymatic and chemical hydroxylations of *aromatic* rings, as evidenced by appropriate deuterium labelling, as in

Note 1: In enzymatic reactions the NIH shift is thought to derive from the rearrangement of arene oxide *intermediate*s, but other pathways have been suggested.

Note 2: NIH stands for National Institutes of Health, where the shift was discovered.

See [333].

[3]

nitrene

Generic name for the species HN and substitution derivatives thereof, containing an electrically neutral univalent nitrogen atom with four nonbonding electrons.

Note 1: Two nonbonding electrons may have antiparallel spins (singlet state) or parallel spins (triplet state).

Note 2: The name is the strict analogue to *carbene* and, as a generic name, it is preferred to a number of alternative proposed (imene, imine radical, aminylene, azene, azylene, azacarbene, imin, imidogen).

See [97,334].

[3]

1 **no-bond resonance**

2 double-bond-no-bond resonance

3 Inclusion of one or more contributing structures that lack the σ bond of another

4 contributing structure.

5   *Example:*

6

7   See *hyperconjugation*.

8   rev[3]

9

10 **nonclassical carbocation**

11 *Carbocation* that has delocalized (bridged) bonding σ electrons.

12   See [89,335].

13   rev[3]

14

15 **non-Kekulé structure**

16 Compound with unpaired electrons for which no *Lewis structure*s are possible with all

17 bonding electrons paired in single or double bonds.

18   *Examples:*

19

20
21

22   *Note*: For the second example ("trimethylenemethane") the *isomer* shown (valence

23 tautomer methylidenecyclopropane) is a *Kekulé structure*.

24   See [336].

25

26 **nucleofuge**

27 *Leaving group* that carries away the bonding electron pair in a *nucleophilic substitution*

28 reaction.

29   Example: In the *hydrolysis* of a chloroalkane, Cl⁻ is the nucleofuge.

30

31   R–Cl + H_2O → ROH + HCl

32

Note 1: Nucleofugality, commonly called leaving-group ability, characterizes the relative rates of atoms or groups to depart with the bonding electron pair from a reference substrate. Nucleofugality depends on the nature of the reference reaction and is not the reverse of *nucleophilicity*.

Note 2: Protofugality is a special type of nucleofugality, characterizing the relative rates of proton transfer from a series of *Brønsted acid*s H–X to a common *Brønsted base*.

See [194].

See also *electrofuge*, *nucleophile*.

rev[3]

nucleophile (n.), nucleophilic (adj.)

Reactant that forms a bond to its reaction partner (the *electrophile*) by donating both of its bonding electrons.

Note 1: A "*nucleophilic substitution* reaction" is a heterolytic reaction in which the reagent supplying the entering group acts as a nucleophile.

Example:

MeO^- (nucleophile) + EtCl → MeOEt + Cl$^-$ (*nucleofuge*)

Note 2: Nucleophilic reagents are *Lewis base*s.

Note 3: The term "nucleophilic" is also used to designate the apparent polar character of certain *radical*s, as inferred from their higher relative reactivity with reaction sites of lower electron density.

See also *nucleophilicity*, *order of reaction*.

[3]

nucleophilic catalysis

Catalysis by a *Lewis base*, involving conversion of a substrate with low *electrophilicity* into an *intermediate* with higher electrophilicity.

Example 1: hydrolysis of acetic anhydride in aqueous solution, catalysed by 4-(dimethylamino)pyridine

$Me_2NC_5H_4N + (CH_3CO)_2O \rightarrow (Me_2NC_5H_4NCOCH_3)^+ + CH_3CO_2^-$

then $(Me_2NC_5H_4COCH_3)^+ + H_2O \rightarrow Me_2NC_5H_4N + CH_3CO_2H + H^+_{aq}$

Example 2: S_N2 reaction of CH_3CH_2Cl with HO^-, catalyzed by I^-:

$CH_3CH_2Cl + I^- \rightarrow Cl^- + CH_3CH_2I$, then $CH_3CH_2I + HO^- \rightarrow CH_3CH_2OH + I^-$

See also *nucleophilicity*.

1
2
3   1   rev[3]
4
5   2
6   3   **nucleophilic substitution**
7   4   Heterolytic reaction in which an entering group adds to the electrophilic part of the
8   5   substrate and in which the leaving group, or *nucleofuge*, retains both electrons of the
9   6   bond that is broken, whereupon it becomes another potential *nucleophile*.
10   7   *Example*:
11
12   8
13   9 CH_3Br (substrate) + HO^- (nucleophile) → CH_3OH + Br^- (nucleofuge)
14
15   10
16   11   *Note 1:* It is arbitrary to emphasize the nucleophile and ignore the feature that this is
17   12   also an electrophilic substitution, but the distinction depends on the nucleophilic nature
18   13   of the reactant that is considered to react with the *substrate*.
19   14   *Note 2:* Nucleophilic substitution reactions are designated as S_N1 or S_N2, depending
20   15   on whether they are unimolecular or bimolecular, respectively. Mechanistically, these
21   16   correspond to two-step and one-step processes, respectively. S_N1 reactions follow first-
22   17   order kinetics but S_N2 reactions do not always follow second-order kinetics.
23   18   See *order of reaction*, *rate coefficient*.
24
25   19
26   20
27   21   **nucleophilicity**
28   22   Relative reactivity of a *nucleophile* toward a common *electrophile*.
29   23   *Note 1*: The concept is related to *Lewis basicity*. However, whereas the Lewis
30   24   basicity of a base B: is measured by its *equilibrium* constant for *adduct* formation with
31   25   a common acid A, the nucleophilicity of a *Lewis base* B: is measured by the *rate*
32   26   *coefficient* for reaction with a common *substrate* A–Z, often involving formation of a
33   27   bond to carbon.
34   28   *Note 2*: *Protophilicity* is a special case of nucleophilicity, describing the relative rates
35   29   of reactions of a series of Lewis bases B: with a common *Brønsted acid* H–Z. The term
36   30   "protophilicity" is preferred over the alternative term "kinetic basicity" because *basicity*
37   31   refers to equilibrium constants, whereas "philicity" (like "fugality") refers to *rate*
38   32   *constant*s.
39   33   See [192,193,307].
40   34   See also *Brønsted basicity*, *electrophilicity*, *Lewis basicity*, *Mayr-Patz equation*,
41   35   *Ritchie equation*, *Swain-Scott equation*.
42   36   rev[3]
43
44   37
45   38   **n-σ* delocalization (n-σ* no-bond resonance)**
46   39   *Delocalization* of a lone pair (*n*) into an antibonding σ-orbital (σ*).
47   40   See also *anomeric effect*, *hyperconjugation*, *resonance*.

1   [3]

2

3   **octanol-water partition ratio** (K_{OW}):

4   Equilibrium concentration of a substance in octan-1-ol divided by its equilibrium

5   concentration in water.

6   *Note:* This is a measure of the *lipophilicity* of a substance. It is used in

7   pharmacological studies and in the assessment of environmental fate and transport of

8   organic chemicals.

9   See [337,338].

10   See also *partition ratio*.

11

12   **octet rule**

13   Electron-counting rule that the number of lone-pair electrons on a first-row atom plus

14   the number of electron pairs in that atom's bonds should be 8.

15

16   **onium ion**

17   (1) Cation derived by addition of a *hydron* to a mononuclear parent hydride of the

18   nitrogen, chalcogen, and halogen family, e.g., H_4N^+ ammonium ion.

19   (2) Derivative formed by substitution of the above parent ions by univalent groups, e.g.,

20   $(CH_3)_2SH^+$ dimethylsulfonium (dimethylsulfanium), $(CH_3CH_2)_4N^+$ tetraethylammonium.

21   See [97].

22   See also *carbenium ion*, *carbonium ion*.

23   rev[3]

24

25   **optical yield**

26   Ratio of the optical purity of the product to that of the *chiral* precursor or reactant.

27   *Note 1:* This should not be confused with *enantiomeric excess*.

28   *Note 2:* The optical yield is not related to the chemical yield of the reaction.

29   See [11].

30   See *stereoselectivity*.

31   [3]

32

33   **orbital (atomic or molecular)**

34   *Wavefunction* depending on the spatial coordinates of only one electron.

35   *Note:* An orbital is often illustrated by sketching contours, often very approximate, on

36   which the wavefunction has a constant value or by indicating schematically the

37   envelope of the region of space in which there is an arbitrarily fixed high probability (say

38   95 %) of finding the electron occupying that region, and affixing also the algebraic sign

39   (+ or –) of the wavefunction in each part of that region, or suggesting the sign by

40   shading.

1   1   *Examples:*

2   2

1s   2p$_z$ sp^3 hybrid   bonding MO

3   3

      4

5   See *atomic orbital*, *molecular orbital*.

6   See [8].

7   rev[3]

8

orbital steering

10   Concept expressing the principle that the energetically favourable stereochemistry of
11   approach of two reacting species is governed by the most favourable overlap of their
12   appropriate *orbital*s.

13   rev[3]

14

orbital symmetry

16   Behaviour of an *atomic orbital* or *molecular orbital* under molecular symmetry
17   operations, such that under reflection in a symmetry plane or rotation by 180º around a
18   symmetry axis the phase of the orbital is either unchanged (symmetric) or changes sign
19   (antisymmetric), whereby positive and negative lobes are interchanged.

20   *Examples:*

21   (1) The orbital of an idealized single bond is σ, with cylindrical symmetry.

22   (2) A p-orbital or π-bond orbital has π symmetry, i.e., it is antisymmetric with respect
23   to reflection in a plane passing through the atomic centres with which it is associated.

24   (3) The *HOMO* of 1,3-butadiene (illustrated below by its component atomic orbitals)
25   is antisymmetric with respect to 180º rotation about an axis through the C2–C3 bond
26   and perpendicular to the molecular plane.

27

28

29

30

31

32

33   See [107,123].

34   See also *conservation of orbital symmetry*, *sigma*, *pi*.

35   rev[3]

36

order of reaction

1 Exponent α, independent of concentration and time, in the differential rate equation
2 (*rate law*) relating the macroscopic (observed, empirical, or phenomenological) rate of
3 reaction v to c_A the concentration of one of the chemical species present, as defined by
4

5
$$\alpha = \left(\frac{\partial \ln \{v\}}{\partial \ln \{c_A\}}\right)_{[B],...}$$

6 The argument in the ln function should be of dimension 1. Thus, reduced quantities
7 should be used, i.e., the quantity divided by its unit, $\{v\} = v/(\text{mol dm}^{-3} \text{ s}^{-1})$ and $\{c_A\} =$
8 $c_A/(\text{mol dm}^{-3})$.
9   *Note 1:* A rate equation can often be expressed in the form $v = k [A]^{\alpha}[B]^{\beta}...$,
10 describing the dependence of the rate of reaction on the concentrations [A], [B],...,
11 where exponents α, β, ... are independent of concentration and time and k is
12 independent of [A], [B], ... In this case the reaction is said to be of order α with respect
13 to A, of order β with respect to B,..., and of (total or overall) order $n = \alpha + \beta +...$. The
14 exponents α, β,... sometimes called "partial orders of reaction", can be positive or
15 negative, integral, or rational nonintegral numbers.
16   *Note 2:* For an *elementary reaction* a partial order of reaction is the same as the
17 stoichiometric number. The overall order is then the same as the *molecularity*. For
18 stepwise reactions there is no general connection between stoichiometric numbers and
19 partial orders. Such reactions may have more complex rate laws, so that an apparent
20 order of reaction may vary with the concentrations of the *chemical species* involved and
21 with the progress of the reaction: in such cases it is not useful to speak of orders of
22 reaction, although apparent orders of reaction may be deducible from initial rates.
23   *Note 3:* In a *stepwise reaction*, orders of reaction may in principle be assigned to the
24 elementary steps.
25   *Note 4:* For chemical rate processes occurring in systems for which concentration
26 changes are not measurable, as in the case of a dynamic equilibrium $aA \rightleftarrows pP$, and if a
27 *chemical flux* ϕ_{-A} is found experimentally (e.g., by NMR *line-shape analysis*) to be
28 related to the concentration of A and to concentrations of other species B, ..., by the
29 equation
30

31     $\phi_{-A} = k[A]^{\alpha}[B]^{\beta} ...$
32

33 then the reaction is of order α with respect to A... and of total (or overall) order
34 (=α + β +...).
35 *Note 5:* If the overall rate of reaction is given by
36

37     $v = k[A]^{\alpha}[B]^{\beta}$

1
2
3   1
4
5   2   but [B] remains constant in any particular sample (but can vary from sample to sample),
6   3   then the order of the reaction in A will be α, and the rate of disappearance of A can be
7   4   expressed in the form
8
9   5
10   6 $v_A = k_{obs}[A]^{\alpha}$
11
12   7
13   8   The proportionality factor k_{obs} is called the "observed rate coefficient" and is related to
14   9   the *rate constant k* by
15
16   10
17   11 $k_{obs} = k[B]^{\beta}$
18
19   12
20   13   *Note 6:* For the frequent case where α = 1, k_{obs} is often referred to as a "pseudo-first-
21   14   order rate coefficient".
22   15   See [13].
23   16   See also *kinetic equivalence*, *rate coefficient*, *rate constant*.
24   17   rev[3]
25
26   18
27   19
28
29   20
30   21   **organocatalysis**
31   22   *Catalysis* by small organic molecules, as distinguished from catalysis by (transition)
32   23   metals or enzymes.
33   24   *Note 1:* Frequently used organocatalysts are secondary amines (covalent catalysis
34   25   by generation of enamines or of iminium ions as *reactive intermediates*) and thioureas
35   26   (hydrogen-bonding catalysis).
36   27   *Note 2*: Organocatalysts are often employed for *enantioselectivity*.
37   28   *Note 3*: The mechanisms employed by organocatalysts are examples of *general acid
38   29   catalysis*, *general base catalysis*, *nucleophilic catalysis*, *specific acid catalysis*, *specific
39   30   base catalysis*.
40   31   See [339,340,341,342].
41
42   32
43   33   **outer-sphere electron transfer**
44   34   Feature of an *electron transfer* between redox centres not sharing a common atom or
45   35   group.
46   36   *Example:*
47   37 $MnO_4^- + Mn^*O_4^{2-} \rightleftarrows MnO_4^{2-} + Mn^*O_4^-$
48   38   *Note 1:* In the *transition state* the interaction between the relevant electronic orbitals
49   39   of the two centres is weak (below 20 kJ mol^{-1}), and the electron(s) must tunnel through
50   40   space.

Note 2: If instead the donor and the acceptor exhibit a strong electronic coupling, often through a *ligand* that bridges both, the reaction is described as *inner-sphere electron transfer*.

Note 3: These two terms derive from studies of metal complexes, and for organic reactions the terms "nonbonded' and 'bonded" electron transfer are often used.

See [9,182,343].

rev[3]

oxidation

(1) Removal of one or more electrons from a *molecular entity*.

(2) Increase in the *oxidation number* of an atom within a *substrate*, see [344].

(3) Gain of oxygen and/or loss of hydrogen by an organic substrate.

Note 1: All oxidations meet criterion (2) and many meet criterion (3), but this is not always easy to demonstrate. Alternatively, an oxidation can be described as the *transformation* of an organic substrate by removal of one or more electrons from the substrate, often accompanied by gain or loss of water, *hydrons*, and/or hydroxide, or by *nucleophilic* substitution, or by *molecular rearrangement*.

Note 2: 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 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

$$CH_4 - 2e^- - H^+ + HO^- = CH_3OH \qquad \text{(oxidation)},$$

followed by

$$CH_3OH + HCl = CH_3Cl + H_2O \quad \text{(neither oxidation nor reduction)}$$

rev[3]

oxidation number

oxidation state

Number assigned to a carbon atom in a *covalent* organic compound according to

$$N_{Ox} = N_X + N_O + N_N - N_H - N_M$$

where N_X, N_O, N_N, N_H, and N_M are the numbers of bonds to halogen, oxygen (or sulfur), nitrogen, hydrogen, and a metal, respectively.

Examples:

CH_3MgBr (-4), CH_3CH_3 (-3), $CH_2=CH_2$ (-2), CH_3OH (-2), CH_2Cl_2 (0), CH_3**C**$H=O$ (+1), HCN (+2), CCl_4 (+4).

1

2 *Note 1:* This assignment is based on the convention that each attached atom more

3 electronegative than carbon contributes +1, while each atom less electronegative

4 (including H) contributes -1, and an attached carbon contributes zero.

5 *Note 2:* Oxidation numbers are not significant in themselves, but changes in oxidation

6 number are useful for recognizing whether a reaction is an oxidation or a reduction or

7 neither.

8 *Note 3*: A different system is used for transition-metal species [345].

9 See also *electronegativity*, *oxidation*.

10 rev[3]

11

12 **oxidative addition**

13 *Insertion* of the metal of a metal complex into a *covalent bond* involving formally an

14 overall two-electron loss on one metal or a one-electron loss on each of two metals,

15 i.e.,

16 $\qquad L_nM^m + XY \rightarrow L_nM^{m+2}(X)(Y)$

17 or $\quad 2\,L_nM^m + XY \rightarrow L_nM^{m+1}(X) + L_nM^{m+1}(Y)$

18 rev[3]

19

20 **oxidative coupling**

21 Coupling of two *molecular entities* through an oxidative process, usually catalysed by a

22 transition-metal compound.

23 *Example* (where the oxidant can be O_2 or Cu(II) or others):

24

25 $$2\ PhC\equiv CH \xrightarrow[NH_3]{CuCl} 2\ PhC\equiv CCu \xrightarrow{[Ox]} PhC\equiv C\text{-}C\equiv CPh$$

26 rev[3]

27

28 **parallel effect**

29 Change of the position of the *transition state* upon stabilization or destabilization of a

30 structure (or structures) along the assumed *minimum-energy reaction path*.

31 See *Hammond postulate*, *More O'Ferrall - Jencks diagram*.

32

33 **parallel reaction**

34 See *composite reaction*.

35 [3]

36

37 **paramagnetism**

1 Property of substances having a magnetic susceptibility greater than 0, whereby they
2 are drawn into a magnetic field.
3   See also *diamagnetism*.
4 [3]
5

6 **partial rate factor** p_f^Z, m_f^Z
7 *Rate constant* for substitution at one specific site in an *aromatic* compound divided by
8 the rate constant for substitution at one position in benzene.
9   *Note 1:* The partial rate factor p_f^Z for para-substitution in a monosubstituted benzene
10 C_6H_5Z is related to the rate constants $k(C_6H_5Z)$ and $k(C_6H_6)$ for the total reactions (i.e.,
11 at all positions) of C_6H_5Z and benzene, respectively, and f_{para} (the fraction of para-
12 substitution in the total product formed from C_6H_5Z, usually expressed as a percentage)
13 by the relation
14

15
$$p_f^Z = \frac{6k(C_6H_5Z)}{k(C_6H_6)} f_{para}$$

16
17 Similarly for meta-substitution:
18

19
$$m_f^Z = \frac{6k(C_6H_5Z)}{2k(C_6H_6)} f_{meta}$$

20
21 The symbols f_p^Z, f_m^Z, f_o^Z are also in use.
22   *Note 2*: The term applies also to the *ipso* position, and it can be extended to other
23 substituted *substrate*s undergoing parallel reactions at different sites with the same
24 reagent according to the same *rate law*.
25   See [262,346,347].
26   See also *selectivity*.
27   rev[3]
28

29 **partition ratio** (partition constant, distribution ratio) *P*
30 Concentration of a substance in one phase divided by its concentration in another
31 phase, at equilibrium.
32   *Example*, for an aqueous/organic system the partition ratio (or distribution ratio *D*) is
33 given by
34    $P = c_{org}(A)/c_{aq}(A)$
35   *Note 1:* The most common way of applying *P* in *correlation analysis* or *quantitative*
36 *structure-activity relationships* is as lg *P*.
37   *Note 2:* The parameter *P* is extensively used as an indicator of the capacity of a
38 molecular entity to cross biological membranes by passive diffusion.

1
2
3   1   *Note 3:* The term *partition coefficient* is in common usage in toxicology but is not
4   2   recommended for use in chemistry and should not be used as a synonym for partition
5   3   constant, partition ratio, or distribution ratio.
6   4   See [167,232].
7
8   5   See also *Hansch constant, octanol-water partition ratio*.
9
10   6
11   7   **pericyclic reaction**
12
13   8   *Chemical reaction* in which *concerted* reorganization of bonding takes place throughout
14   9   a cyclic array of continuously bonded atoms.
15   10   *Note 1*: It may be viewed as a reaction proceeding through a fully *conjugated* cyclic
16
17   11   transition state.
18   12   *Note 2*: The term embraces a variety of processes, including *cycloaddition*,
19   13   *cheletropic reaction*, *electrocyclic reaction* and *sigmatropic rearrangement*, etc.
20
21   14   (provided they are *concerted*).
22   15   See also *pseudopericyclic*.
23   16   [3]
24   17
25
26   18   **permittivity, relative** ε_r
27   19   dielectric constant (obsolete)
28   20   Measure of the reduction of the magnitude of the potential energy of interaction between
29
30   21   two charges on going from vacuum to a condensed medium, expressed as the ratio of
31   22   the former to the latter.
32   23   *Note*: The term dielectric constant is obsolete. Moreover, the dielectric constant is
33
34   24   not a constant since it depends on frequency.
35   25   See [12].
36   26
37
38   27   **perpendicular effect**
39   28   Change of the position of the transition state upon stabilization or destabilization of a
40
41   29   structure (or structures) that lies off the assumed *minimum-energy reaction path*.
42   30   See *anti-Hammond effect*, *Hammond postulate*, *More O'Ferrall - Jencks diagram*.
43   31   rev[3]
44   32
45
46   33   **persistence**
47   34   Characteristic of a *molecular entity* that has an appreciable *lifetime* (minutes or
48   35   nanoseconds or other, depending on context).
49
50   36   *Note 1*: Dilute solution or inert solvent may be required for persistence.
51   37   *Note 2*: Persistence is a kinetic or reactivity property, whereas, in contrast, stability
52   38   (being *stable*) is a thermodynamic property.
53
54   39   See [348].
55   40   See also *transient*.
56
57
58
59
60

1   rev[3]

2

pH-rate profile

Plot of observed *rate coefficient*, or more usually the decadic logarithm of its numerical value, against solution pH, other variables being kept constant.

    [3]

phase-transfer catalysis

Enhancement of the rate 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, into the other phase so that reaction can proceed.

    Note 1: These catalysts are often *onium ion*s (e.g., tetraalkylammonium ions) or complexes of inorganic cations (e.g., as *crown ether* complexes).

    Note 2: The catalyst cation is not consumed in the reaction although an anion exchange does occur.

    Example:

        $CH_3(CH_2)_7Cl$ in decane + aqueous Na^+CN^- + catalytic $PhCH_2N(CH_2CH_3)_3^+$

        = $CH_3(CH_2)_7CN$ + aqueous Na^+Cl^-

    rev[3]

phenonium ion

    See *bridged carbocation*.

    [3]

photochromism

Reversible transformation of a *molecular entity* between two forms, A and B, having different absorption spectra, induced in one or both directions by absorption of electromagnetic radiation.

    Note 1: The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (photochromism of type T) or photochemically (photochromism of type P).

    Note 2: The spectral change is typically, but not necessarily, of visible colour.

    Note 3: An important parameter is the number of cycles that a photochromic system can undergo.

    See [9].

photolysis

Bond cleavage induced by ultraviolet, visible, or infrared radiation.

    Example:

1       $Cl_2 \rightarrow 2\ Cl^\bullet$

2   *Note*: The term is used incorrectly to describe irradiation of a sample without any

3 bond cleavage, although in the term "flash photolysis" this usage is accepted.

4   See [9].

5   [3]

6

7 photostationary state

8 Steady state reached by a chemical system undergoing photochemical reaction, such

9 that the rates of formation and disappearance are equal for each of the transient

10 *molecular entities* formed.

11   See [9].

12

13 pi-adduct

14   See *π-adduct*.

15

16 pi-bond

17   See *σ, π*.

18

19

20 polar aprotic solvent

21   See *dipolar non-HBD solvent*.

22   [3]

23

24 polar effect

25 All the interactions whereby a *substituent* on a reactant molecule RY modifies the

26 electrostatic forces operating at the reaction centre Y, relative to the reference standard

27 R_oY.

28   *Note 1*: These forces may be governed by charge separations arising from

29 differences in the *electronegativity* of atoms (leading to the presence of dipoles), by the

30 presence of monopoles, or by electron *delocalization*.

31   *Note 2*: It is distinguished from a *steric effect*.

32   *Note 3*: Sometimes, however, the term polar effect is taken to refer to the influence,

33 other than steric, that non-conjugated substituents exert on reaction rates or equilibria,

34 thus excluding effects of electron delocalization between a substituent and the

35 molecular framework to which it is attached.

36   See also *electronic effects (of substituents)*, *field effect*, *inductive effect*.

37   [3]

38

39 polar solvent

1 Liquid composed of molecules with a significant dipole moment, capable of dissolving
2 ions or other molecules with significant dipole moments.
3   See *polarity*.
4 rev[3]
5

6 **polarity (**of a bond**)**
7 Characteristic of a bond between atoms of different *electronegativity*, such that the
8 electrons in that bond are not shared equally.
9

10 **polarity (**of a solvent**)**
11 Overall solvation capability (solvation power) of a solvent toward solutes, which
12 depends on the action of all possible intermolecular interactions between solute ions or
13 molecules and solvent molecules, excluding interactions leading to definite chemical
14 alterations of the ions or molecules of the solute.
15   *Note:* Quantitative measures of solvent polarity include relative *permittivity* (dielectric
16 constant) and various spectroscopic parameters.
17   See [17].
18   See *solvent parameter*.
19 rev[3]
20

21 **polarizability**
22 α
23 (SI unit: C m^2 V^{-1})
24 electric polarizability
25 Induced dipole moment, $\mu_{induced}$, divided by applied electric field strength $\boldsymbol{E}$

26    $\alpha = \mu_{induced}/\boldsymbol{E}$

27   *Note 1*: The polarizability represents the ease of distortion of the electron cloud of a
28 *molecular entity* by an electric field (such as that due to the proximity of a charged
29 species).
30   *Note 2*: Polarizability is more often expressed as polarizability volume, with unit cm^3,
31 where ε_0 is the *permittivity* of vacuum:
32

33    $$\alpha/\text{cm}^3 = \frac{10^6}{4\pi\varepsilon_0}\frac{\text{d}\boldsymbol{\mu}}{\text{d}E}$$

34

35   *Note 3*: In general, polarizability is a tensor that depends on direction, for example,
36 depending on whether the electric field is along a bond or perpendicular to it, and the
37 induced dipole may not even be along the direction of the electric field. However, in
38 ordinary usage the term refers to the mean polarizability, the average over three
39 rectilinear axes of the molecule.

1　rev[3]

2

3　**polydent**

4　polydentate

5　　See *ambident*.

6　　[3]

7

8　**potential-energy profile**

9　Curve describing the variation of the potential energy of a system of atoms as a function

10　of a single coordinate.

11　　*Note 1*: For an *elementary reaction* the relevant coordinate is the *reaction coordinate*,

12　which is a measure of progress along the *minimum-energy reaction path* (MERP) from

13　a saddle point on a *potential-energy surface* in each direction toward adjacent energy

14　minima. For a stepwise reaction it is the succession of reaction coordinates for the

15　successive individual reaction steps. For a reaction involving a *bifurcation* each branch

16　requires a different reaction coordinate and has its own profile.

17　　*Note 2*: A profile constructed as a function of an arbitrary internal coordinate (for

18　example, a bond distance) is not guaranteed to pass through a saddle point on the

19　corresponding potential-energy surface; in order to do so, it must be smooth,

20　continuous, and follow the path of lowest energy connecting the reactant and product

21　energy minima.

22　　*Examples:* (one-step reaction, two-step reaction)

23

24

25

26　　See [349].

27　　See also *Gibbs energy diagram*, *potential-energy surface*.

28　　rev[3]

29

30　**potential-energy surface** (**PES**)

31　Surface describing the variation within the *Born-Oppenheimer approximation* of the

32　potential energy of a system of atoms as a function of a set of internal coordinates.

Note 1: A minimum on a PES is characterized by positive curvature in all directions and corresponds to a structure that is stable with respect to small displacements away from its equilibrium geometry; for this structure (a reactant, *intermediate* or product) all vibrational frequencies are real. A saddle point is characterized by positive curvature in all directions except for one with negative curvature and corresponds to a transition structure, for which one vibrational frequency is imaginary. A local maximum is characterized by negative curvatures in two (or more) directions and has two (or more) imaginary frequencies; it is sometimes called a second-order (or higher-order) saddle point.

Note 2: It is usual to select only two coordinates in order to represent the surface, with potential energy as the third dimension, or alternatively as a two-dimensional contour map. For example, a PES for a simple reacting triatomic system A–B + C → A + B–C, could be constructed using the A···B and B···C distances as two internal coordinates; the third independent coordinate could be the ABC angle or the A···C distance, and its value could either be kept fixed or else be relaxed to minimize the energy at each point on the (A···B, B···C) surface.

Note 3: The path of steepest-descent from a saddle point in each direction towards adjacent energy minima defines a *minimum-energy reaction path* (MERP) that is equivalent to the energetically easiest route from reactants to products. The change in potential energy along this path across the PES defines a *potential-energy profile* for the *elementary reaction*. Progress along this path is measured by the value of the *reaction coordinate*.

Note 4: In general there is neither a unique set of internal coordinates nor a unique choice of two coordinates with which to construct a PES of reduced dimensionality. Consequently there is no guarantee of a smooth and continuous PES containing a saddle point connecting reactant and product minima.

See [8,73,350,351].

See: *bifurcation*, *minimum-energy reaction path*, *potential-energy profile*, *reaction coordinate*, *transition structure*.

rev[3]

potential of mean force (PMF)

Free energy as a function of a set of coordinates, the negative gradient of which gives the average force acting on that configuration averaged over all other coordinates and momenta within a statistical distribution. If the averaging is performed within a canonical ensemble (constant volume, temperature, and number of particles) the PMF is equivalent to the Helmholtz energy, but if it is performed within an isobaric-isothermal ensemble (constant pressure, temperature, and number of particles) the PMF is equivalent to the Gibbs energy.

1   *Note 1*: Commonly, the PMF acting upon a selected geometric variable and averaged
2   over the coordinates and momenta of all other geometric variables is evaluated for a
3   succession of constrained values of the selected variable, thereby generating
4   (generically) a *free-energy* profile with respect to the selected *reaction coordinate* (e.g.,
5   a bond distance or angle, or a combination of internal coordinates); specifically this is
6   either a Helmholtz-energy or a Gibbs-energy profile, depending upon the choice of
7   ensemble for the statistical averaging within a computational simulation.
8   *Note 2:* Selection of two geometric variables as reaction coordinates allows a free-
9   energy surface to be computed as a two-dimensional PMF.
10   *Note 3:* Molecular simulations often yield Helmholtz energies, not Gibbs energies,
11   but for condensed phases the difference is usually neglected.
12   See: *free energy*, *reaction coordinate*.

13

14   **pre-association**
15   Step on the *reaction path* of some *stepwise reaction*s in which the *molecular entity* C
16   forms an encounter pair or *encounter complex* with A prior to the reaction of A to form
17   product.
18   *Example:*

$$A + C \underset{\text{Pre-association}}{\rightleftharpoons} \underset{\substack{\text{encounter}\\\text{complex}}}{(A\cdots\cdots C)} \longrightarrow \underset{\substack{\text{encounter}\\\text{complex}}}{(B\cdots\cdots C)} \xrightarrow{\text{rapid}} \text{Product}$$

19
20

21   *Note 1*: In this mechanism the *chemical species* C may but does not necessarily
22   assist the formation of B from A, which may itself be a *bimolecular* reaction with some
23   other reagent.
24   *Specific example* (aminolysis of phenyl acetate)*:*

25

26
27

Note 2: Pre-association is important when B is too short-lived to permit B and C to come together by diffusion. In the specific example, T$^\pm$ would dissociate faster than general acid HA can diffuse to it. Experimentally, the Brønsted *α* is > 0, which is inconsistent with *rate-limiting* diffusion and *hydron* transfer.

   See [352].

   See also *Brønsted relation*, *microscopic diffusion control*, *spectator mechanism*.

   rev[3]

precursor complex

   See *encounter complex*.

   [3]

pre-equilibrium

prior equilibrium

Rapid reversible step preceding the *rate-limiting step* in a *stepwise reaction*.

   Example:
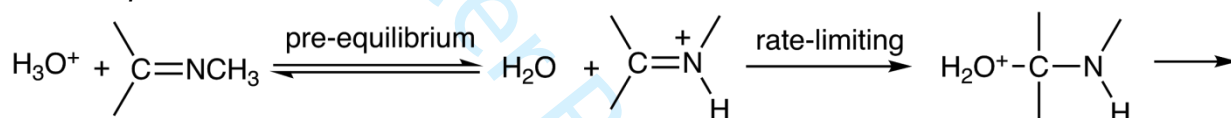
   See also *kinetic equivalence, steady state*.

   [3]

pre-exponential factor

   See *energy of activation*, *entropy of activation*.

   [3]

principle of nonperfect synchronization

Consideration applicable to reactions in which there is a lack of synchronization between bond formation or bond rupture and other changes that affect the stability of products and reactants, such as *resonance*, *solvation*, electrostatic, *hydrogen bonding* and *polarizability* effects.

   Note: 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 *rate constant* of a reaction. For a product-stabilizing factor whose development is ahead of bond changes, or a reactant-stabilizing factor whose loss lags behind bond changes, the opposite relations hold. The reverse effects are observable for factors that destabilize a reactant or product.

   See [108].

See also *imbalance*, *synchronous*.

prior equilibrium
See *pre-equilibrium*.
[3]

product-determining step
Step of a *stepwise reaction* in which the product distribution is determined.
Note: The product-determining step may be identical to, or may occur later than, the *rate-determining step* in the reaction.
[3]

product-development control
Case of *kinetic control* in which the *selectivity* of a reaction parallels the relative (thermodynamic) stabilities of the products.
Note: Product-development control arises because whatever effect stabilizes or destabilizes a product is already operative at the *transition state*. Therefore it is usually associated with a transition state occurring late on the *minimum-energy reaction path*.
See also *steric-approach control*, *thermodynamic control*.
[3]

promotion
See *pseudo-catalysis*.
[3]

propagation
See *chain reaction*.
[3]

propargylic substitution
See *allylic substitution reaction*.

protic
See *protogenic*.
[3]

protic solvent
Solvent that is capable of acting as a *hydrogen-bond* donor.
See *HBD solvent*.

1 **protofugality**

2 special case of *nucleofugality*, describing the relative rates of transfer of a proton (more

3 generally: *hydron*) from a series of *Brønsted acid*s H–X to a common *Brønsted base*.

4 *Note:* This term has the advantage over the commonly used "kinetic acidity" that

5 philicity and fugality are associated with kinetics, while acidity and basicity are

6 associated with thermodynamics.

7 See [194].

8 See also *Brønsted acidity, nucleofugality, protophilicity*.

9

10 **protogenic** (solvent)

11 HBD (hydrogen bond donor) solvent.

12 Capable of acting as a proton (*hydron*) donor.

13 *Note 1*: Such a solvent may be a strong or weak *Brønsted acid*.

14 *Note 2*: The term is preferred to the synonym *protic* or to the more ambiguous

15 expression acidic.

16 See *protophilic solvent*.

17 [3]

18

19 **protolysis**

20 proton (*hydron*)-transfer reaction.

21 *Note*: Because of its misleading similarity to *hydrolysis*, *photolysis*, etc., this use is

22 discouraged.

23 See also *autoprotolysis*.

24 rev[3]

25

26 **proton affinity**

27 Negative of the enthalpy change in the gas phase reaction between a proton (more

28 appropriately *hydron*) and the *chemical species* concerned, usually an electrically

29 neutral or anionic species, to give the *conjugate acid* of that species.

30 *Note 1*: For an anion A^-, the proton affinity is the negative of the enthalpy of the

31 heterolytic dissociation (in the gas phase) of the *Brønsted acid* HA.

32 *Note 2*: Proton affinity is often, but unofficially, abbreviated as PA.

33 *Note 3:* Affinity properly refers to Gibbs energy.

34 See also *gas phase basicity, gas phase acidity*.

35 See [2]. See also [213,353].

36 rev[3]

37

38 **protonation**

39 Attachment of the ion $^1H^+$ (of relative atomic mass ≈ 1).

40 See also *hydronation*.

proton–transfer reaction

Chemical reaction, the main feature of which is the intermolecular or intramolecular transfer of a proton (*hydron*) from one binding site to another.

   Example:

   $CH_3COOH + (CH_3)_2C=O \rightarrow CH_3CO_2^- + (CH_3)_2C=OH^+$

   Note: 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) or just to the proton-transfer event (including solvent rearrangement) by itself.

   See also *autoprotolysis*, *microscopic diffusion control*, *tautomerism*.

   [3]

protophilic (solvent)

   See *HBA (hydrogen bond acceptor) solvent*.

   rev[3]

protophilicity

Special case of *nucleophilicity*, describing the relative rates of reactions of a series of *Lewis base*s with a common *Brønsted acid*. This term has the advantage over the commonly used "kinetic basicity" that philicity and fugality are associated with kinetics, while acidity and basicity are associated with thermodynamics.

   See [194].

   See also *Brønsted basicity, nucleophilicity, protofugality*.

prototropic rearrangement (prototropy)

   See *tautomerization*.

   [3]

pseudo-catalysis

Increase of the rate of a reaction by an acid or base present in nearly constant concentration throughout a reaction in solution (owing to buffering or to the use of a large excess), even though that acid or base is consumed during the process, so that the acid or base is not a *catalyst* and the phenomenon strictly cannot be called *catalysis* according to the established meaning of these terms in chemical kinetics.

   Note 1: Although the *mechanism* of such a process is often closely related to that of a catalysed reaction, it is recommended that the term pseudo-catalysis be used in these

1   and analogous cases. For example, if a *Brønsted acid* accelerates the hydrolysis of an
2   ester to a carboxylic acid and an alcohol, this is properly called acid catalysis, whereas
3   the acceleration, by the same acid, of the hydrolysis of an amide should be described
4   as pseudo-catalysis because the acid pseudo-catalyst is stoichiometrically consumed
5   during the reaction through formation of an ammonium ion.

6   *Note 2*: The terms general-acid pseudo-catalysis and general-base pseudo-catalysis
7   may be used as the analogues of *general acid catalysis* and *general base catalysis*.

8   *Note 3*: The terms acid- and base-promoted, acid- and base-accelerated, and acid-
9   and base-induced are sometimes used for reactions that are pseudo-catalysed by or
10   bases. However, the term promotion also has a different meaning in other chemical
11   contexts.

12   rev[3]

13

14   **pseudo-first-order rate coefficient**

15   See *order of reaction*, *rate coefficient*.

16   [3]

17

18

19

20

21   **pseudopericyclic**

22   *Feature of a concerted transformation* in which the primary changes in bonding occur
23   within a cyclic array of atoms but in which one (or more) nonbonding and bonding
24   *atomic orbital*s interchange roles.

25   *Examples:* enol-to-enol *tautomerism* of 4-hydroxypent-3-en-2-one (where the
26   electron pairs in the O–H bond and in the lone pair on the other O are in σ orbitals
27   whereas the other three electron pairs are in π orbitals) and hydroboration (where the
28   B uses an sp^2 bonding orbital and a vacant p orbital)

29

30
31

32   *Note:* Because the atomic orbitals that interchange roles are orthogonal, such a
33   reaction does not proceed through a fully *conjugated transition state* and is thus not a
34   pericyclic reaction. It is therefore not governed by the rules that express *orbital*
35   *symmetry* restrictions applicable to pericyclic reactions.

36   See [354,355].

37   See also *coarctate*.

38   rev[3]

1

2 **push-pull conjugation**

3 Feature of an extended conjugated π system bearing an electron donor group at one

4 end and an electron acceptor group at the other end.

5   See [356].

6   See also *cross-conjugation*.

7

8 **pyrolysis**

9 *Thermolysis*, usually associated with exposure to a high temperature.

10   See also *flash vacuum pyrolysis*.

11   [3]

12

13 **π-adduct (pi-adduct)**

14 *Adduct* formed by electron-pair donation from a π *orbital* into a σ^* orbital, or from a σ

15 orbital into a π^* orbital, or from a π orbital into a π^* orbital.

16   *Example:*

17

18   *Note*: Such an adduct has commonly been known as a π *complex*, but, as the

19 bonding is not necessarily weak, it is better to avoid the term complex, in accordance

20 with the recommendations in this Glossary.

21   See also *coordination*.

22   [3]

23

24 **π-bond** (pi bond)

25 Interaction between two atoms whose p *orbital*s overlap sideways.

26   *Note:* The designation as π is because the p orbitals are antisymmetric with respect

27 to a defining plane containing the two atoms.

28   See *sigma, pi*.

29   rev[3]

30

31 **π-complex**

32   See *π-adduct*.

33   [3]

34

1 **π-electron acceptor**
2 *Substituent* capable of electron withdrawal by resonance (e.g., NO_2).
3   See *electronic effect*, *polar effect*, *π-electron donor*, *σ-constant.*
4   rev[3]
5

6 **π-electron donor**
7 *Substituent* capable of electron donation by resonance (e.g., OCH_3).
8   See *electronic effect*, *polar effect*, *π-electron acceptor*, *σ-constant.*
9   rev[3]
10

11 **quantitative structure-activity relationship** (QSAR)
12 Regression model to correlate biological activity or chemical reactivity with predictor
13 parameters based on measured or calculated features of molecular structure.
14   See [357,358].
15   See also *correlation analysis*.
16   rev[3]
17

18 **quantitative structure-property relationship** (QSPR)
19 Regression model to correlate chemical properties such as boiling point or
20 chromatographic retention time with predictor parameters based on measured or
21 calculated features of molecular structure.
22   See [359].
23   See also *correlation analysis*.
24

25 **quantum yield**
26 Number of defined events that occur per photon absorbed by the system.
27   *Note 1:* The integral quantum yield Φ is the number of events divided by the number
28 of photons absorbed in a specified wavelength range.
29   *Note 2:* For a photochemical reaction $\Phi(\lambda)$ is the amount of reactant consumed or
30 product formed divided by the number of photons absorbed at wavelength λ.
31   *Note 3:* The differential quantum yield for a homogeneous system is
32

33
$$\Phi(\lambda) = \frac{\left|\dfrac{\mathrm{d}x}{\mathrm{d}t}\right|}{q_{p,\lambda}[1 - 10^{A(\lambda)}]}$$

34

35 where $|\mathrm{d}x/\mathrm{d}t|$ is the rate of change of a quantity x that measures the progress of a
36 reaction, $q_{p,\lambda}$ is the spectral photon flux (mol or its non-SI equivalent einstein) incident

1   per unit time at wavelength λ, and $A(\lambda)$ is the decadic absorbance at the excitation

2   wavelengthλ.

3   *Note 4:* When the quantity x is an amount concentration, it is convenient to use in

4   the denominator the rate (in moles) of photons absorbed per volume.

5   See [9,10].

6   rev[3]

7

8   **radical**

9   free radical (obsolete)

10   *Molecular entity* possessing an unpaired electron.

11   *Examples:* •CH_3, •SnR_3, Cl•

12   *Note 1*: In these formulae the dot, symbolizing the unpaired electron, should be

13   placed so as to indicate the atom of highest spin density, if possible.

14   *Note 2*: Paramagnetic metal ions are not normally regarded as radicals. However, in

15   the *isolobal* analogy the similarity between certain paramagnetic metal ions and radicals

16   becomes apparent.

17   *Note 3*: Depending upon the core atom that possesses the highest spin density, the

18   radicals can be described as carbon-, oxygen-, nitrogen-, or metal-centred radicals.

19   *Note 4*: If the unpaired electron occupies an orbital having considerable s or more or

20   less pure p character, the respective radicals are termed σ or π radicals.

21   *Note 5*: The term radical has also been used to designate a *substituent* group within

22   a molecular entity, as opposed to "free radical", which is now simply called radical. The

23   bound entities may be called *groups* or substituents, but should no longer be called

24   radicals.

25   See [40,97].

26   See also *diradical*.

27   rev[3]

28

29   **radical combination**

30   Formation of a *covalent bond* by reaction of one *radical* with another.

31   See *colligation*.

32   rev[3]

33

34   **radical ion**

35   *Radical* that carries a net electric charge.

36   *Note 1*: A positively charged radical is called a radical cation (e.g., the benzene

37   radical cation $C_6H_6^{•+}$); a negatively charged radical is called a radical anion (e.g., the

38   benzene radical anion $C_6H_6^{•-}$ or the benzophenone radical anion $Ph_2C–O^{•-}$).

39   *Note 2*: Unless the positions of unpaired spin and charge can be associated with

40   specific atoms, superscript dot and charge designations should be placed in the order

•+ or •–, as suggested by the name radical ion. However, the usage in mass spectrometry is to place the charge symbol before the dot [7].

Note 3: In the first edition of this Glossary it was recommended to place the charge designation directly above the dot. This format is now discouraged because of the difficulty of extending it to ions bearing more than one charge and/or more than one unpaired electron.

[3]

radical pair

geminate pair

Two *radical*s in close proximity in solution, within a solvent *cage*.

Note 1: The two radicals may be formed simultaneously by some *unimolecular* process, e.g., peroxide decomposition or *photolysis*, or they may have come together by diffusion.

Note 2: 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*.

See [9,40].

[3]

radiolysis

Cleavage of one or several *bond*s resulting from exposure to high-energy radiation.

Note: The term is also often used loosely to specify the method of irradiation (e.g., pulse radiolysis) used in any radiochemical reaction, not necessarily one involving bond cleavage.

[3]

rate coefficient

Empirical constant k in the equation for the rate of a reaction that is expressible by an equation of the form

$$v = k[A]^a[B]^b....$$

Note 1: It is recommended that the term *rate constant* be confined to reactions that are believed to be *elementary reaction*s.

Note 2: When a rate coefficient relates to a reaction occurring by a composite mechanism, it may vary not only with temperature and pressure but also with the concentration of reactants. For example, in the case of a *unimolecular* gas reaction the rate at sufficiently high pressures is given by

1
2
3

1

4
5

2          $v = k[A]$

6

3

7
8

4   whereas at low pressures the rate expression is

9

5

10
11

6          $v = k'[A]^2$

12
13

7

14

8   Similarly, for a second-order reaction, the rate is given by

15
16

9

17

10         $v = k_2[A][B]$

18

11

19
20

12   But under conditions where [B] remains constant at $[B]_0$, as when B is a _catalyst_ or is

21
22

13   present in large excess,

23

14

24
25

15         $v = k_2[A][B]_0 = k[A]$

26

16

27
28

17   where the rate coefficient $k = k_2[B]_0$, which varies with $[B]_0$.

29

18   Such a rate coefficient k, which varies with the concentration [B], is called a first-

30

19   order rate coefficient for the reaction, or a _pseudo first-order rate constant_ even though

31

20   it is not a rate constant.

32
33

21   _Note_: _Rate constant_ and _rate coefficient_ are often used as synonyms, see [12],

34

22   section 2.12, p.63.

35

23   See [13].

36
37

24   See _order of reaction._

38

25   rev[3]

39

26

40
41

27   **rate constant**

42

28   _k_

43

29   Term generally used for the _rate coefficient_ of a reaction that is believed to be an

44
45

30   _elementary reaction_. See [13].

46

31   _Note 1_: In contrast to a rate coefficient, a rate constant should be independent of

47

32   concentrations, but in general both rate constant and rate coefficient vary with

48
49

33   temperature.

50

34   _Note 2_: Rate constant and rate coefficient are often used as synonymous, see [12],

51

35   section 2.12, p.63.

52
53

36   See _order of reaction_.

54

37   rev[3]

55
56

38

57

39   **rate-controlling step**

58
59

40   See _rate-determining states, rate-limiting step_.

60

1   rev[3]

2

3   **rate law**

4   empirical differential rate equation

5   Expression for the *rate of reaction* in terms of concentrations of *chemical species* and

6   constant parameters (normally *rate coefficients* and partial *orders of reaction*) only.

7   For examples of rate laws see the equations under *kinetic equivalence*, and under

8   *steady state*.

9   [3]

10

11   **rate-limiting step**

12   rate-controlling step

13   rate-determining step

14   Step in a multistep reaction that is the last step in the sequence whose *rate constant*

15   appears in the rate equation.

16   See [13].

17   *Example*: Two-step reaction of A with B to give *intermediate* C, which then reacts

18   further with D to give products:

19

$$A + B \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; C \;\; (\text{Step 1})$$

$$C + D \; \xrightarrow{k_2} \; \text{products} \;\; (\text{Step 2})$$

20   If [C] reaches a *steady state*, then the observed rate is given by

21

22    $v = -d[A]/dt = k_1 k_2 [A][B][D]/(k_{-1} + k_2[D])$

23

24   *Case 1:* If $k_2[D] \gg k_{-1}$, then the observed rate simplifies to

25

26    $v = -d[A]/dt = k_1[A][B]$

27

28   Because k_2 disappears from the rate equation and k_1 is the last rate constant to remain,

29   step (1) is said to be rate-limiting.

30   *Case 2:* If $k_2[D] \ll k_{-1}$, then the observed rate is given by

31

32    $v = k_1 k_2 [A][D]/k_{-1} = K k_2 [A][B][D]$

33

34   where K, equal to k_1/k_{-1}, is the *equilibrium* constant for the *pre-equilibrium* (Step 1).

35   Because k_2 remains in the rate equation, Step 2 is said to be rate-limiting. Notice that

36   in this case, where Step 2 involves another reactant D, which step is rate-limiting can

37   depend on [D]: Step 1 at high [D] and Step 2 at low [D].

Specific example: Acid-catalyzed bromination of a methyl ketone

where $k_1 = k_1'[H+]$, $k_{-2} = k_{-2}'[H+]$, $k_3 = k_3'[Br_2]$, $k_{-3} = k_{-3}'[Br^-]$.

According to the *steady-state* approximation,

$$v = k_{obs}[RCOCH_3] = k_1 k_2 k_3 k_4 [RCOCH_3]/\{k_2 k_3 k_4 + k_{-1} k_3 k_4 + k_{-1} k_{-2}(k_{-3} + k_4)\}.$$

or $k_{obs} = k_1 k_2 k_3 k_4/\{k_2 k_3 k_4 + k_{-1} k_3 k_4 + k_{-1} k_{-2}(k_{-3} + k_4)\}.$

If $k_4 \gg k_{-3}$, k_{-3} can be ignored in the parentheses, so that k_{obs} simplifies to $k_1 k_2 k_3 k_4/\{k_2 k_3 k_4 + k_{-1} k_3 k_4 + k_{-1} k_{-2} k_4\}$. Then if $k_3 \gg k_{-2}$, k_{obs} simplifies further to $k_1 k_2 k_3 k_4/\{k_2 k_3 k_4 + k_{-1} k_3 k_4\}$, where $k_3 k_4$ cancels and k_{obs} becomes $k_1 k_2/\{k_{-1} + k_2\}$, so that k_2 is the last rate constant remaining in k_{obs}. The second step is rate-limiting, and the rate is independent of k_3 or of $[Br_2]$.

Note 1: Although the expressions rate-controlling, rate-determining, and rate-limiting are often regarded as synonymous, rate-limiting is to be preferred, because in Case 2 all three rate constants enter into the rate equation, so that all three are rate-controlling and rate-determining, but the first step is not rate-limiting.

Note 2: If the concentration of any intermediate builds up to an appreciable extent, then the steady-state approximation no longer holds, and the reaction should be analyzed as though that intermediate is the reactant.

Note 3: It should be noted that a *catalytic cycle* does not have a rate-determining step. Instead, under steady-state conditions, all steps proceed at the same rate because the concentrations of all intermediates adjust so as to offset the differences in the corresponding rate constants [360].

See also *Gibbs energy diagram*, *microscopic diffusion control*, *mixing control*.

rev[3]

rate of reaction

v

(unit: mol dm^{-3} s^{-1} or mol L^{-1} s^{-1})

For the general *chemical reaction*

$$a\,A + b\,B\ =\ p\,P + q\,Q\ ...$$

occurring under constant-volume conditions, without an appreciable build-up of reaction *intermediate*s, 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 inside square brackets denote concentrations (conventionally expressed in unit $mol\ dm^{-3}$). The symbols R and r are also used instead of v. It is recommended that the unit of time be the second.

Example:

$$Cr_2O_7^{2-} + 3\ (CH_3)_2CHOH + 8\ H^+ = 2\ Cr^{3+} + 3\ (CH_3)_2C=O + 7\ H_2O$$

$$v = -\frac{d[Cr_2O_7^{2-}]}{dt} = -\frac{1}{3}\frac{d[(CH_3)_2CHOH]}{dt} = \frac{1}{2}\frac{d[Cr^{3+}]}{dt} = \frac{1}{3}\frac{d[(CH_3)_2C=O]}{dt}$$

Note: For a *stepwise reaction* this definition of rate of reaction 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., $-d[A]/dt$) or rate of appearance of P (i.e., $d[P]/dt$) be used, depending on the particular *chemical species* that is actually observed. In some cases reference to the *chemical flux* observed may be more appropriate.

See [13].

See also *chemical relaxation*, *lifetime*, *order of reaction*.

rev[3]

reaction coordinate

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 as a measure of the progress along a *minimum-energy reaction path*.

Note 1: The term "reaction coordinate" is often used to refer to a geometric variable itself (typically a bond distance or bond angle, or a combination of distances and/or angles) as well as (or instead of) the value of that variable. Although strictly incorrect, this usage is very commonly encountered.

Note 2: In cases where the location of the transition structure is unknown, an internal coordinate of the system (e.g., a geometric variable or a bond order, or an energy gap between reactant-like and product-like valence-bond structures) is often selected as a reaction coordinate. A *potential-energy profile* obtained by energy minimization over

other coordinates for a succession of fixed values of an arbitrary reaction coordinate is not guaranteed to pass through the *transition structure* unless it is a continuous function of that reaction coordinate. Similarly, a free-energy profile obtained as a *potential of mean force* with respect to an arbitrary reaction coordinate is not guaranteed to pass through the lowest-energy *transition state*.

Note 3: "Reaction coordinate" is sometimes used as an undefined label for the horizontal axis of a *potential-energy profile* or a *Gibbs energy diagram*.

See [349,361].

See also *Gibbs energy diagram*, *potential-energy profile*, *potential-energy surface*.

rev[3]

reaction path

(1) Synonym for *mechanism*.

(2) Trajectory on the *potential-energy surface*.

rev[3]

reaction step

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.

[3]

reactive intermediate

intermediate

reactivity (n.), reactive (adj.)

Kinetic property of a *chemical species* by which (for whatever reason) it has a different rate constant for a specified *elementary reaction* than some other (reference) species.

Note 1: 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.

Note 2: Term also used more loosely as a phenomenological description not restricted to elementary reactions. When applied in this sense, the property under consideration may reflect not only rate constants but also equilibrium constants.

See also *stable*, *unreactive*, *unstable*.

[3]

reactivity index

Numerical quantity derived from quantum-mechanical model calculations or from a *linear Gibbs-energy relationship (linear free-energy relationship)* that permits the prediction or correlation of relative reactivities of different molecular sites.

Note: 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 π-electron energy and π-*electron density*.

rev[3]

reactivity-selectivity principle (RSP)

Idea that the more *reactive* a reagent is, the less *selective* it is.

Note: There are many examples in which the RSP is followed, but there are also many counterexamples. Although the RSP is in accord with intuitive feeling, it is now clear that selectivity can decrease, increase, or remain constant as *reactivity* increases, so that the RSP is unreliable as a guide to reactivity.

See [126,346,362,363,364,365].

rev[3]

rearrangement

See *degenerate rearrangement*, *molecular rearrangement*, *sigmatropic rearrangement*.

[3]

reduction

(1) Transfer of one or more electrons to a *molecular entity*, usually inorganic.

(2) Decrease in the *oxidation number* of any atom within any *substrate* [344].

(3) Loss of oxygen or halogen and/or gain of hydrogen of an organic *substrate*.

See *oxidation.*

rev[3]

reductive elimination

Reverse of *oxidative addition*.

[3]

regioselectivity (*n.*), **regioselective** (*adj.*)

Property of a reaction in which one position of *bond* making or breaking occurs preferentially over all other possible positions.

Note 1: The resulting regioisomers are *constitutional isomers*.

Note 2: Reactions are termed completely (100 %) regioselective if the discrimination is complete, or partially (*x* %) if the product of reaction at one site predominates over

1   1 the product of reaction at other sites. The discrimination may also be referred to semi-
2   2 quantitatively as high or low regioselectivity.

3   *Note 3*: Historically the term was restricted to *addition reaction*s of unsymmetrical
4 reagents to unsymmetrical alkenes.

5 *Note 4*: In the past, the term regiospecificity was proposed for 100 % regioselectivity.
6 This terminology is not recommended, owing to inconsistency with the terms
7 *stereoselectivity* and *stereospecificity*.

8 See [366,367].

9 See also *chemoselectivity*.

10 rev[3]

11

Reichardt E_T parameter

13 See *Dimroth-Reichardt $E_T(30)$ parameter*.

14

relaxation

16 Passage of a system that has been perturbed from *equilibrium*, by radiation excitation
17 or otherwise, toward or into thermal equilibrium with its environment.

18 See [9].

19 See also *chemical relaxation*.

20 rev[3]

21

reorganization energy

23 Gibbs energy required to distort the reactants (and their associated solvent molecules)
24 from their relaxed nuclear configurations to the relaxed nuclear configurations of the
25 products (and their associated solvent molecules).

26 *Note 1:* This approach was originally formulated for one-electron transfer reactions,
27 A + D → A⁻· + D⁺·, in the framework of the *Marcus equation*, assuming weak coupling
28 between the reactants [368].

29 *Note 2:* Reorganization energy is not the same as distortion energy, which is the
30 energy required to distort the reactants to the nuclear configuration of the *transition*
31 *state*.

32 *Note 3:* This approach has been extended to enzyme-catalysed reactions [369].

33 *Note 4:* Marcus theory has been shown to be valid for some complex reactions
34 (*cycloaddition*, S_N2), even though the weak-coupling assumption is clearly not valid. In
35 these cases the reorganization energy (in terms of activation strain) is counteracted by
36 stabilizing interactions (electrostatic and orbital) [166].

37 See also *distortion interaction model*, *intrinsic barrier*, *Marcus equation*.

38 rev[3]

39

resonance

Representation of the electronic structure of a *molecular entity* in terms of contributing *Lewis structure*s.

Note 1: Resonance means that the *wavefunction* is represented by mixing the wavefunctions of the contributing Lewis structures.

Note 2: The contributing Lewis structures are represented as connected by a double-headed arrow (↔), rather than by the double arrow (⇄) representing *equilibrium* between species.

Note 3: This 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.

Note 4: This term has a completely different meaning in physics.

See [75,370].

See also [371].

rev[3]

resonance effect

Experimentally observable influence (on reactivity, etc.) of a *substituent* through electron *delocalization* to or from the substituent.

See [126,173,191].

See also *inductive effect*.

rev[3]

resonance energy

Difference in potential energy between the actual *molecular entity* and the contributing *Lewis structure* of lowest potential energy.

Note: The resonance energy cannot be measured experimentally, but only estimated, since contributing Lewis structures are not observable molecular entities.

See *resonance*.

rev[3]

resonance form

resonance structure, contributing structure, canonical form

One of at least two *Lewis structure*s,with fixed single, double, and triple bonds, that is a contributing structure to the valence-bond *wavefunction* of a molecule that cannot be described by a single Lewis structure.

Note 1: Although the valence-bond wavefunction is a linear combination of the wavefunctions of the individual resonance forms, the coefficients and the relative contributions of the various resonance forms are usually kept qualitative. For example,

1　the major resonance forms for the conjugate base of acetone are $CH_2=C(CH_3)–O^-$ and

2　$H_2C^-–C(CH_3)=O$, with the former contributing more.

3　　*Note 2:* Resonance forms are connected by a double-headed arrow ($\leftrightarrow$). This must

4　not be confused with the double arrow connecting species in *equilibrium* ($\rightleftharpoons$).

5　　See also *delocalization*, *Kekulé structure*, *resonance*.

6

resonance hybrid

7

8　*Molecular entity* whose electronic structure is represented as the superposition of two

9　or more *resonance form*s (or *Lewis structure*s) with different formal arrangements of

10　electrons but identical arrangements of nuclei.

11　　*Note 1:* Whereas each contributing resonance form represents a localized

12　arrangement of electrons which, considered by itself, would imply different bond lengths

13　(say) for formal single and double bonds, *resonance* between two or more contributors

14　requires each to have the same geometry, namely that of the resulting hybrid, which

15　represents a delocalized arrangement of electrons. A particular bond in the hybrid may

16　have a length that is, loosely, an "average" of formal single-bond and double-bond

17　values implied by its contributing individual resonance forms, but the hybrid does not

18　oscillate among these as if they were in *equilibrium*.

19　　*Note 2*: The resonance forms are connected by a double-headed arrow ($\leftrightarrow$), rather

20　than by the double arrow ($\rightleftharpoons$) representing equilibrium between species.

21

retrocycloaddition

22

23　deprecated

24　*Cycloelimination*.

25　　[3]

26

Ritchie equation

27

28　*Linear Gibbs-energy relation (linear free-energy relation)*

29

30　　$$\lg\{k_N\} = \lg\{k_0\} + N_+$$

31

32　applied to the reactions between nucleophiles and certain large and relatively stable

33　organic cations, e.g., arenediazonium, triarylmethyl, and aryltropylium cations, in

34　various solvents, where $\{k_N\}$ is the (reduced) second-order *rate constant* for reaction of

35　a given cation with a given nucleophilic system (i.e., given *nucleophile* in a given

36　solvent). $\{k_0\}$ is the (reduced) first-order rate constant for the same cation with water in

37　water, and N_+ is a parameter characteristic of the nucleophilic system and independent

38　of the *electrophilic* reaction partner.

39　　The discrepancy between second-order and first-order rate constants must be

40　reconciled by writing the equation with arguments of the logarithms of dimension 1, i.e.,

by using reduced rate constants (as denoted by the curly brackets in the defining equation):

$$\lg\,[k_N/(dm^3\,mol^{-1}s^{-1})] = \lg\,(k_0/s^{-1}) + N_+$$

Note 1: 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 decadic log (lg) units. The equation thus involves a gigantic breakdown of the *reactivity-selectivity principle*.

Note 2: The Ritchie equation is a special case of the more general *Mayr-Patz equation*.

See [193,372,373]. See also [125,374].

rev[3]

ρ-value (rho-value)

Quantitative measure of the susceptibility of the *rate constant* or *equilibrium* constant of an organic reaction to the influence of *substituent* groups, usually on an *aromatic* ring.

Note 1: Defined by Hammett to describe the effects of substituents at the *meta*- and *para*-positions on rate or equilibrium of a reaction on the side chain of a substituted benzene, the empirical equation has the general form

$$\lg(k_X/k_H)\text{ or }\lg(K_X/K_H) = \rho\sigma_X$$

in which σ_X is a constant characteristic of the substituent X and of its position in the reactant molecule.

Note 2: More generally (not only for aromatic series), ρ-values (modified with appropriate subscripts and superscripts) are used to designate the susceptibility to substituent effects of reactions of families of organic compounds, as given by the modified set of σ-constants in an empirical correlation.

Note 3: Reactions with a positive ρ-value are accelerated (or the equilibrium constants 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 involve a *transition state* (or reaction product) with an increased *electron density* at the *reactive* site of the substrate.

See also *Hammett equation*, σ-*constant*, *Taft equation*.

rev[3]

$\rho\sigma$-equation (rho-sigma equation)
See *Hammett equation*, *ρ-value*, *σ-constant*, *Taft equation*.
[3]

salt effect
See *kinetic electrolyte effect*.
[3]

saturation transfer
See *magnetization transfer*.
rev[3]

Saytzeff rule
Preferential removal of a hydrogen from the β carbon that has the fewest hydrogens in dehydrohalogenation of secondary and tertiary haloalkanes.
Note 1: The rule was originally formulated by A. Saytzeff (Zaitsev) to generalize the orientation in *β-elimination* reactions of haloalkanes. It 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.
Note 2: Exceptions to the Saytzeff rule are exemplified by the *Hofmann rule*.
See [375].
See also *Markovnikov rule*.
[3]

scavenger
Substance that reacts with (or otherwise removes) a trace component (as in the scavenging of trace metal ions) or traps a *reactive intermediate*.
See also *inhibition*.
[3]

selectivity
Discrimination shown by a reagent in competitive attack on two or more *substrate*s or on two or more positions or diastereotopic or enantiotopic faces of the same substrate.
Note 1: Selectivity is quantitatively expressed by the ratio of *rate constant*s of the competing reactions, or by the decadic logarithm of such a ratio.
Note 2: In the context of *aromatic substitution* (usually *electrophilic*, for monosubstituted benzene derivatives), the selectivity factor S_f (expressing discrimination between *p*- and *m*-positions in PhZ) is defined as

$$S_f = \lg (p_f^Z/m_f^Z)$$

where the *partial rate factors* p_f^Z and m_f^Z express the *reactivity* of para and meta positions in the aromatic compound PhZ relative to that of a single position in benzene.

See [347].

See also *isoselective relationship*, *partial rate factor*, *regioselectivity*, *stereoselectivity*.

rev[3]

self-assembly

Process whereby a system of single-molecule components spontaneously forms an organized structure, owing to *molecular recognition*.

shielding

Extent to which the effective magnetic field is reduced for a nucleus in a molecule immersed in an external magnetic field, relative to that experienced by a bare nucleus in that field.

Note 1: The reduction is due to the circulation of the electrons around the observed and the neighbouring nuclei. The external field induces a magnetic moment that 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).

Note 2: This phenomenon is the origin of the structural dependence of the resonance frequencies of the nuclei.

See also *chemical shift*.

[3]

shift reagent

Paramagnetic substance that induces an additional change of the NMR resonance frequency of a nucleus near any site in a molecule to which the substance binds.

See *chemical shift*.

sigma, pi

See σ, π

rev[3]

sigmatropic rearrangement

Molecular rearrangement that involves both the creation of a new σ *bond* between atoms previously not directly linked and the breaking of an existing σ bond.

Note 1: There is normally a concurrent relocation of π bonds in the molecule concerned, but neither the number of π bonds nor the number of σ bonds changes.

Note 2: The *transition state* of such a reaction may be visualized as an *association*

1   of two fragments connected at their termini by two partial σ bonds, one being broken

2   and the other being formed as, for example, the two allyl fragments in (a'). Considering

3   only atoms within the (real or hypothetical) cyclic array undergoing reorganization, if the

4   numbers of these in the two fragments are designated *i* and *j*, then the rearrangement

5   is said to be a sigmatropic change of order [*i*,*j*] (conventionally *i* ≤ *j*). Thus rearrangement

6   (a) is of order [3,3], whereas rearrangement (b) is a [1,5]sigmatropic shift of hydrogen.

7   (By convention the square brackets [...] here refer to numbers of atoms, in contrast with

8   current usage in the context of *cycloaddition*.)

11   The descriptors a and s (*antarafacial* and *suprafacial*) may also be annexed to the

12   numbers *i* and *j*; (b) is then described as a [1$_s$,5$_s$] sigmatropic rearrangement, since it is

13   suprafacial with respect to both the hydrogen atom and the pentadienyl system:

17   See also *cycloaddition*, *tautomerization*.

18   rev[3]

20   **silylene**

21   (1) Generic name for H_2Si**:** and substitution derivatives thereof, containing an

22   electrically neutral bivalent silicon atom with two non-bonding electrons. (The definition

23   is analogous to that given for *carbene*.)

24   (2) The silanediyl group ($H_2Si<$), analogous to the methylene group ($H_2C<$).

25   [3]

27   **single-electron transfer mechanism (SET)**

28   Reaction *mechanism* characterized by the transfer of a single electron between two

1 species, occurring in one of the steps of a multistep reaction.

2 [3]

3

single-step reaction

5 one-step reaction

6 Reaction that proceeds through a single *transition state* (or no transition state).

7 [3]

8

9

skeletal formula

11 bond-line formula

12 Two-dimensional representation of a *molecular entity* in which bonds are indicated as

13 lines between vertices representing octet carbon atoms with attached hydrogens

14 omitted and in which other atoms are represented by their chemical symbols.

15 *Examples:* ethanol, cyclohexene, 4-pyridone

16

17

18

19 See *line formula*.

20

Slater-type orbital (STO)

22 Function centred on an atom for which the radial dependence has the form $\phi(r) \propto r^{n-1}$

23 $\exp(-\zeta r)$, used to approximate *atomic orbital*s in the LCAO-MO method.

24 *Note 1*: n is the effective principal quantum number and ζ is the orbital exponent

25 (screening constant) derived from empirical considerations.

26 *Note 2*: The angular dependence is usually introduced by multiplying the radial

27 function by a spherical harmonic $Y_{1m}(\theta, \phi)$.

28 *Note 3*: Owing to difficulties in computing the integrals of STOs analytically for

29 molecules with more than two atoms they are often replaced by linear combinations of

30 *Gaussian orbitals*.

31 See [8].

32 rev[3]

33

solvation

1 Stabilizing interaction between a solute (or solute moiety) and the solvent.

2 *Note*: Such interactions generally involve electrostatic forces and *van der Waals*

3 *forces*, as well as chemically more specific effects such as *hydrogen bond* formation.

4 See also *cybotactic region*.

5 [3]

6

solvatochromic relationship

8 *Linear Gibbs-energy relationship (linear free-energy relationship)* based on

9 *solvatochromism*.

10 See also *Dimroth-Reichardt E_T parameter*, *Kamlet-Taft solvent parameters*.

11 [3]

12

solvatochromism

14 Pronounced change in position and sometimes intensity of an electronic absorption or

15 emission band, accompanying a change in the *polarity* of the *medium*.

16 *Note*: Negative (positive) solvatochromism corresponds to a *hypsochromic shift*

17 (*bathochromic shift*) with increasing solvent polarity.

18 See [9,17,376].

19 See also *Dimroth-Reichardt E_T parameter*, *Z-value*.

20 [3]

21

solvatomers

23 *Isomers* that differ in their solvation environment.

24 *Note 1:* Because the solvation environment fluctuates rapidly, solvatomers

25 interconvert rapidly.

26 *Note 2:* Species that differ in the type of solvent molecules should not be called

27 solvatomers, because they are not isomers.

28

solvent parameter

30 Quantity that expresses the capability of a solvent for interaction with solutes, based on

31 experimentally determined physicochemical quantities, in particular: relative

32 *permittivity*, refractive index, *rate constant*s, Gibbs energies and enthalpies of reaction,

33 and ultraviolet-visible, infrared, and NMR spectra.

34 *Note 1*: Solvent parameters are used in *correlation analysis* of solvent effects, either

35 in single-parameter or in multiple-parameter equations.

36 *Note 2:* Solvent parameters include those representing a bulk property, such as

37 relative *permittivity* (dielectric constant) as well as those that describe a more localized

38 solute/solvent interaction, such as hydrogen-bonding acceptance or donation and

39 Lewis acid/base adduct formation.

40 See [17,377].

1   See also: *acceptor number*, *Catalán solvent parameters*, *Dimroth-Reichardt E_T*
2 *parameter*, *Grunwald-Winstein equation*, *Kamlet-Taft solvent parameters*, *Laurence*
3 *solvent parameters*, *Koppel-Palm solvent parameters*, *linear solvation energy*
4 *relationship*, *Z-value*.
5   rev[3]
6

solvolysis

7
8 Reaction with solvent.
9   *Note 1*: Such a reaction generally involves the rupture of one or more *bond*s in the
10 solute. More specifically the term is used for *substitution*, *elimination,* and *fragmentation*
11 reactions in which a solvent species serves as *nucleophile* or *base*.
12   *Note 2:* A solvolysis can also be classified as a *hydrolysis*, alcoholysis, or
13 ammonolysis, etc., if the solvent is water, alcohol, or ammonia, etc.
14   *Note 3:* Often a solvolysis is a *nucleophilic substitution* (usually S_N1, accompanied
15 by E1 *elimination*), where the nucleophile is a solvent molecule.
16   rev[3]
17

SOMO

18
19 **S**ingly **O**ccupied **M**olecular **O**rbital (such as the half-filled *HOMO* of a radical).
20   See also *frontier orbitals*.
21   [3]
22

special salt effect

23
24 Steep increase of the rate of certain solvolysis reactions observed at low concentrations
25 of some non-common-ion salts.
26   *Note*: The effect is attributed to trapping of an intimate *ion pair* that would revert to
27 reactant in the absence of the salt.
28   See also *kinetic electrolyte effect*.
29   rev[3]
30

specific catalysis

31
32 Acceleration of a reaction by a unique *catalyst*, rather than by a family of related
33 substances.
34   *Note*: The term is most commonly used in connection with specific hydrogen-ion or
35 hydroxide-ion (*lyonium ion* or *lyate ion*) catalysis.
36   See also *general acid catalysis*, *general base catalysis*, *pseudo-catalysis*.
37   [3]
38

spectator mechanism

39
40 *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.,

A + C ⇌ (Pre-association) → (A·····C) encounter complex → (B·····C) encounter complex → (rapid) Product

Note: The formation of B from A may itself be a bimolecular reaction with some other reagent. Since C does not assist the formation of B, it is described as being present as a spectator.

See also *microscopic diffusion control*.

[3]

spin adduct

See *spin trapping*.

[3]

spin counting

See *spin trapping*.

[3]

spin density

Unpaired *electron density* at a position of interest, usually at carbon, in a *radical* or a *triplet state*.

Note: Spin density is often measured experimentally by electron paramagnetic resonance/electron spin resonance (EPR/ ESR) spectroscopy through hyperfine splitting of the signal by neighbouring magnetic nuclei.

See also *radical centre*.

[3]

spin label

Stable paramagnetic *group* (typically an *aminoxy* radical, $R_2NO^•$) that is attached to a part of a *molecular entity* whose chemical environment may be revealed by its electron spin resonance (ESR) spectrum.

Note: When a paramagnetic molecular entity is used without covalent attachment to the molecular entity of interest, it is frequently referred to as a spin probe.

[3]

spin trapping

Formation of a more *persistent* radical from interaction of a *transient radical* with a

1 diamagnetic reagent.

2 *Note 1*: The product radical accumulates to a concentration where detection and,
3 frequently, identification are possible by EPR/ESR spectroscopy.

4 *Note 2*: The key reaction is usually one of *attachment*; the diamagnetic reagent is
5 said to be a spin trap, and the persistent product radical is then the spin *adduct*. The
6 procedure is referred to as spin trapping, and is used for monitoring reactions involving
7 the intermediacy of *reactive* radicals at concentrations too low for direct observation.
8 Typical spin traps are *C*-nitroso compounds and nitrones, to which reactive radicals will
9 rapidly add to form *aminoxy* radicals.

10 *Example:*

11

12 *Note 3*: A quantitative development in which essentially all reactive radicals
13 generated in a particular system are intercepted has been referred to as spin counting.

14 *Note 4*: Spin trapping has also been adapted to the interception of radicals generated
15 in both gaseous and solid phases. In these cases the spin adduct is in practice
16 transferred to a liquid solution for EPR/ESR observation.

17 [3]

18

19 **stable**

20 Having a lower standard Gibbs energy, compared to a reference *chemical species*.

21 *Note 1*: Quantitatively, in terms of Gibbs energy, a chemical species A is more stable
22 than its isomer B if $\Delta_r G°$ is positive for the (real or hypothetical) reaction A → B.

23 *Note 2*: For the two reactions

24

25   P → X + Y $\Delta_r G_1°$
26 and   Q → X + Z $\Delta_r G_2°$

27

28 if $\Delta_r G_1° > \Delta_r G_2°$, then P is more stable relative to its product Y than is Q relative to Z.

29 *Note 3*: Both in qualitative and quantitative usage the term stable is therefore always
30 used in reference to some explicitly stated or implicitly assumed standard.

31 *Note 4*: The term should not be used as a synonym for *unreactive* or less *reactive*
32 since this confuses thermodynamics and kinetics. A relatively more stable chemical
33 species may be more reactive than some reference species towards a given reaction
34 partner.

35 See also *inert*, *unstable*.

36 [3]

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2 **stationary state**

3 (1) (in quantum mechanics): _Wavefunction_ whose probability density $|\Psi|^2$ remains
4 constant and whose observable properties do not evolve with time.
5 (2) (in kinetics): See _steady state_.
6   [3]

7

8 **steady state (or stationary state)**
9 (1) Approximation that the kinetic analysis of a complex reaction involving _unstable_
10 intermediates in low concentration can be simplified by setting the rate of change of
11 each such _intermediate_ equal to zero, so that the rate equation can be expressed as a
12 function of the concentrations of _chemical species_ present in macroscopic amounts.
13   For example, if X is an _unstable_ intermediate in the reaction sequence:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$$

$$X + C \xrightarrow{k_2} D$$

14
15

16 Since [X] is negligibly small, d[X]/dt, the rate of change of [X], can be set equal to zero.
17 The steady state approximation then permits solving the following equation
18

19   d[X]/dt = k_1[A] − k_{-1}[X] − k_2[X][C] = 0
20

21 to obtain the steady-state [X]:
22

23   [X] = k_1[A]/(k_{-1} + k_2[C])
24

25 whereupon the rate of reaction is expressed:
26

27   d[D]/dt = k_2[X][C] = $k_1 k_2$[A][C]/(k_{-1} + k_2[C])
28

29   _Note_: The steady-state approximation does not imply that [X] is even approximately
30 constant, only that its absolute rate of change is very much smaller than that of [A] and
31 [D].
32 (2) Regime in a stirred flow reactor such that all concentrations are independent of time.
33   See [13].
34   [3]
35

36 **stepwise reaction**
37 _Chemical reaction_ with at least one reaction _intermediate_ and involving at least two
38 consecutive _elementary reaction_s.

1   See also *composite reaction*, *reaction step*.

2   [3]

3

stereoelectronic

Pertaining to the dependence of the properties (especially energy or *reactivity*) of a *molecular entity* or of a *transition state* on the relative disposition of electron pairs owing to the nuclear geometry.

    Note: Stereoelectronic effects are ascribed to the differing overlaps of *atomic orbital*s in different *conformation*s.

    See [11].

    [3]

stereogenic centre

Atom within a molecule bearing groups such that interchanging any two of them leads to a *stereoisomer* of the original molecule.

    See [11,378].

stereoisomers

Isomers that have the same bonds (*connectivity*) but differ in the arrangement of their atoms and cannot be interconverted by rapid rotation around single bonds.

    See [11].

stereoselectivity (stereoselective)

Preferential formation in a *chemical reaction* of one *stereoisomer* over another.

    Note 1: When the stereoisomers are *enantiomer*s, the phenomenon is called enantioselectivity and is quantitatively expressed by the enantiomeric excess or enantiomeric ratio; when they are *diastereoisomers*, it is called *diastereoselectivity* and is quantitatively expressed by the diastereomeric excess or diastereomeric ratio.

    Note 2: Reactions are termed 100 % stereoselective if the preference is complete, or partially (*x* %) stereoselective if one product predominates. The preference may also be referred to semiquantitatively as high or low stereoselectivity

    See [11,140].

    [3]

stereospecificity (stereospecific)

Property of those *chemical reaction*s in which different stereoisomeric reactants are converted into different stereoisomeric products.

    Example: electrocyclization of *trans,cis,trans*-octa-2,4,6-triene produces *cis*-5,6-dimethylcyclohexa-1,3-diene, whereas *cis,cis,trans*-octa-2,4,6-triene produces racemic *trans*-5,6-dimethylcyclohexa-1,3-diene.

1

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Note 1: A stereospecific process is necessarily *stereoselective* but not all stereoselective processes are stereospecific. Stereospecificity may be total (100 %) or partial.

Note 2: The term is also applied to situations where reaction can be performed with only one stereoisomer. For example the exclusive formation of racemic *trans*-1,2-dibromocyclohexane upon bromination of cyclohexene is a stereospecific process, even though the analogous reaction with (*E*)-cyclohexene has not been performed.

Note 3: Stereospecificity does NOT mean very high stereoselectivity. This usage is unnecessary and is strongly discouraged.

See [11,140].

For the term stereospecific polymerization see [379].

rev[3]

steric-approach control

Situation in which the *stereoselectivity* of a reaction under *kinetic control* is governed by steric hindrance to attack of the reagent, which is directed to the less hindered face of the molecule.

Note: Partial bond making at the *transition state* must be strong enough for steric control to take place, but the transition state should not be so close to products that the steric demand of the reagent at the transition state is the same as the steric demand of the group as present in the product.

An example is LiAlH$_4$ reduction of 3,3,5-trimethylcyclohexan-1-one, where steric hindrance by an axial methyl directs hydride addition to the equatorial position, even though the more stable product has the H axial and the OH equatorial.

See also *product-development control*.

rev[3]

steric effect

Consequences for molecular geometry, thermochemical properties, spectral features, solvation, or reaction rates resulting from the fact that atoms repel each other at close distance. The repulsion is due to the quantum-mechanical Pauli exclusion principle. Substitution of hydrogen atoms by groups with a larger van der Waals radius may lead to situations where atoms or groups of atoms repel each other, thereby affecting distances and angles.

Note 1: It is in principle difficult to separate the steric effect from other electronic effects.

Note 2: For the purpose of *correlation analysis* or *linear Gibbs-energy relations* (*linear free-energy relation*s) various scales of steric parameters have been proposed, notably *A values*, Taft's E_S and Charton's *v* scales.

Note 3: A steric effect on a rate process may result in a rate increase (steric acceleration) or a decrease (steric retardation) depending on whether the transition state or the reactant state is more affected by the steric effect.

Note 4: Bulky groups may also attract each other if at a suitable distance.

See [290,380].

See *Taft equation*, *van der Waals forces*.

rev[3]

steric hindrance

Steric effect whereby the crowding of substituents around a reaction centre retards the attack of a reagent.

rev[3]

stopped flow

Technique for following the kinetics of reactions in solution (usually in the millisecond time range) in which two, or more, 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 a method with a rapid response (e.g., optical absorption spectroscopy).

See *mixing control*.

rev[3]

strain

Feature of a *molecular entity* or *transition structure* for which the energy is increased because of unfavourable non-bonded (steric) interactions, bond lengths, bond angles, or dihedral angles (torsional strain), relative to a standard.

1   *Note 1*: The strain energy is quantitatively defined as the standard enthalpy of a
2   structure relative to that of a strainless structure (real or hypothetical) made up from the
3   same atoms with the same types of bonding.

4   For example, the enthalpy of formation of cyclopropane is +53.6 kJ mol^{-1}, whereas
5   the hypothetical enthalpy of formation based on three "normal" methylene groups, from
6   acyclic models, is -62 kJ mol^{-1}. On this basis cyclopropane is destabilized by ca. 115 kJ
7   mol^{-1} of strain energy.

8   See *molecular mechanics*.

9   [3]

10

11   **structural isomers**
12   discouraged term for *constitutional isomers*.

13

14   **subjacent orbital**
15   **N**ext-to-**H**ighest **O**ccupied **M**olecular **O**rbital (NHOMO, also called HOMO–1).
16   *Note*: Subjacent and *superjacent* orbitals sometimes play an important role in the
17   interpretation of molecular interactions according to the *frontier orbital* approach.
18   See [381].
19   [3]

20

21   **substituent**
22   Any atom or *group* of bonded atoms that can be considered to have replaced a
23   hydrogen atom (or two hydrogen atoms in the special case of bivalent groups) in a
24   parent *molecular entity* (real or hypothetical).
25   [3]

26

27   **substitution**
28   *Chemical reaction*, elementary or stepwise, of the form A–B + C → A–C + B, in which
29   one atom or group in a molecular entity is replaced by another atom or group.
30   *Examples*
31   $CH_3Cl + HO^- \rightarrow CH_3OH + Cl^-$
32   $C_6H_6 + NO_2^+ \rightarrow C_6H_5NO_2 + H^+$

33   *Note:* A substitution reaction can be distinguished as an *electrophilic substitution* or
34   a *nucleophilic substitution*, depending on the nature of the reactant that is considered
35   to react with the *substrate*.
36   rev[3]

37

38   **substrate**
39   *Chemical species*, the reaction of which with some other chemical reagent is under
40   observation (e.g., a compound that is transformed under the influence of a catalyst).

Note: The term should be used with care. Either the context or a specific statement should always make it clear which chemical species in a reaction is regarded as the substrate.

See also *transformation*.

[3]

successor complex

Chemical species formed by the transfer of an electron or of a hydrogen (atom or ion) from a donor D to an acceptor A after these species have diffused together to form the precursor or *encounter complex*:

$$A + D \longrightarrow (A\ D) \longrightarrow (A^{\cdot -}\ D^{\cdot +})$$

$$A + DH \longrightarrow (A\ DH) \longrightarrow (AH^{\cdot -}\ D^{\cdot +})\ or\ (AH^+\ D^-)$$

rev[3]
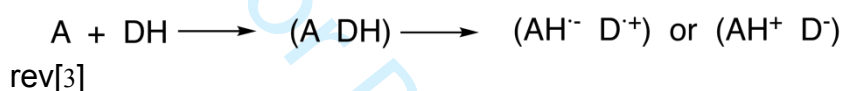
suicide inhibition

See *mechanism-based inhibition*.

[3]

superacid

Medium having a high *acidity*, generally greater than that of 100 % sulfuric acid. The common superacids are made by dissolving a powerful *Lewis acid* (e.g., SbF_5) in a suitable *Brønsted acid*, such as HF or HSO_3F.

Note 1: An equimolar mixture of HSO_3F and SbF_5 is known by the trade name Magic Acid.

Note 2: An uncharged gas-phase substance having an endothermicity (enthalpy) of deprotonation (dehydronation) lower than that of H_2SO_4 is also called a superacid. Nevertheless such a superacid is much less acidic in the gas phase than similar cationic acids.

See [18,382,383,384].

See *acidity, superbase*.

rev[3]

superbase

Compound having a very high *basicity*.

Examples include amide bases such as LDA, potassium *tert*-butoxide + organolithium, some phosphazenes.

See *superacid*.

See [385].

rev[3]

1 **superjacent orbital**

2 **S**econd **L**owest **U**noccupied **M**olecular **O**rbital (SLUMO).

3 *Note*: *Subjacent* and superjacent orbitals sometimes play an important role in the

4 interpretation of molecular interactions according to the *frontier orbital* approach.

5 See [381].

6

7 **suprafacial**

8 See *antarafacial*.

9 [3]

10

11 **supramolecular**

12 Description of a system of two or more *molecular entities* that are held together and

13 organized by means of intermolecular (noncovalent) binding interactions.

14 See [386].

15 [3]

16

17 **Swain-Lupton equation**

18 Dual-parameter approach to the correlation analysis of substituent effects, which

19 involves a field constant (F) and a resonance constant (R).

20

21 $$\lg(k_X/k_H) \; = \; fF_X \; + \; rR_X$$

22

23 See [191,387].

24 *Note 1*: The original treatment was modified later.

25 *Note 2*: The procedure has often been applied, but also often criticized.

26 See [388,389,390,391,392].

27 [3]

28

29 **Swain-Scott equation**

30 *Linear Gibbs-energy relation* (*linear free-energy relation*) of the form

31

32 $$\lg(k/k_0) = sn$$

33

34 applied to the variation of *reactivity* of a given *electrophilic* substrate towards a series

35 of *nucleophilic* reagents, where k_0 is a *rate constant* for reaction with water, k is the

36 corresponding rate constant for reaction with any other nucleophilic reagent, n is a

37 measure of the *nucleophilicity* of the reagent (n = 0.0 for water) and s is a measure of

38 the sensitivity of the substrate to the nucleophilicity of the reagent (s = 1.0 for CH_3Br).

39 See [192].

40 See also *Mayr-Patz equation, Ritchie equation*.

1 [3]

2

3 **symproportionation**

4 *comproportionation*

5   [3]

6

7 ***syn***

8   See *anti*.

9   See [11].

10   [3]

11

12 **synartetic acceleration**

13   See *neighbouring group participation*.

14   [3]

15

16 **synchronization**

17   See *principle of nonperfect synchronization*.

18   rev[3]

19

20 **synchronous**

21 Feature of a *concerted* process in which all the changes (generally bond rupture and

22 bond formation) have progressed to the same extent at the *transition state*.

23   *Note 1:* A synchronous reaction is distinguished from (1) a concerted reaction, which

24 takes place in a single kinetic step without being synchronous, (2) a reaction where

25 some of the changes in bonding take place earlier, followed by the rest, and (3) a two-

26 step reaction, which takes place in two kinetically distinct steps, via a stable

27 *intermediate*

28   *Note 2*: The progress of the bonding changes (or other primitive changes) is not

29 defined quantitatively in terms of a single parameter applicable to different bonds. The

30 concept therefore does not admit an exact definition except in the case of concerted

31 processes involving changes in two identical bonds. If the bonds are not identical, the

32 process should simply be described as concerted.

33   See [393,394,395]. For an index of synchronicity see [396].

34   See also *imbalance*.

35   rev[3]

36

37 σ, π

38 Symmetry designations that distinguish *molecular orbital*s as being symmetric (σ) or

39 antisymmetric (π) with respect to a defining plane containing at least one atom.

40   *Note 1*: In practice the terms are used both in this rigorous sense (for orbitals

encompassing the entire molecule) and for localized two-centre orbitals or bonds. In the case of localized two-centre bonds, a π bond has a nodal plane that includes the internuclear bond axis, whereas a σ bond has no such nodal plane. (A δ bond in organometallic or inorganic chemical species has two nodes.) *Radical*s are classified by analogy into σ and π radicals.

Note 2: Such two-centre orbitals may take part in molecular orbitals of σ or π symmetry. For example, the methyl group in propene contains three C–H bonds, each of which is of local σ symmetry (i.e., without a nodal plane including the internuclear axis), but these three σ bonds can in turn be combined to form a set of group orbitals one of which has π symmetry with respect to the principal molecular plane and can accordingly interact with the two-centre orbital of π symmetry (π bond) of the double-bonded carbon atoms, to form a molecular orbital of π symmetry. Such an interaction between the CH_3 group and the double bond is an example of *hyperconjugation*. This cannot rigorously be described as σ-π conjugation since σ and π here refer to different defining planes, and interaction between orbitals of different symmetries (with respect to the same defining plane) is forbidden.

Note 3: Conjugation between a π system and a lone pair of (for example) an ether oxygen involves a lone pair of π symmetry with respect to the defining plane. It is incorrect to consider this as an interaction between the π system and one of two identical sp^3-hybrid lone pairs, which are neither σ nor π.

Note 4: The two lone pairs on a carbonyl oxygen are properly classified as σ or π with respect to the plane perpendicular to the molecular plane (dotted line perpendicular to the plane of the page), rather than as two sp^2-hybridized lone pairs. This distinction readily accounts for the facts that there are two different lone-pair *ionization energies* and two different *n*-π^* *excited state*s.

See also [397].

σ-adduct

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 σ bond is formed and the original *conjugation* is disrupted.

Note 1: This has generally been called a σ complex, or a Wheland complex from

1 electrophilic addition, but adduct is more appropriate.

2 *Note* 2: The term may also be used for analogous adducts to π systems.

3 See also *Meisenheimer adduct*.

4 rev[3]

5

6 **σ-constant**

7 Substituent constant for *meta*- and *para*-substituents in benzene derivatives as defined

8 by Hammett on the basis of the *ionization* constant of a substituted benzoic acid, i.e.,

9 lg(K_a^X/K_a^H), where K_a^X is the ionization constant (acid-dissociation constant) of a *m*- or

10 *p*-substituted benzoic acid and K_a^H that of benzoic acid itself.

11 *Note 1:* A large positive σ-value implies high electron-withdrawing power by an

12 inductive and/or resonance effect, relative to H; a large negative σ-value implies high

13 electron-releasing power relative to H.

14 *Note 2:* The term is also used as a collective description for related electronic

15 substituent constants based on other standard reaction series, of which, σ^+, σ^- and σ_o

16 are typical; also for constants which represent dissected electronic effects, such as σ_I

17 and σ_R. For example, σ^- (sigma-minus) constants are defined on the basis of the

18 ionization constants of *para*-substituted phenols, where such substituents as nitro show

19 enhanced electron-withdrawing power.

20 See [124,125,126,191,226,398].

21 See also *Hammett equation*, ρ-value, *Taft equation*.

22 [3]

23

24 **Taft equation**

25 *Linear free-energy relation* (*linear Gibbs-energy relation*) involving the polar substituent

26 constant σ^* and the steric substituent constant E_s, as derived from reactivities of

27 aliphatic esters

28

29 $$\lg \{k\} = \lg \{k_0\} + \rho^*\sigma^* + \delta E_s$$

30

31 The argument of the lg function should be of dimension 1. Thus, the reduced rate

32 constants should be used, i.e., the *rate coefficient* divided by its units: $\{k\} = k/[k]$ and

33 $\{k_0\} = k_0/[k_0]$.

34 *Note*: The standard reaction (k_0) is the *hydrolysis* of methyl acetate, whereby E_s is

35 evaluated from the rate of acid-catalyzed hydrolysis, relative to that of methyl acetate,

36 and σ^* is evaluated from the ratio of the rates of base- and acid-catalyzed hydrolysis.

37 See [172,380,399,400].

38 See also *Hammett equation*, ρ-value, σ-constant.

39 rev[3]

40

1
2
3   1   **tautomerization**
4
5   2   Rapid *isomerization* of the general form
6
7   3   G–X–Y=Z ⇌   X=Y–Z–G
8
9   4   where the isomers (called *tautomers*) are readily interconvertible.
10   5   *Note 1*: The atoms of the groups X,Y, Z are typically any of C, H, N, O, or S, and G
11   6   is a group that becomes an *electrofuge* or *nucleofuge* during isomerization.
12   7   *Note 2*: The commonest case, when the electrofuge is H^+, is also known as a
13   8   *prototropic rearrangement*.
14   9   *Examples*:
15
16   10

enol   keto

11
12
13   *Note 3*: The group Y may itself be a three-atom (or five-atom) chain extending the
14   conjugation, as in
15

16
17
18   *Note 4*: Ring-chain tautomerization is the case where addition across a double bond
19   leads to ring formation, as in
20

α-D-glucose

21
22   *Note 5*: *Valence tautomerization* is the case of rapid isomerization involving the
23   formation and rupture of single and/or double bonds, without *migration* of atoms: for
24   example

1

2　　　See [346,401].

3　　　See also *ambident*, *fluxional, sigmatropic rearrangement*, *valence tautomerization*.

4　　　rev[3]

5

6　tautomers

7　*Constitutional isomers* that can interconvert more or less rapidly, often by *migration* of

8　a *hydron*.

9　　　See *tautomerization*.

10

11　*tele*-substitution

12　*Substitution* reaction in which the *entering group* takes up a position more than one

13　atom away from the atom to which the *leaving group* was attached.

14　　*Example*

15

16

17　　　See also *cine-substitution*.

18　　　See [402,403].

19　　　rev[3]

20

21　termination

22　Step(s) in a *chain reaction* in which *reactive intermediate*s are destroyed or rendered

23　inactive, thus ending the chain.

24　　　[3]

25

26　tetrahedral intermediate

27　Reaction *intermediate* in which the bond arrangement around an initially double-bonded

28　carbon atom (typically a carbonyl carbon) has been transformed from tricoordinate to

29　tetracoordinate (with a *coordination number* of 4).

30　　*Example:*

31

32　　rev[3]

33

34

1 **thermodynamic control (of product composition)**

2 equilibrium control

3 Conditions (including reaction times) that lead to reaction products in a proportion

4 specified by the *equilibrium* constant for their interconversion.

5   See also *kinetic control*.

6   rev[3]

7

8 **thermolysis**

9 Uncatalysed cleavage of one or more *covalent bond*s resulting from exposure of a

10 *molecular entity* to a raised temperature, or a process of which such cleavage is an

11 essential part.

12   See also *pyrolysis*.

13   [3]

14

15 **through-conjugation**

16 Phenomenon whereby electrons can be delocalized from any of three (or more) groups

17 to any other.

18   *Example:* p-XC_6H_4Y, where an electron pair can be delocalized from electron-

19 donating X not only to ring carbons but also to electron-withdrawing Y.

20   *Note 1*: This may be contrasted with *cross-conjugation*.

21   *Note 2*: In Hammett-type correlations (*linear Gibbs-energy relationship*s) this

22 situation can lead to exalted substituent constants σ^+ or σ^-, as in solvolysis of p-

23 $CH_3OC_6H_4C(CH_3)_2Cl$ or acidity of p-nitrophenol, respectively.

24

25 **TICT**

26   See *twisted intramolecular charge transfer*.

27

28 **torquoselectivity**

29 Preference for inward or outward rotation of substituents in *conrotatory* or *disrotatory*

30 *electrocyclic* ring-opening and ring-closing reactions, often owing to a preference for

31 electron donors (especially including large groups) to rotate outward and acceptors to

32 rotate inward.

33   See [404,405].

1

2   rev[3]

3

transferability

5   Assumption that a chemical property associated with an atom or group of atoms in a
6   molecule will have a similar (but not identical) value in other circumstances.

7   *Examples*: equilibrium bond length, bond force constant, NMR chemical shift.

8   [3]

9

transformation

11   Conversion of a *substrate* into a particular product, irrespective of the specific reagents
12   or *mechanisms* involved.

13   *Example*: transformation of aniline ($C_6H_5NH_2$) into *N*-phenylacetamide
14   ($C_6H_5NHCOCH_3$), which may be effected with acetyl chloride or acetic anhydride or
15   ketene.

16   *Note:* A transformation is distinct from a reaction, the full description of which would
17   state or imply all the reactants and all the products.

18   See [406].

19   [3]

20

transient (chemical) species

22   Short-lived reaction *intermediate*.

23   *Note 1*: Transiency can be defined only in relation to a time scale fixed by the
24   experimental conditions and by the limitations of the technique employed in the
25   detection of the intermediate. The term is a relative one.

Note 2: 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*.

[3]

transition dipole moment

Vector quantity describing the oscillating electronic moment induced by an electromagnetic wave, given by an integral involving the dipole moment operator **m** and the ground- and excited-state *wavefunction*s:

$$\boldsymbol{M} = \int \Psi_{exc}\, \mathbf{m}\, \Psi_{gnd}\, d\tau$$

Note: The magnitude of this quantity describes the allowedness of an electronic transition. It can often be separated into an electronic factor and a nuclear-overlap factor known as the Franck-Condon factor.

See [9].

transition state

State of a molecular system from which there are equal probabilities of evolving toward states of lower energy, generally considered as reactants and products of an *elementary reaction*.

Note 1: The transition state corresponds to the maximum along the minimum-Gibbs-energy path connecting reactants and products.

Note 2: The transition state can be considered to be a *chemical species* of transient existence.

Note 3: The term transition-state structure refers to a structure inferred from kinetic and stereochemical investigations; it does not necessarily coincide with a transition state or with a *transition structure*, which corresponds to a saddle point on a *potential-energy surface*, although it may represent an average structure.

Note 4: The assembly of atoms at the transition state has also been called an *activated complex*, although it is not a *complex* according to the definition in this Glossary.

Note 5: There are also reactions, such as the gas-phase *colligation* of simple *radical*s or the reactions of some *reactive intermediate*s in solution, that do not require activation and do not involve a transition state.

Note 6: Ultrafast spectroscopy permits observation of transition states in some special cases.

See [349,407].

1   See also *Gibbs energy of activation*, *potential-energy profile*, *reaction coordinate*,
2 *transition structure*.
3   rev[3]
4

5 **transition-state analogue**
6 Species designed to mimic the geometry and electron density of the *transition state* of
7 a reaction, usually enzymatic.
8   *Note*: A transition-state analogue is usually not a substrate for the enzyme, but rather
9 an inhibitor.
10   rev[3]
11

12 **transition structure**
13 *Molecular entity* corresponding to a saddle point on a *potential-energy surface*, with one
14 negative force constant and its associated imaginary frequency.
15   *Note 1*: Whereas the *transition state* is not a specific molecular structure, but a set
16 of structures between reactants and products, a transition structure is one member of
17 that set with a specific geometry and energy.
18   Note 2: Although the saddle point coincides with the potential-energy maximum
19 along a *minimum-energy reaction path*, it does not necessarily coincide with the
20 maximum of Gibbs energy for an ensemble of *chemical species*.
21   *Note 3:* The term transition-state structure is not a synonym for transition structure.
22   See [349,408].
23   See also *activated complex*, *transition state*.
24   rev[3]
25

26 **transition vector**
27 Normal mode of vibration of a *transition structure* corresponding to the single imaginary
28 frequency and tangent to the *intrinsic reaction coordinate* at the saddle point.
29 Sometimes called the reaction-coordinate vibrational mode.
30   *Note*: Infinitesimal motion along the transition vector in the two opposite senses
31 determines the initial direction leading either toward reactants or toward products.
32   *Note 2*: The term "transition coordinate" was used in the 1994 Glossary of Terms in
33 Physical Organic Chemistry in the sense defined here for transition vector, but
34 apparently this usage was unique in the literature at that time and has not been
35 generally adopted since.
36   See [349,409].
37   See *reaction coordinate*, *transition state*.
38

39

40

transport control
 See *encounter-controlled rate*, *microscopic diffusion control*.
 [3]

trapping
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.
 See also *scavenger*.
 [3]

triplet state
State having a total electron spin quantum number of 1.
 See [9].

tunnelling
Quantum-mechanical phenomenon by which a particle or a set of particles penetrates a barrier on its *potential-energy surface* without having the energy required to surmount that barrier.
 Note 1: In consequence of Heisenberg's Uncertainty Principle, a molecular entity has a nonzero probability of adopting a geometry that is classically forbidden because it corresponds to a potential energy greater than the total energy.
 Note 2: Tunnelling is often considered to be a correction to an (over)simplified version of transition-state theory.
 Note 3: Because the rate of tunnelling increases with decreasing mass, it is significant in the context of *isotope effect*s, especially of hydrogen isotopes.
 See [410,411].
 rev[3]

twisted intramolecular charge transfer (TICT)
Feature of an excited electronic state formed by intramolecular electron transfer from an electron donor (D) to an electron acceptor (A), where interaction between electron and hole is restricted because D^+ and A^- are perpendicular to each other.
 See [412].

umpolung
Process by which the nucleophilic or electrophilic property of a functional group is reversed.
 Note: Umpolung is often achieved by temporary exchange of heteroatoms N or O by others, such as P, S, or Se, as in the conversion of electrophilic $RCH=O$ to $RCH(SR')_2$

1 and then with base to nucleophilic RC(SR')$_2^-$. Also the transformation of a haloalkane
2 RX into a Grignard reagent RMgCl is an umpolung.
3   See [413].
4   rev[3]
5

6 **unimolecular**
7 Feature of a reaction in which only one *molecular entity* is involved.
8   See *molecularity*.
9   rev[3]
10

11 **unreactive**
12 Failing to react with a specified *chemical species* under specified conditions.
13   *Note*: The term should not be used in place of *stable*, which refers to a
14 thermodynamic property, since a relatively more stable species may nevertheless be
15 more *reactive* than some reference species towards a given reaction partner.
16   [3]
17

18 **unstable**
19 Opposite of *stable*, i.e., the *chemical species* concerned has a higher molar Gibbs
20 energy than some assumed standard.
21   *Note*: The term should not be used in place of *reactive* or transient, although more
22 reactive or *transient species* are frequently also more unstable.
23   rev[3]
24

25 **upfield**
26 superseded but still widely used to mean shielded.
27   See *chemical shift*.
28   [3]
29

30 **valence**
31 Maximum number of single bonds that can be commonly formed by an atom or ion of
32 the element under consideration.
33   *Note*: Often there is a most common maximum for a given element, and atoms in
34 compounds where this number is exceeded, such as pentacoordinate carbocations
35 ("carbonium ions") and iodine(III) compounds, are called *hypervalent*.
36   rev[3]
37

38 **valence isomer**
39 *Constitutional isomer* related to another by *pericyclic reaction*.

1   *Examples*: Dewar benzene, prismane, and benzvalene are valence isomers of
2   benzene.
3   *Note*: Valence isomers are separable, as distinguished from valence tautomers,
4   which interconvert rapidly. See *valence tautomerization*.
5   rev[3]
6

valence tautomerization
7
8   Rapid isomerization involving the formation and rupture of single and/or double bonds,
9   without *migration* of atoms.
10   *Example:*

11
12   See *tautomerization*.
13   rev[3]
14

van der Waals forces
15
16   Attractive or repulsive forces between *molecular entities* (or between groups within the
17   same molecular entity) other than those due to *bond* formation or to the electrostatic
18   interaction of ions or of ionic *group*s with one another or with neutral molecules.
19   *Note 1*: The term includes dipole-dipole, dipole-induced dipole, and London
20   (instantaneous induced dipole-induced dipole) forces, as well as quadrupolar *forces.*
21   *Note 2*: The term is sometimes used loosely for the totality of nonspecific attractive
22   or repulsive intermolecular forces.
23   *Note 3*: In the context of molecular mechanics, van der Waals forces correspond only
24   to the London dispersion forces plus the Pauli repulsion forces. Interactions due to the
25   average charge distribution (and not to fluctuations around the average or to induced
26   dipoles), including dipole-dipole, ion-ion and ion-dipole forces, are called Coulombic
27   forces.
28   See [290,414].
29   See also *dipole-dipole interaction*, *dipole-induced dipole forces, London forces.*
30   rev[3]
31

volume of activation, $\Delta^{\ddagger}V$
32
33   Quantity derived from the pressure dependence of the *rate constant* of a reaction,
34   defined by the equation
35

36   $$\Delta^{\ddagger}V = -RT\,[\partial\ln(k/[k])/\partial p]_T$$

37

provided that 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 argument in the lg function should be of dimension 1. Thus, the rate constant should be divided by its units, [k].

Note: The volume of activation is interpreted as the difference between the partial molar volume $^{\ddagger}V$ of the *transition state* and the sums of the partial molar volumes of the reactants at the same temperature and pressure, i.e.,

$$\Delta^{\ddagger}V = {}^{\ddagger}V - \Sigma(\rho V_R)$$

where ρ is the order in the reactant R and V_R its partial molar volume.

See [13].

See *order of reaction*.

rev[3]

water/octanol partition coefficient (partition ratio)

See *octanol-water partition ratio*

wavefunction

A mathematical expression whose form resembles the wave equations of physics, supposed to contain all the information associated with a particular atomic or molecular system. In particular, a solution of the Schrödinger wave equation, $H\psi = E\psi$, as an eigenfunction ψ of the hamiltonian operator H, which involves the electronic and/or nuclear coordinates.

Note 1: The wavefunction contains all the information describing an atomic or molecular system that is consistent with the Heisenberg Uncertainty Principle.

Note 2: When a wavefunction is operated on by certain quantum-mechanical operators, a theoretical evaluation of physical and chemical observables for that system (the most important one being energy) can be carried out.

See [8,12].

Wheland intermediate

See *Meisenheimer adduct, σ-adduct*.

[3]

Woodward-Hoffmann rules

See *orbital symmetry*.

1 **ylide**
2 Chemical species that can be produced by loss of a *hydron* from an atom directly
3 attached to the central atom of an *onium ion*.
4   *Example:*
5         $Ph_3P^+–CHRR' \rightarrow [Ph_3P^+–C^–RR' \leftrightarrow Ph_3P=CRR'] + H^+$
6   See [40].
7   [3]
8

9 **Yukawa-Tsuno equation**
10 Multiparameter extension of the *Hammett equation* to quantify the role of enhanced
11 *resonance* effects on the reactivity of *para*–substituted benzene derivatives,
12

13         $\lg \{k\} = \lg \{k_o\} + \rho[\sigma^o + r(\sigma^+ - \sigma^o)]$
14 or $\lg \{k\} = \lg \{k_o\} + \rho[\sigma^o + r(\sigma^- - \sigma^o)]$
15

16 where the parameter *r* expresses the enhancement and where σ^o is a *substituent*
17 *constant* based on reactivities of phenylacetic acids and similar substrates, where
18 resonance interaction is weak or absent. The argument in the lg function should be of
19 dimension 1. Thus, reduced rate constants should be used $\{k\}= k/[k]$ and $\{k_o\} = k_o/[k_o]$.
20   See [398,415,416].
21   See also *dual substituent-parameter equation*, *ρ-value*, *σ-constant*, *through-*
22 *conjugation*.
23   rev[3]
24

25 **Zaitsev rule**
26   See *Saytzeff rule*.
27   [3]
28

29 **zero-point energy**
30 Extent, in consequence of Heisenberg's Uncertainty Principle, by which a particle or a
31 set of particles has an energy greater than that of the minimum on the *potential-energy*
32 *surface*.
33   *Note 1*: Because of zero-point energy a molecular entity has a nonzero probability of
34 adopting a geometry whose energy is greater than that of the energy minimum.
35   *Note 2:* A molecular entity with zero-point energy may even adopt a geometry with
36 a potential energy greater than its total energy, a possibility that permits *tunnelling*.
37   *Note 3*: Because the magnitude of zero-point energy increases with decreasing
38 mass, it is significant in the context of *isotope effect*s, especially of hydrogen isotopes.
39

40 **Zucker-Hammett hypothesis**

1 Assumption that if lg $\{k_1\}$ (= $k_1/[k_1]$, reduced pseudo-first-order rate constant of an acid-
2 catalyzed reaction) is linear in H_o (Hammett *acidity function*), then water is not involved
3 in the *transition state* of the *rate-controlling step*, whereas if lg $\{k_1\}$ is linear in lg $\{[H^+]\}$
4 then water is involved. The argument in the lg function should be of dimension 1. Thus,
5 reduced concentration = $\{[H^+]\}$ should be used, i.e., concentration of protons divided by
6 its units.

7   *Note*: This has been shown to be an overinterpretation.

8   See [22,417].

9   See also *Bunnett-Olsen equation*, *Cox-Yates equation*.

10   rev[3]

11

12 **Z-value**

13 Quantitative measure of solvent polarity based on the UV-vis spectrum of 1-ethyl-4-
14 (methoxycarbonyl)pyridinium iodide.

15   See [143].

16   See *solvent parameter*.

17   rev[3]

18

19 **zwitterion**

20 Highly dipolar, net uncharged (neutral) molecule having full electrical charges of
21 opposite sign, which may be delocalized within parts of the molecule but for which no
22 uncharged canonical resonance structure can be written.

23   *Examples*: glycine (H_3N^+–CH_2–CO_2^-), betaine (Me_3N^+–CH_2–CO_2^-).

24   *Note 1*: Sometimes also referred to as inner salts or ampholytes.

25   *Note 2:* Mesoionic compounds, such as sydnones, in which both positive and
26 negative charge are delocalized, are sometimes considered as zwitterions, but species
27 with a localized nonzero formal charge, such as a nitrone, $CH_3CH=N^+(-O^-)CH_3$, are
28 not.

29   See [418].

30   rev[3]

31

1

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GLOSSARY OF TERMS USED IN
PHYSICAL ORGANIC CHEMISTRY

Abstract. This Glossary contains definitions, explanatory notes, and sources for terms used in physical organic chemistry. Its aim is to provide guidance on the terminology of physical organic chemistry, with a view to achieving a consensus on the meaning and applicability of useful terms and the abandonment of unsatisfactory ones. Owing to the substantial progress in the field, this 2021 revision of the Glossary is much expanded relative to the previous edition, and it includes terms from cognate fields.

INTRODUCTION TO THE 2021 REVISION
General Remarks

The first Glossary of Terms Used In Physical Organic Chemistry was published in provisional form in 1979 [1] and in revised form in 1983, incorporating modifications agreed to by IUPAC Commission III.2 (Physical Organic Chemistry) [2].

A further revision was undertaken under the chairmanship of Paul Müller, which was published in 1994 [3]. The work was coordinated with that of other Commissions within the Division of Organic Chemistry. In 1999 Gerard P. Moss, with the assistance of Charles L. Perrin, converted this glossary to a World Wide Web version [4]. The Compendium of Chemical Terminology [5] (Gold Book) incorporated many of the terms in the later version.

This Glossary has now been thoroughly revised and updated, to be made available as a Web document. The general criterion adopted for the inclusion of a term in this Glossary has been its wide use in the present or past literature of physical-organic chemistry and related fields, with particular attention to those terms that have been ambiguous. It is expected that the terms in this Glossary will be incorporated within the on-line version of the IUPAC Gold Book, which is the merged compendium of all glossaries [5].

The aim of this Glossary is to provide guidance on the terminology of physical-organic chemistry, with a view to achieving a far-reaching consensus on the definitions of useful terms and the abandonment of unsatisfactory ones. According to Antoine Lavoisier "Comme ce sont les mots qui conservent les idées et qui les transmettent, il en résulte qu'on ne peut perfectionner le langage sans perfectionner la science, ni la science sans le langage," (As it is the words that preserve the ideas and convey them, it follows that one cannot improve the language without improving science, nor improve

2

science without improving the language.") [6]. Our approach has been to take or update entries from the previous glossary, whereas new terms were added by virtue of their usage in the current literature and the diverse knowledge of the members of the Task Force.

The Task Force is pleased to acknowledge the generous contributions of many scientists who helped by proposing or defining new terms or by criticizing or modifying existing ones. The following members of the Task Force have contributed to this revision:

Israel Agranat	Charles L. Perrin, Chair
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Arrangement, Abbreviations, and Symbols

The arrangement is alphabetical, terms with Greek letters following those in the corresponding Latin ones. Italicized words in the body of a definition, as well as those cited at the end, point to relevant cross-references. Literature references direct the reader either to the original literature where the term was originally defined or to pertinent references where it is used, including other IUPAC glossaries, where definitions may differ from those here.

Definitions of techniques not directly used for measurements in physical-organic chemistry are not included here but may be consulted in specialized IUPAC texts, including the IUPAC Recommendations for Mass Spectrometry [7], the Glossary of Terms Used In Theoretical Organic Chemistry [8], the Glossary of Terms Used in Photochemistry 3rd edition [9], the Glossary of Terms Used in Photocatalysis and Radiation Catalysis [10] and the Basic Terminology of Stereochemistry [11].

3

1   In accordance with IUPAC recommendations [12] the symbol ‡ to indicate
2 transition state ("double dagger") is used as a prefix to the appropriate quantities, e.g.,
3 $\Delta^{\ddagger}G$ rather than $\Delta G^{\ddagger}$. In equations including a logarithmic function the procedure
4 recommended by IUPAC was adopted, i.e., to divide each dimensioned quantity by its
5 units. Since this procedure often introduces a cluttering of the equations, we have in
6 some cases chosen a short-hand notation, such as ln $\{k(T)\}$, where the curly brackets
7 indicate an argument of dimension one, corresponding to $k(T)/[k(T)]$, where the square
8 brackets indicate that the quantity is divided by its units, as recommended in [12].
9
10 **Note on the identification of new and/or revised terms.**
11 Terms that are found in the previous version of this Glossary [3,4] and currently
12 incorporated in the IUPAC "Gold Book" [5] are identified with a reference to the
13 Glossary of Terms used in Physical Organic Chemistry (1994), i.e., [3]are marked as
14 GB, whereas revised terms are designated as revGBrev[3]. Revised terms from the
15 previous Glossary of Terms in Physical Organic Chemistry are labeled revPOC. Some
16 of them were not incorporated in the Gold Book. Minor changes such as better wording,
17 additional cross-referencing, or reorganization of the text without changing the concept
18 are, in general, not considered revisions. However, the improved version should replace
19 the older one in the "Gold Book". New terms and terms from other IUPAC documents
20 are not identified as such. In many cases new references have been added in the
21 definitions.
22
23
24

4

1 ***A* factor**
2 Arrhenius factor
3 (SI unit same as rate constant: s^{-1} for first-order reaction).
4 Pre-exponential factor in the *Arrhenius equation* for the temperature dependence of a
5 reaction rate constant.
6   *Note 1:* According to collision theory, *A* is the frequency of collisions with the correct
7 orientation for reaction.
8   *Note 2:* The common unit of *A* for second-order reactions is $dm^3\ mol^{-1}\ s^{-1}$.
9   See also *A value*, *energy of activation*, *entropy of activation*.
10   See [12,13].
11 ~~revGB~~-rev~~POC~~[3]
12
13 ***A* value**
14 Steric substituent parameter expressing the conformational preference of an equatorial
15 substituent relative to an axial one in a monosubstituted cyclohexane.
16   *Note 1*: This parameter equals $\Delta_r G^o$ for the equatorial to axial equilibration,
17 in $kJ\ mol^{-1}$. For example, A_{CH3} is 7.28 $kJ\ mol^{-1}$, a positive value because an axial
18 methyl group is destabilized by a *steric effect*.
19   *Note 2*: The values are also known as Winstein-Holness *A* values.
20   See [3,14,15].
21 ~~GB~~
22
23 **abstraction**
24 Chemical reaction or transformation, the main feature of which is the bimolecular
25 removal of an atom (neutral or charged) from a molecular entity.
26   *Examples*:
27        $CH_3COCH_3 + (i\text{-}C_3H_7)_2N^- \rightarrow [CH_3COCH_2]^- + (i\text{-}C_3H_7)_2NH$
28   (hydron abstraction from acetone)
29        $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$
30   (hydrogen atom abstraction from methane)
31   See *detachment*.
32 ~~GB~~[3]
33
34 **acceptor parameter** (*A*, ~~dimensionless~~)
35 acceptor number (deprecated). Unit and dimension 1.
36 Quantitative measure, devised by Gutmann [16] of the *Lewis acidity* of a solvent, based
37 on the ^{31}P chemical shift of dissolved triethylphosphine oxide (triethylphosphane oxide).
38   *Note:* The term acceptor number, designated by AN, is a misnomer and ought to be
39 called acceptor parameter, *A,* because it is an experimental value [17].
40 rev[3]~~RevGB-revPOC~~

5

acid

Molecular entity or *chemical species* capable of donating a hydron (proton) or capable of forming a bond with the electron pair of a Lewis base.

See *Brønsted acid, Lewis acid, Lewis base*.

See also *hard acid*.

~~GB~~[3]

acidity

(1) Of a compound:

Tendency of a *Brønsted acid* to act as a *hydron* (proton) donor, or tendency of a *Lewis acid* to form *Lewis adduct*s and *π-adduct*s.

Note: Acidity can be quantitatively expressed by the acid dissociation constant of the compound in water or in some other specified medium, by the association constants for formation of Lewis adducts and π-adducts, or by the enthalpy or Gibbs energy of deprotonation in the gas phase.

(2) Of a medium, usually one containing Brønsted acids:

Tendency of the medium to hydronate a specific reference base.

Note 1: The acidity of a medium is quantitatively expressed by the appropriate *acidity function*.

Note 2: Media having an acidity greater than that of 100 % H_2SO_4 are often called *superacid*s.

See [18].

~~r~~Rev[3]~~GB-revPOC~~

acidity function

Measure of 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 adduct*s.

Note 1: 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.

Note 2: Commonly used acidity functions are extensions of pH to concentrated acidic or basic solutions. Acidity functions are usually established over a range of compositions of such a system by UV/Vis spectrophotometric or NMR measurements of the degree of hydronation (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 is the Hammett acidity function H_o (for primary aromatic amines as indicator bases).

6

For detailed information on other acidity functions, on *excess acidity*, on the evaluation of acidity functions, and on the limitations of the concept, see [19,20,21,22].
[3]~~GB~~

activated complex
See *activated state*.
~~revGB~~ ~~revPOC~~rev[3]

activated state
In theories of unimolecular reactions an energized *chemical species*, often characterized by the superscript ‡, where the excitation is specific and the molecule is poised for reaction.
Note 1: Often used as a synonym for *activated complex* or *transition state*, but not restricted to transition-state theory.
Note 2: This is distinct from an energized *molecule*, often characterized by the superscript *, in which excitation energy is dispersed among internal degrees of freedom.
Note 3: This is not a *complex* according to the definition in this Glossary.
See also *transition state, transition structure*.

activation energy
See *energy of activation*.
See [12], section 2.12.
[3]~~GB~~

activation strain model
See *distortion interaction model*.

addition reaction
Chemical reaction of two or more reacting *molecular entities*, resulting in a 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.
Note 1: The addition to an entity may occur at only one site (1,1-addition, *insertion*), at two adjacent sites (1,2-addition) or at two non-adjacent sites (1,3- or 1,4-addition, etc.).
Examples
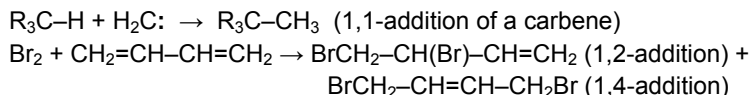
$R_3C–H + H_2C\textbf{:} \rightarrow R_3C–CH_3$ (1,1-addition of a carbene)

$Br_2 + CH_2=CH–CH=CH_2 \rightarrow BrCH_2–CH(Br)–CH=CH_2$ (1,2-addition) +

$BrCH_2–CH=CH–CH_2Br$ (1,4-addition)

Note 2: This is distinguished from *adduct* formation, which is less specific about bonding changes.

Note 3: The reverse process is called an *elimination* reaction.

See also *cheletropic reaction*, *cycloaddition*, *insertion*.

~~revGB-revPOC~~

rev[3]

additivity principle

Hypothesis that each of several structural features of a *molecular entity* makes an independent, transferable, and additive contribution to a property of the substance concerned.

Note 1: 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 *chemical reaction*.

Note 2: The enthalpies of formation of series of compounds can be described by additivity schemes [23].

Note 3: Deviations from additivity may be remedied by including terms describing interactions between atoms or groups.

See *transferability* [24,25].

~~GB~~

rev[3]

adduct

New *chemical species* AB, each *molecular entity* of which is formed by direct combination of two (or more) separate molecular entities A and B in such a way that there is no loss of atoms from A or B.

Example: adduct formed by interaction of a *Lewis acid* with a *Lewis base*:

$(CH_3)_3N^{+}–{}^{-}BF_3$

Note 1: Stoichiometries other than 1:1 are also possible, e.g., a bis-adduct (2:1).

Note 2: An *intramolecular* adduct can be formed when A and B are *groups* contained within the same molecular entity.

Note 3: If adduct formation is prevented by *steric hindrance*, *frustrated Lewis pair*s may result.

See also *addition reaction, frustrated Lewis pair, Lewis adduct, Meisenheimer adduct, π-adduct*.

8

1
2
3 **agostic**
4 Feature of a structure in which a hydrogen atom is bonded to both a main-group atom
5 and a metal atom.
6   *Example,* [(1–3-η)-but-2-en-1-yl-η²-C^4,H^4](η⁵-cyclopentadienyl)cobalt(+1).
7
8
9
10
11
12   *Note*: The expression η-hydrido-bridged is also used to describe the bonding
13 arrangement with a bridging hydrogen, but this usage is deprecated.
14   See [26,27,28,29].
15 revGB-revPOC
16   rev[3]
17
18 **alcoholysis**
19 Reaction with an alcohol solvent.
20   *Examples:*
21
22        $C_3H_5(OCOR)_3$ (triglyceride) + 3 CH_3OH → $C_3H_5(OH)_3$ (glycerol) + 3 RCOOH
23        $(CH_3)_3CCl$ + CH_3OH → $(CH_3)_3COCH_3$ + H^+ + Cl^-
24
25   See *solvolysis*.
26   rev[3]
27   revGB-revPOC
28
29 **allotropes**
30 Different structural modifications of an element, with different bonding arrangements of
31 the atoms.
32   *Examples* for carbon include diamond, *fullerenes*, graphite, and *graphene*.
33   See [29].
34
35 **allylic substitution reaction**
36 *Substitution* reaction on an allylic system with *leaving group* (*nucleofuge*) at position 1
37 and double bond between positions 2 and 3. The incoming group may become attached
38 to atom 1, or else the incoming group may become attached at position 3, with
39 movement of the double bond from 2,3 to 1,2.
40   *Example*:

1   rRev[3]GB-revPOC

9

1   CH$_3$CH=CHCH$_2$Br + HOAc → CH$_3$CH=CHCH$_2$OAc or CH$_3$CH(OAc)CH=CH$_2$

2

3   *Note*: This term can be extended to systems such as:

4

5   CH$_3$CH=CH–CH=CH–CH$_2$Br → CH$_3$CH(OAc)–CH=CH–CH=CH$_2$ +

6   CH$_3$CH=CH–CH(OAc)–CH=CH$_2$ + CH$_3$CH=CH–CH=CH–CH$_2$OAc

7

8 and also to propargylic substitution, with a triple bond between positions 2 and 3 and

9 possible rearrangement to an allenic product.

10   rev[3]

11   revGB-revPOC

12

13 **alternant**

14 Property of a *conjugated system* of π electrons whose atoms can be divided into two

15 sets (marked as "starred" and "unstarred") so that no atom of either set is directly linked

16 to any other atom of the same set.

17   *Examples*

18

19

20

21

22

23

24

25   *Note 1:* According to several approximate theories (including *HMO theory*), the π

26 MOs for an alternant hydrocarbon are paired, such that for an orbital of energy $\alpha + x\beta$

27 there is another of energy $\alpha - x\beta$. The coefficients of paired molecular orbitals at each

28 atom are the same, but with opposite sign for the unstarred atoms, and the π electron

29 density at each atom in a neutral alternant hydrocarbon is unity.

30   See [30,31,32].

31   rev[3]

32   revGB-revPOC

33

34 **ambident**

35 ambidentate, bidentate

36 Characteristic of a *chemical species* whose *molecular entities* each possess two

37 alternative, distinguishable, and strongly interacting reactive centres, to either of which

38 a *bond* may be made.

39   *Note 1*: Term most commonly applied to *conjugated nucleophiles*, for example an

40 enolate ion (which may react with *electrophiles* at either the α-carbon atom or the

10

1   oxygen) or a 4-pyridone, and also to the vicinally ambident cyanide ion and to cyanate
2   ion, thiocyanate ion, sulfinate ions, nitrite ion, and unsymmetrical hydrazines.
3

6   *Note 2*: Ambident electrophiles are exemplified by carboxylic esters RC(O)OR',
7   which react with nucleophiles at either the carbonyl carbon or the alkoxy carbon, and
8   by Michael acceptors, such as enones, that can react at either the carbonyl or the α-
9   carbon.
10   *Note 3*: Molecular entities containing two non-interacting (or feebly interacting)
11   reactive centres, such as dianions of dicarboxylic acids, are not generally considered
12   to be ambident or bidentate and are better described as bifunctional.
13   *Note 4*: The Latin root of the word implies two reactive centres, but the term has also
14   been applied to chemical species with more than two reactive centres, such as an acyl
15   thiourea, RCONHCSNHR', with nucleophilic O, S, and N. For such species the term
16   polydentate (or multidentate) is more appropriate.
17   See [33,34,35,36].
18   GB[3]
19

20   **ambiphilic**
21   Both *nucleophilic* and *electrophilic*.
22   *Example*:
23        $CH_2=O$
24   See also *amphiphilic*, but the distinction between ambi (Latin: both) and amphi
25   (Greek: both) and the application to hydrophilic and lipophilic or to nucleophilic and
26   electrophilic is arbitrary.
27

28   **aminoxyl**
29   Compound having the structure
30        $R_2N–O^{\bullet} \leftrightarrow R_2N^{\bullet+}–O^-$
31   *Note*: The synonymous term 'nitroxyl radical' erroneously suggests the presence of
32   a nitro group; its use is deprecated.
33

34   **amphiphilic**
35   Both hydrophilic and lipophilic, owing to the presence in the molecule of a large organic
36   cation or anion and also a long hydrocarbon chain (or other combination of polar and
37   nonpolar groups, as in nonionic surfactants)
38   *Examples*:

11

$CH_3(CH_2)_nCO_2^-M^+$, $CH_3(CH_2)_nSO_3^-M^+$, $CH_3(CH_2)_nN(CH_3)_3^+X^-$ ($n > 7$).

Note: The presence of distinct polar (hydrophilic) and nonpolar (hydrophobic) regions promotes the formation of *micelles* in dilute aqueous solution.

See also *ambiphilic*.

GB[3]

amphiprotic (solvent)

Feature of a self-ionizing solvent possessing characteristics of both *Brønsted acid* and *base*.

Examples: H_2O, CH_3OH.

GB[3]

amphoteric

Property of a *chemical species* that can behave as either an acid or as a base.

Examples: H_2O, HCO_3^- (hydrogen carbonate)

Note: This property depends upon the medium in which the species is investigated. For example HNO_3 is an acid in water but becomes a base in H_2SO_4.

rev[3]

GB

anchimeric assistance

neighbouring group participation

GB[3]

anionotropy

Rearrangement or *tautomerization* in which the migrating group moves with its electron pair.

See [37].

GB[3]

annelation

Alternative, but less desirable term for *annulation*.

Note: The term is widely used in German and French languages.

GB[3]

annulation

Transformation involving fusion of a new ring to a molecule via two new bonds.

12

1   *Note*: Some authors use the term *annelation* for the fusion of an additional ring to an
2 already existing one, and annulation for the formation of a ring from an acyclic
3 precursor.
4   See [38,39].
5   See also *cyclization*.
6   GB[3]
7

8 **annulene**
9 Conjugated monocyclic hydrocarbon of the general formula C_nH_n (*n* even) with the
10 maximum number of noncumulative double bonds and without side chains.
11   *Note*: In systematic nomenclature an annulene may be named [*n*]annulene, where *n*
12 is the number of carbon atoms, e.g., [8]annulene for cycloocta-1,3,5,7-tetraene.
13   See [40].
14   See *aromatic*, *Hückel (4n + 2) rule*.
15   GB [3]
16

17 **anomeric effect**
18 Tendency of an electronegative substituent alpha to a heteroatom in a six-membered
19 ring to prefer the axial position, as in the *anomers* of glucopyranose.
20   *Note 1*: The effect can be generalized to the conformational preference of an
21 electronegative substituent X to be antiperiplanar to a lone pair of atom Y in a system
22 R–Y–C–X with geminal substituents RY and X.
23   *Note 2:* The effect can be attributed, at least in part, to *n-σ* delocalization* of the lone
24 pair on Y into the C–X σ* orbital.
25   See [11,41,42,43,44].
26   GB
27

28 **anomers**
29 The two stereoisomers (epimers) of a cyclic sugar or glycoside that differ only in the
30 *configuration* at C1 of aldoses or C2 of ketoses (the anomeric or acetal/ketal carbon).
31   *Example:*
32
33
34
35
36   See [11].
37   GB[3]
38

39 **antarafacial, suprafacial**

13

Two spatially different ways whereby bonding changes can occur when a part of a molecule undergoes two changes in bonding (*bond*-making or bond-breaking), either to a common centre or to two related centres external to itself. These are designated as antarafacial if opposite faces of the molecule 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 interacting π orbitals.
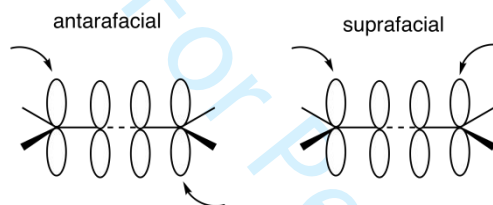
antarafacial   suprafacial

For examples of the use of these terms see *cycloaddition*, *sigmatropic rearrangement*.

See also *anti*, σ, π.

rev[3]

revGB-revPOC

anti

Stereochemical relationship of two substituents that are on opposite sides of a reference plane, in contrast to *syn*, which means "on the same side".

Note 1: 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°, in contrast to *syn* if it is less than 90°.

Note 2: A further distinction is made between antiperiplanar, synperiplanar, anticlinal and synclinal.

See [11,45,46,47].

Note 3: 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:

anti:

syn:

14

(2)   Alkene-forming *elimination*:

(3)   Aldol reaction (where *syn* and *anti* designate the relative orientation of CH_3 and OH in the product)

Note 4: In examples (1) and (2) *anti* processes are always *antarafacial*, and *syn* processes are *suprafacial*.

Note 5: 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*.

See [11].

rev[3]

~~GB-revPOC~~

anti-Hammond effect

If a structure lying off the *minimum-energy reaction path* (MERP) is stabilized, the position of the *transition state* moves toward that structure.

See *Hammond Postulate*, *More O'Ferrall - Jencks diagram*, *perpendicular effect*.

rev[3]

~~revGB-revPOC~~

aprotic (solvent)

non-HBD solvent (non-Hydrogen-Bond Donating solvent)

Solvent that is *not* capable of acting as a hydrogen-bond donor.

15

Note: Although this definition applies to both polar and nonpolar solvents, the distinction between HBD and non-HBD (or between protic and aprotic) is relevant only for polar solvents.

See *HBD solvent*.

rev[3]

revGB-revPOC

aquation

Incorporation of one or more integral molecules of water into a species, with or without displacement of one or more other atoms or groups.

Example: The incorporation of water into the inner *ligand* sphere of an inorganic *complex*.

See [48].

See also *hydration*.

GB[3]

aromatic (*adj*.), **aromaticity** (*n*.)

(1) Having a chemistry typified by benzene (traditionally).

(2) Feature of a cyclically *conjugated molecular entity* whose electronic energy is significantly lower or whose stability is significantly greater (owing to *delocalization*) than that of a hypothetical localized structure (e.g., *Kekulé structure*).

Note 1: If the molecular entity is of higher energy or less stable than a hypothetical localized structure, the entity is said to be antiaromatic.

Note 2: A geometric parameter indicating bond-length equalization has been used as a measure of aromatic character, as expressed in the harmonic oscillator model of aromaticity [49].

Note 3: The magnitude of the magnetically induced ring current, as observed experimentally by NMR spectroscopy or by the calculated nucleus-independent chemical shift (NICS) value, is another measure of aromaticity [50].

Note 4: 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, whereby a cycle with ($4n+2$) electrons and a Möbius cycle with $4n$ electrons are aromatic. Reactions of molecules in the *ground state* involving antiaromatic transition states proceed much less easily than those involving aromatic transition states.

See [51,52,53]. See 19 articles in [54].

See also *Hückel (4n + 2) rule*, *Möbius aromaticity*.

16

1   [3]

2   ~~revGB-revPOC~~

3

Arrhenius equation

Empirical expression for the temperature dependence of a reaction rate constant k as

$$k(T) = A \exp(-E_A/RT),$$

with A the pre-exponential factor (Arrhenius *A factor*) and E_A the Arrhenius *energy of activation*, both considered to be temperature-independent.

revGB[3]

aryne

Hydrocarbon derived from an arene by formal removal of two vicinal hydrogen atoms.

   Example: 1,2-didehydrobenzene (benzyne)

   Note 1: 1,4-Didehydrobenzene ("*p*-benzyne *diradical*", structure above right). Despite common usage this is not an aryne because there is no triple bond, and the usage is deprecated.

   Note 2: Arynes are usually *transient species*.

   Note 3: The analogous heterocyclic compounds are called heteroarynes or hetarynes.

   See [40,55].

rev[3]

~~revGB-revPOC~~

association

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.

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

~~GB~~[3]

asymmetric induction

17

Preferential formation in a *chemical reaction* of one *enantiomer* or *diastereoisomer* over the other as a result of the influence of a *chiral centre* (*stereogenic centre*, *chiral feature*) in the substrate, reagent, *catalyst*, or environment.

Note: The term also refers to the formation of a new chiral centre or chiral feature preferentially in one *configuration* under such influence.

See [11].

rev[3]

revGB-revPOC

atomic charge

Net charge due to the nucleus and the average electronic distribution in a given region of space. This region is considered to correspond to an atom in a *molecular entity*.

Note 1: The boundary limits of an atom in a polyatomic molecular entity cannot be defined, as they are not a quantum-mechanical observable. Therefore, different conceptual schemes of dividing a molecule into individual atoms will result in different atomic charges.

Note 2: The atomic charge on an atom should not be confused with its *formal charge*. For example, the N in NH_4^+ is calculated to carry a net negative charge even though its formal charge is +1, and each H is calculated to carry a net positive charge even though its formal charge is 0.

See [8].

atomic orbital

Wavefunction that depends explicitly on the spatial coordinates of only one electron around a single nucleus.

See also *molecular orbital*.

See [8].

[3]

atropisomers

Stereoisomers that are enantiomeric owing to hindered rotation about a single bond.

Example (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, BINAP):

See [11].

18

attachment

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.

Example: formation of an acyl cation by attachment of carbon monoxide to a *carbenium* ion (R^+):

$$R^+ + CO \rightarrow (RCO)^+$$
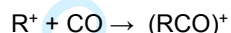
See also *colligation*.
revGB[3]

autocatalytic reaction

Chemical reaction in which a product (or a reaction *intermediate*) also functions as *catalyst*.

Note: In such a reaction the observed *rate of reaction* is often found to increase with time from its initial value.

Example: acid-catalyzed bromination of acetophenone, $PhCOCH_3$, because the reaction generates HBr, which functions as a catalyst.
rev[3]
revGB-revPOC

automerization

degenerate rearrangement
GB[3]

autoprotolysis

Proton transfer reaction (*hydron* transfer reaction) between two identical *amphoteric* molecules (usually of a solvent), one acting as a *Brønsted acid* and the other as a *Brønsted base*.

Example:

$$2 H_2O \rightarrow H_3O^+ + HO^-$$
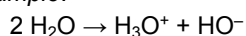
[3]
revGB-revPOC

autoprotolysis constant

Product of the activities of the species produced as the result of *autoprotolysis*.

Example: The autoprotolysis constant for water, K_w (or K_{AP}), is equal to the product of the relative activities of the hydronium and hydroxide ions at equilibrium in pure water.

19

$K_w = a(H_3O^+)a(HO^-) = 1.0 \times 10^{-14}$ at 25 °C and 1 standard atmosphere.

Note: Since the relative activity $a(H_2O)$ of water at equilibrium is imperceptibly different from unity (with mole fraction as the activity scale and pure un-ionized water as the standard state), the denominator in the expression for the thermodynamic equilibrium constant $K_w°$ for autoprotolysis has a value very close to 1.

$$K_w° = \frac{a(H^3O^+)a(HO^-)}{a(H_2O)^2}$$

Furthermore, owing to the low equilibrium extent of dissociation, and if infinite dilution is selected as the standard state, the activity coefficients of the hydronium and hydroxide ions in pure water are very close to unity. This leads to the relative activities of H_3O^+ and HO^- being virtually identical with the numerical values of their molar concentrations, if the molar scale of activity is used and an activity of 1 mol dm^{-3} is chosen as the standard state. Thus

$K_w \approx [H_3O^+][HO^-]$

where $[H_3O^+]$ and $[HO^-]$ are the numerical values of the molar concentrations. The autoprotolysis constant has the unit (and dimension) 1 because each relative activity has dimension 1, being a quotient of an absolute activity (including units) divided by a common unit standard state activity (including units).
See [56,57].
   rev[3]
   revGB-revPOC

α (alpha)
(1) Designation applied to the carbon to which a functional group is attached.
(2) In carbohydrate nomenclature a stereochemical designation of the *configuration* at the anomeric carbon.
(3) Parameter in a *Brønsted relation* expressing the sensitivity of the rate of protonation to *acidity.*
(4) Parameter in *Leffler's relation* expressing the sensitivity of changes in Gibbs activation energy to changes in overall Gibbs energy for an elementary reaction.
   See [11].
   rev[3]
   revGB

20

1 **α-effect**

2 Positive deviation of an α nucleophile (one bearing an unshared pair of electrons on an
3 atom adjacent to the nucleophilic site) from a Brønsted-type plot of lg $\{k_{nuc}\}$ vs. pK_a. The
4 argument in the lg function should be of dimension 1. Thus, reduced *rate coefficient*s
5 should be used. Here $\{k_{nuc}\} = k_{nuc}/[k_{nuc}]$ is the reduced k_{nuc}.

6   *Note 1*: More generally, it is the influence on the reactivity at the site adjacent to the
7 atom bearing a lone pair of electrons.

8   *Note 2*: The term has been extended to include the effect of any substituent on an
9 adjacent reactive centre, e.g., the α-silicon effect.

10   See [58,59,60].

11   See also *Brønsted relation*.

12 rev[3]

13 revGB

14

15 **α-elimination**

16 1,1-elimination

17 *Transformation* of the general type

18

19   RR'ZXY → RR'Z + XY (or X + Y, or X⁺ + Y⁻)

20

21 where the central atom Z is commonly carbon.

22   See also *elimination*.

23 revGB[3]

24

25 **Baldwin's rules**

26 Set of empirical rules for closures of 3- to 7-membered rings.

27   *Note*: The favoured pathways are those in which the length and nature of the linking
28 chain enable the terminal atoms to achieve the proper geometry and *orbital* overlaps
29 for reaction.

30   *Example*: Hex-5-en-1-yl radical undergoes 5-exo-trig cyclization to cyclopentylmethyl
31 radical rather than 6-endo-trig cyclization to cyclohexyl radical.

32

33

34

35   See [61,62].

36 rev[3]

37 revGB-revPOC

38

21

base

Chemical species or *molecular entity* having an available pair of electrons capable of forming a *bond* with a *hydron* (proton) (see *Brønsted base*) or with the vacant orbital of some other species (see *Lewis base*).

See also *hard base*, *superbase*.

~~GB~~[3]

basicity

(1) Tendency of a *Brønsted base* to act as *hydron* (proton) acceptor.

Note 1: The basicity of a *chemical species* is normally expressed by the *acidity* or acid-dissociation constant of its conjugate acid (see *conjugate acid-base pair*).

Note 2: To avoid ambiguity, the term pK_{aH} should be used when expressing basicity by the acid-dissociation constant of its conjugate acid. Thus the pK_{aH} of NH_3 is 9.2, while its pK_a, expressing its acidity, is 38.

(2) Tendency of a *Lewis base* to act as a *Lewis acid* acceptor.

Note 3: For Lewis bases, basicity is expressed by the association constants of *Lewis adduct*s and *π-adduct*s, or by the enthalpy of an acid/base reaction.

Note 4: Spectroscopic shifts induced by acid/base adduct formation can also be used as a measure of the strength of interaction.

See [63].

rev[3]

~~revGB-revPOC~~

bathochromic shift (effect)

Shift of a spectral band to lower frequencies (longer wavelengths).

Note: This is informally referred to as a red shift and is opposite to a *hypsochromic shift* ("blue shift"), but these historical terms are discouraged because they apply only to visible transitions.

See [9].

~~GB~~[3]

Bell-Evans-Polanyi principle

Linear relation between energy of activation (E_A) and enthalpy of reaction ($\Delta_r H$), sometimes observed within a series of closely related reactions.

$$E_A = a + b\,\Delta_r H$$

See [64,65,66,67].

rev[3]

~~revGB-revPOC~~

22

benzyne

1,2-Didehydrobenzene (a C_6H_4 *aryne* derived from benzene) and its derivatives formed by substitution.

 Note: The terms *m*- and *p*-benzyne are occasionally used for 1,3- and 1,4-didehydrobenzene, respectively, but these are incorrect because there is no triple bond.

 See [40,55].

 ~~GB~~[3]

bidentate

Feature of a *ligand* with two potential binding sites.

bifunctional catalysis

Catalysis (usually of *hydron* transfer) by a *chemical species* involving a mechanism in which two *functional groups* are implicated in the *rate-limiting step*, so that the corresponding *catalytic coefficient* is larger than that expected for catalysis by a chemical species containing only one of these functional groups.

 Example: Hydrogen carbonate is a particularly effective *catalyst* for the hydrolysis of 4-hydroxybutyranilide (*N*-phenyl-4-hydroxybutanamide), because it catalyzes the breakdown of the tetrahedral intermediate to expel aniline:
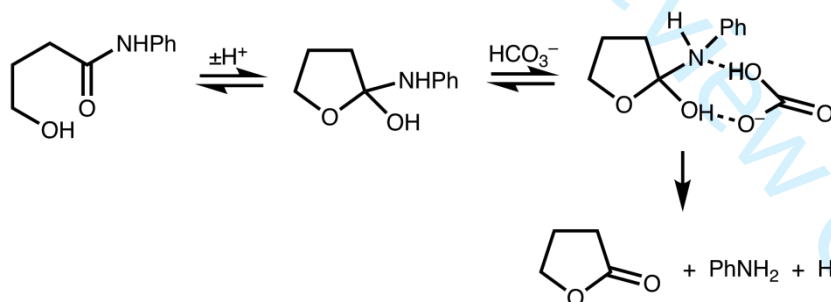
 Note: The term should not be used to describe a *concerted process* involving the action of two different catalysts.

 See [68,69,70,71,72].

 rev[3]

 ~~revGB-revPOC~~

bifurcation

Feature on a *potential-energy surface* whereby a *minimum-energy reaction path* (MERP) emanating from a saddle point (corresponding to a *transition structure*) splits

23

in two and leads to alternative products without intervening minima or secondary barriers to overcome. A bifurcation arises when the curvature of the surface in a direction perpendicular to the MERP becomes zero and then negative; it implies the existence of a lower-energy transition structure with a *transition vector* orthogonal to the original MERP.

See [73,74].

bimolecular

See *molecularity*.

~~GB~~[3]

binding site

Specific region (or atom) in a *molecular entity* that is capable of entering into a stabilizing interaction with another atomic or molecular entity.

Example: an active site in an enzyme that interacts with its *substrate*.

Note 1: Typical modes of interaction are by *covalent bonding*, *hydrogen bonding*, *coordination*, and *ion-pair* formation, as well as by dipole-dipole interactions, dispersion forces, hydrophobic interactions, and desolvation.

Note 2: Two binding sites in different molecular entities are said to be complementary if their interaction is stabilizing.

~~GB~~[3]

biradical

diradical

See [9].

rev[3]

~~GB-revPOC~~

blue shift

Informal expression for *hypsochromic shift*, but this historical term is discouraged because it applies only to visible transitions.

rev[3]

~~revGB~~

Bodenstein approximation

See *steady state*.

~~GB~~[3]

bond

24

1 Balance of attractive and repulsive forces between two atoms or groups of atoms,
2 resulting in sufficient net stabilization to lead to the formation of an aggregate
3 conveniently considered as an independent *molecular entity*.
4   *Note*: The term usually refers to the *covalent bond*.
5   See [75].
6   See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.
7   rev[3]
8   revGB-revPOC
9

10 **bond dissociation**
11   See *heterolysis*, *homolysis*.
12   *Note*: In ordinary usage the term refers to homolysis. If not, it should be specified as
13 heterolytic.
14   GB[3]
15

16 **bond-dissociation energy**
17 D_e
18 (SI unit: kJ mol^{-1})
19 Energy required to break a given *bond* of some specific *molecular entity* by *homolysis*
20 from its potential-energy minimum.
21   *Note:* This is the quantity that appears in the *Morse potential*.
22   See also *bond-dissociation enthalpy*.
23   rev[3]
24   revGB-revPOC
25

26 **bond-dissociation enthalpy**
27 DH^0, $\Delta_{diss}H^0$
28 (SI unit: kJ mol^{-1})
29 Standard molar enthalpy required to break a given *bond* of some specific *molecular*
30 *entity* by *homolysis*.
31   *Example*: For CH$_4$ → CH$_3$· + H· the bond-dissociation enthalpy is symbolized as
32 DH^0(CH$_3$–H).
33   *Note:* Although DH^0 is commonly used, $\Delta_{diss}H^0$ is more consistent with the notation
34 for other thermodynamic quantities.
35   See also *bond-dissociation energy*, *bond energy*, *heterolytic bond-dissociation*
36 *enthalpy*.
37

38 **bond energy**
39 D_0
40 (SI unit: kJ mol^{-1})

25

1   Enthalpy of bond dissociation at 0 K.

2   See *bond-dissociation enthalpy*.

3   rev[3]

4   revGB-revPOC

5

bond enthalpy (mean bond enthalpy, mean bond energy)

6

7   Average value of the gas-phase *bond-dissociation enthalpies* (usually at a temperature

8   of 298 K) for all *bond*s of the same type within the same *chemical species*.

9   *Example*: For methane, the mean bond enthalpy is 415.9 kJ mol^{-1}, one-fourth the

10   enthalpy of reaction for

11       $CH_4(g) \rightarrow C(g) + 4\ H(g)$

12   *Note*: More commonly, tabulated mean bond energies (which are really enthalpies)

13   are values of bond enthalpies averaged over a number of selected chemical species

14   containing that type of bond, such as 414 kJ mol^{-1} for C–H bonds in a group of R_3CH

15   (R = H, alkyl).

16   See [76].

17

bond order

18

19   Theoretical index of the degree of bonding between two atoms, relative to that of a

20   normal single *bond*, i.e., the bond provided by one localized electron pair.

21   *Example*: In ethene the C–C bond order is 2, and the C–H bond order is 1.

22   *Note 1*: In valence-bond theory it is a weighted average of the bond orders between

23   the respective atoms in the various resonance forms. In molecular-orbital theory it is

24   calculated from the weights of the atomic orbitals in each of the occupied molecular

25   orbitals. For example, in valence-bond theory the bond order between adjacent carbon

26   atoms in benzene is 1.5; in *Hückel molecular orbital theory* it is 1.67.

27   *Note 2:* Bond order is often derived from the electron distribution.

28   *Note 3:* The Pauling bond order *n* (as often used in the *bond-energy-bond-order*

29   *model*) is a simple function of change in bond length *d*, where the value of the coefficient

30   *c* is often 0.3 Å (for *n* > 1) or 0.6 Å (for *n* < 1).

31

32      $n = \exp[(d_1 - d_n)/c]$

33   rev[3]

34   revGB-revPOC

35

bond-energy-bond-order model (BEBO):

36

37   Empirical procedure for estimating *activation energy*, involving relationships among

38   bond length, *bond-dissociation energy*, and *bond order*.

39   See [13,77].

40   GB

26

bond-stretch isomers
Two (or more) molecules with the same spin multiplicity but with different lengths for one or more bonds.
   Note: This feature arises because the potential-energy surface, which describes how the energy of the molecule depends on geometry, shows two (or more) minima that are not merely symmetry-related.
   See [78,79,80,81].

borderline mechanism
Mechanism intermediate between two extremes, for example a *nucleophilic substitution* intermediate between S_N1 and S_N2, or intermediate between electron transfer and S_N2.
   GB[3]

Born-Oppenheimer approximation
Representation of the complete *wavefunction* as a product of electronic and nuclear parts, $\Psi(r,R) = \psi_{el}(r,R)\ \psi_{nuc}(R)$, so that the two wavefunctions can be determined separately by solving two different Schrödinger equations.
   See [8].
   GB

Bredt's rule
Prohibition of placing a double bond with one terminus at the *bridgehead* atom of a polycyclic system unless the rings are large enough to accommodate the double bond without excessive *strain*.
   Example: Bicyclo[2.2.1]hept-1-ene (A), which is capable of existence only as a *transient species*, although its higher homologues, bicyclo[3.3.1]non-1-ene (B) and bicyclo[4.2.1]non-1(8)-ene (C), with double bond at the bridgeheads, have been isolated.

A   B   C

   See [82,83,84,85].
   For limitations see [86].
   Note: For an alternative formulation, based on the instability of a *trans* double bond in a small ring (fewer than 8 atoms), see [87].
   rev[3]

27

bridged carbocation

Carbocation (real or hypothetical) in which there are two (or more) carbon atoms that could in alternative *Lewis formula*s 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.

Note: Electron-sufficient bridged carbocations are distinguished from electron-deficient bridged carbocations. Examples of the former, where the bridging uses π electrons, are phenyl-bridged ions (for which the trivial name phenonium ion has been used), such as **A**. These ions are straightforwardly classified as *carbenium ion*s. The latter type of ion necessarily involves three-centre bonding because the bridging uses σ electrons. The hydrogen-bridged carbocation **B** contains a two-coordinate hydrogen atom, whereas structures **C**, **D**, and **E** (the 2-norbornyl cation) contain five-coordinate carbon atoms.

See [88].
See also *carbonium ion*, *multi-centre bond*, *neighbouring group participation*.
For the definitive X-ray structure of the norbornyl cation see [89].
rev[3]

bridgehead (atom)

Atom that is part of two or more rings in a polycyclic molecule and that is separated from another bridgehead atom by bridges all of which contain at least one other atom.

Example: C1 and C4 in bicyclo[2.2.1]heptane, but not C4a and C8a in decahydronaphthalene.

bridging ligand

Ligand attached to two or more, usually metallic, central atoms.
See [29].

28

1 ~~GB~~[3]
2
Brønsted acid (Brönsted acid)
Molecular entity capable of donating a *hydron* (proton) to a base (i.e., a hydron donor), or the corresponding *chemical species*.
   Examples: H_2O, H_3O^+, CH_3COOH, H_2SO_4, HSO_4^-, HCl, CH_3OH, NH_3.
   See also *conjugate acid-base pair*.
~~GB~~[3]

Brønsted base (Brönsted base)
Molecular entity capable of accepting a *hydron* (proton) from a Brønsted acid (i.e., a hydron acceptor), or the corresponding *chemical species*.
   Examples: HO^-, H_2O, $CH_3CO_2^-$, HSO_4^-, SO_4^{2-}, Cl^-, CH_3O^-, NH_2^-.
   See also *conjugate acid-base pair*.
~~GB~~[3]

Brønsted relation (Brönsted relation)
Either of the equations

$$\lg(\{k_{HA}\}/p) = C \; + \; \alpha \lg(q\{K_{HA}\}/p)$$

$$\lg(\{k_A\}/q) \;\; = C \; - \; \beta \lg(q\{K_{HA}\}/p)$$

where α, β, and C are constants for a given reaction series (α and β are called Brønsted exponents or Brønsted parameters). The arguments in the lg functions should be of dimension 1. Thus, reduced *rate coefficients* should be used: $\{k_A\} = k_A/[k_A]$ and $\{k_{HA}\} = k_{HA}/[k_{HA}]$, which are the reduced catalytic coefficients of reactions whose rates depend on the concentrations of acid HA or of its conjugate base A^-, $\{K_{HA}\} = K_{HA}/[K_{HA}]$ is the reduced acid dissociation constant of HA, p is the number of equivalent acidic protons in HA, and q is the number of equivalent basic sites in A^-. The chosen values of p and q should always be specified. (The charge designations of HA and A^- are only illustrative.).
   Note 1: The equations are often written without reduced variables, whereupon the slope α or β, obtained from a graph or least-squares analysis, is correct because it is the ~~dimensionless~~ derivative of a logarithmic quantity, ~~is~~ of dimension 1.
   Note 2: The Brønsted relation is often termed the Brønsted catalysis law. Although justifiable on historical grounds, use of 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).

29

Note 3: The term pseudo-Brønsted relation is sometimes used for reactions that involve *nucleophilic catalysis* instead of acid-base catalysis. Various types of Brønsted parameters have been proposed such as β_{nuc} or β_{lg} for nucleophile or leaving group, respectively.

See also *linear free-energy relation* (*linear Gibbs energy relation*).

rev[3]

~~revGB-revPOC~~

Bunnett-Olsen equations

Relations between $lg([SH^+]/[S]) + H_o$ and $H_o + lg\{[H^+]\}$ for base S in aqueous acid solutions, 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. and where ϕ is an empirical parameter that is determined by the slope of the linear correlation of $lg([SH^+]/[S]) - lg\{[H^+]\}$ vs. $H_o + lg\{[H^+]\}$.

$$lg([SH^+]/[S]) - lg\{[H^+]\} = (\phi - 1)(H_o + lg\{[H^+]\}) + pK_{SH+}$$

$$lg([SH^+]/[S]) + H_o = \phi(H_o + lg\{[H^+]\}) + pK_{SH+}$$

Arguments in the lg functions should be of dimension 1. Thus, concentrations should be divided by the respective unit (unless they are eliminated as in the ratio of two concentrations), i.e., the reduced quantity should be used, indicated by curly brackets.

Note 1: These equations avoid using (or defining) an acidity function for each family of bases, including those for which such a definition is not possible. In many cases, ϕ (or $\phi - 1$) values for base families defining an acidity function are very similar. Broadly, the value of ϕ is related to the degree of solvation of SH^+.

Note 2: These equations are obsolete, and the *Cox-Yates equation*, with the equivalent parameter m^* (= $1 - \phi$), is now preferred.

See [21,90].

See also *Cox-Yates equation*.

rev[3]

~~revGB-revPOC~~

β, β_{nuc}, β_{lg}

Parameter in a *Brønsted relation* expressing the sensitivity of the rate of deprotonation to *basicity*.

Note: β_{nuc} and β_{lg} are used to correlate *nucleophilic* reactivity and leaving-group ability, respectively.

β-elimination

30

1,2-elimination

Transformation of the general type

$$XABY \rightarrow A=B + XY \text{ (or } X + Y, \text{ or } X^+ + Y^-)$$
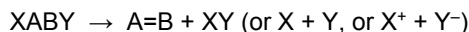
where the central atoms A and B are commonly, but not necessarily, carbon.

See also *elimination*.

cage

Aggregate of molecules, generally solvent molecules in the condensed phase, that surrounds fragments formed by thermal or photochemical dissociation.

Note: Because the cage hinders the separation of the fragments by diffusion, they may preferentially react with one another ("cage effect") although not necessarily to re-form the precursor species.

Example:

$$RN=NR \xrightarrow{\Delta} [R\cdot \ N_2 \ R\cdot]_{cage} \longrightarrow R\text{-}R + N_2$$

See also *geminate recombination*.

GB[3]

cage compound

Polycyclic compound capable of encapsulating another compound

Example (adamantane, where the central cavity is large enough to encapsulate He, Ne, or Na$^+$):

Note: A compound whose cage is occupied is called an *inclusion complex*.

See [91,92].

rev[3]

revGB-revPOC

canonical form

resonance form

rev[3]

revGB-revPOC

captodative effect

31

Combined action of an electron-withdrawing ("captor") substituent and an electron-releasing ("dative") substituent, both attached to a *radical* centre, on the stability of a carbon-centred radical.

Example:
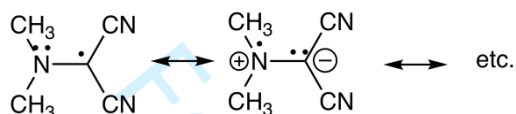
See [93,94,95].

rev[3]

~~revGB-revPOC~~

carbanion

Generic name for an anion containing an even number of electrons and having an unshared pair of electrons on a carbon atom which satisfies the *octet rule* and bears a negative *formal charge* in its *Lewis structure* or in at least one of its *resonance form*s.

Examples:
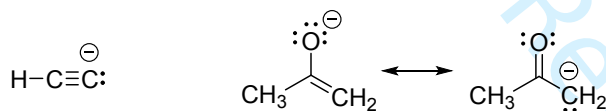
See also *radical ion*.

See [40,96].

rev[3]

~~revGB-revPOC~~

carbene

Generic name for the species $H_2C:$ ("methylidene") and substitution derivatives thereof, containing an electrically neutral bivalent carbon atom with two nonbonding electrons.

Note 1: The nonbonding electrons may have antiparallel spins (singlet state) or parallel spins (*triplet state*).

Note 2: Use of the alternative name "methylene" as a generic term is not recommended.

See [40].

See also *diradical*.

~~GB~~[3]

carbenium ion

32

1   Generic name for a *carbocation* whose electronic structure can be adequately
2   described by two-electron-two-centre bonds.
3   *Note 1*: The name implies a hydronated carbene or a substitution derivative thereof.
4   *Note 2*: The term is a replacement for the previously used term *carbonium ion*, which
5   now specifies a carbocation with penta- or higher-coordinate carbons. The names
6   provide a useful distinction between tricoordinate and pentacoordinate carbons.
7   *Note 3*: To avoid ambiguity, the name should be avoided as the root for the
8   nomenclature of *carbocation*s. For example, the term "ethylcarbenium ion" might refer
9   to either $CH_3CH_2^+$ (ethyl cation, ethylium) or $CH_3CH_2CH_2^+$ (propyl cation, propylium).
10   See [40,97].
11   rev[3]
12   ~~GB-revPOC~~
13
14 **carbenoid**
15 *Carbene*-like *chemical species* but with properties and *reactivity* differing from the free
16 carbene, arising from additional substituents bonded to the carbene carbon.
17   *Example*: $R_1R_2C(Cl)M$ (M = metal)
18   rev[3]
19   ~~revGB~~
20
21 **carbocation**
22 Positive ion containing an even number of electrons and with a significant portion of the
23 excess positive charge located on one or more carbon atoms.
24   *Note 1*: This is a general term embracing *carbenium ion*s, all types of *carbonium*
25 *ion*s, vinyl cations, etc.
26   *Note 2*: Carbocations may be named by adding the word "cation" to the name of the
27 corresponding *radical* [97,98].
28   *Note 3*: Such names do not imply structure (e.g., whether three-coordinated or five-
29 coordinated carbon atoms are present) [98].
30   See also *bridged carbocation*, *radical ion*.
31   See [40].
32   ~~GB~~[3]
33
34 **carbonium ion**
35 (1) Carbocation that contains at least one carbon atom with a *coordination number* of
36 five or greater.
37 (2) Carbocation whose structure cannot adequately be described by only two-electron
38 two-centre *bond*s.
39   *Example*: methanium (CH_5^+).

33

Note 1: In most of the earlier literature this term was used for all types of carbocations, including those that are now defined as a (tricoordinate) *carbenium ion*.

Note 2: To avoid ambiguity, the term should be avoided as the root for the nomenclature of *carbocation*s. For example, the name "ethylcarbonium ion" might refer to either $CH_3CH_2^+$ (ethyl cation) or $CH_3CH_2CH_2^+$ (propyl cation).

See [98,99].

rev[3]

revGB-revPOC

carbyne

methylidyne

Generic name for the species HC·: and substitution derivatives thereof, such as EtOCO–C·: (2-ethoxy-2-oxoethylidyne), containing an electrically neutral univalent carbon atom with three non-bonding electrons.

Note: Use of the alternative name "methylidyne" as a generic term is not recommended.

GB[3]

Catalán solvent parameters

Quantitative measure of solvent polarity, based on the solvent's hydrogen-bond-donor ability, hydrogen-bond-acceptor ability, polarizability, and dipolarity.

See [100,101].

See also *solvent parameter*.

catalyst

Substance that increases the rate of a *chemical reaction* (owing to a change of mechanism to one having a lower Gibbs energy of activation) without changing the overall standard Gibbs energy change (or position of equilibrium).

Note 1: The catalyst is both a reactant and product of the reaction, so that there is no net change in the amount of that substance.

Note 2: 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.

Note 3: The requirement that there be no net change in the amount of catalyst is sometimes relaxed, as in the base catalysis of the bromination of ketones, where base is consumed, but this is properly called *pseudo-catalysis*.

Note 4: *Catalysis* can be classified as homogeneous, in which only one phase is involved, and heterogeneous, in which the reaction occurs at or near an interface between phases.

34

Note 5: Catalysis brought about by one of the products of a reaction is called autocatalysis.

Note 6: The terms catalyst and catalysis should not be used when the added substance reduces the rate of reaction (see *inhibition*).

Note 7: The above definition is adequate for isothermal-isobaric reactions, but under other experimental conditions the state function that is lowered by the catalyst is not the Gibbs activation energy but the quantity corresponding to those conditions (e.g., the Helmholtz energy under isothermal-isochoric conditions).

See [13].

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*.

rev[3]

revGB-revPOC

catalytic antibody (abzyme)

monoclonal antibody with enzymatic activity

Note 1: A catalytic antibody acts by binding its antigen and catalyzing a chemical reaction that converts the antigen into desired products. Despite the existence of natural catalytic antibodies, most of them were specifically designed to catalyze desired chemical reactions.

Note 2: Catalytic antibodies are produced through immunization against a transition-state analogue for the reaction of interest. The resulting antibodies bind strongly and specifically the transition-state analogue, so that they become *catalyst*s for the desired reaction.

Note 3: The concept of catalytic antibodies and the strategy for obtaining them were advanced by W. P. Jencks [102]. The first catalytic antibodies were finally produced in 1986 [103,104].

catalytic coefficient

If the *rate of reaction* v is expressible in the form

$$v = (k_0 + \Sigma k_i[C_i]^{ni})\ [A]^a\ [B]^b...$$

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.

Note: Normally the partial *order of reaction* (n_i) with respect to a catalyst will be unity, so that k_i is an $(a + b+...+1)^{th}$-order *rate coefficient*.

GB[3]

35

catalytic cycle

Sequence of reaction steps in the form of a loop. One step is binding of a reactant to the active *catalyst* (sometimes formed from a precatalyst), and another step is the release of product and regeneration of catalyst.

Example: A + B → C, catalyzed by X formed from precatalyst X'.

cation/π interaction

Noncovalent attractive force between a positive ion (metal cation, protonated *Brønsted base*, etc.) and a π electron system.

See [105].

chain reaction

Reaction in which one or more reactive *reactive intermediates* (frequently *radical*s) are continuously regenerated through a repetitive cycle of elementary steps ("propagation steps").

Example: Chlorination of methane by a radical *mechanism*, where Cl· is continually regenerated in the chain-propagation steps:

Cl· + CH$_4$ → HCl + H$_3$C·

H$_3$C· + Cl$_2$ → CH$_3$Cl + Cl·

Note: In chain polymerization reactions, *reactive intermediate*s of the same types, generated in successive steps or cycles of steps, differ in molecular mass, as in

RCH$_2$C·HPh + H$_2$C=CHPh → RCH$_2$CHPhCH$_2$C·HPh

See [106].

See also *chain transfer*, *initiation*, *termination*.

~~GB~~[3]

chain transfer

36

Chemical reaction during a chain polymerization in which the active centre is transferred from the growing macromolecule to another molecule or to another site on the same molecule, often by abstraction of an atom by the *radical* end of the growing macromolecule.

Note 1: 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

$$RCH_2C \cdot HPh + CCl_4 \rightarrow RCH_2CHClPh + Cl_3C \cdot$$

represents a chain transfer, the radical $Cl_3C \cdot$ inducing further polymerization:

Note 2: Chain transfer also occurs in other chain reactions, such as cationic or anionic polymerization, in which case the abstraction is by the reactive cationic or anionic end of the growing chain.

See [106].

See also *telomerization*.

~~GB~~[3]

charge density

See *electron density*.

See [12].

~~GB~~[3]

charge-transfer (CT) complex

Ground-state *adduct* that exhibits an electronic absorption corresponding to light-induced transfer of electronic charge from one region of the adduct to another.

See [9].

rev[3]

~~revPOC~~

chelation

Formation or presence of *bond*s (or other attractive interactions) between a single central atom (or ion) and two or more separate *binding site*s within the same *ligand*.

Note 1: A *molecular entity* in which there is chelation (and the corresponding *chemical species*) is called a chelate, while the species that binds to the central atom is called a chelant.

Note 2: The terms *bidentate*, tridentate, ... *multident*ate 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 Cu^{+2} in which both nitrogen atoms of ethylenediamine are bonded to copper.

Note 3: The use of the term is often restricted to metallic central atoms or ions.

37

1   *Note 4*: The phrase "separate binding sites" is intended to exclude cases such as
2    $[PtCl_3(CH_2=CH_2)]^-$, ferrocene, and (benzene)tricarbonylchromium, in which ethene, the
3   cyclopentadienyl group, and benzene, respectively, are considered to present single
4   binding sites to the respective metal atom.
5   See also *ambident*, *cryptand*.
6   See also [29].
7   GB[3]
8

9   **cheletropic reaction**
10   *Cycloaddition* across the terminal atoms of a π system with formation of two new σ
11   bonds to a single atom of a monocentric reagent. There is formal loss of one π bond in
12   the substrate and an increase in *coordination number* of the relevant atom of the
13   reagent.
14   *Example: addition* of sulfur dioxide to butadiene:

$$CH_2=CH\text{-}CH=CH_2 \ + \ SO_2 \ \longrightarrow \ \text{(cyclic structure)}\;SO_2$$

15
16   *Note*: The reverse of this type of reaction is designated "cheletropic elimination".
17   See [107].
18   GB[3]
19

20   **chelotropic reaction**
21   Alternative (and etymologically more correct) name for *cheletropic reaction*.
22   See [51].
23   GB[3]
24

25   **chemical flux, ϕ**
26   Unidirectional *rate of reaction*, applicable to the progress of component reaction steps
27   in a complex system or to the progress of reactions in a system at dynamic equilibrium
28   (in which there are no observable concentration changes with time), excluding the
29   reverse reaction and other reaction steps.
30   *Note 1*: Chemical flux is a derivative with respect to time, and has the dimensions of
31   amount of substance per volume transformed per time.
32   For example, for the mechanism
33         $A + B \rightleftarrows C$
34         $C + D \rightarrow E$
35   ϕ_1 is the chemical flux due to forward reaction step 1, or the rate of formation of C or
36   the rate of loss of A or B due to that step, and similarly for ϕ_{-1} and ϕ_2.

38

Note 2: The sum of all the chemical fluxes leading to C is designated the "total chemical flux into C" (symbol $\Sigma\phi_C$), and the sum of all the chemical fluxes leading to destruction of C is designated the "total chemical flux out of C" (symbol $\Sigma\phi_{-C}$), and similarly for A and B. It then follows for this example that $\Sigma\phi_C = \phi_1$ and $\Sigma\phi_{-C} = \phi_{-1} + \phi_2$,

Note 3: The net rate of appearance of C is then given by

$$d[C]/dt = \Sigma\phi_C - \Sigma\phi_{-C}$$

Note 4: In this system ϕ_1 (or $\Sigma\phi_C$) can be regarded as the hypothetical rate of formation of C due to the single (unidirectional) reaction 1 proceeding in the assumed absence of all other reactions, and $\Sigma\phi_{-C}$ can be regarded as the hypothetical rate of destruction of C due to the two (unidirectional) reactions −1 and 2.

Note 5: Even when there is no net reaction, chemical flux can often be measured by NMR methods.

See [1].

See also *order of reaction*, *rate-limiting step*, *steady state*.

rev[3]

revGB-revPOC

chemical reaction

Process that results in the interconversion of *chemical species*.

Note 1: This definition includes experimentally observable interconversions of *conformer*s and *degenerate rearrangement*s.

Note 2: Chemical reactions may be *elementary reaction*s or *stepwise reaction*s.

Note 3: 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"), whose reactions can now be observed experimentally.

See also *identity reaction*.

rev[3]

revGB-revPOC

chemical relaxation

Passage of a perturbed system toward or into chemical equilibrium.

Note 1: A *chemical reaction* at equilibrium can be disturbed from equilibrium by a sudden change of some external parameter such as temperature, pressure, or electric-field strength.

Note 2: 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 process

1
2
3
4
5   39
6
7
8
9
1
10
2          $c(t) - (c_{eq})_2 = [(c_{eq})_1 - (c_{eq})_2] \exp(-t/\tau)$
11
3
12
4   where $(c_{eq})_1$ and $(c_{eq})_2$ are the equilibrium amount concentrations of one of the chemical
13
5   species before and after the change in the external parameter, and $c(t)$ is its amount
14
6   concentration at time t. The time parameter τ, called relaxation time, is related to the
15
7   *rate coefficients* of the chemical reaction involved. Such measurements are commonly
16
8   used to follow the kinetics of very fast reactions.
17
9   *Note 3: Relaxation,* or the passage toward equilibrium, is more general than chemical
18
10   relaxation, and includes relaxation of nuclear spins.
19
11   See [108,109].
20
12   See *relaxation*.
21
13   rev[3]
22
14   revGB-revPOC
23
15
24
16   **chemical shift (NMR)**
25
17   δ
26
18   Variation of the resonance frequency of a nucleus in nuclear magnetic resonance
27
19   (NMR) spectrometry as a consequence of its environment.
28
20   *Note 1*: The chemical shift of a nucleus X, δ_X, expressed as its frequency, ν_X, relative
29
21   to that of a standard, ν_{ref}, and defined as
30
22
31
23       $\delta_X = (\nu_X - \nu_{ref})/\nu_{ref}$
32
24
33
25   For ^1H and ^{13}C NMR the reference signal is usually that of tetramethylsilane (SiMe$_4$).
34
26   *Note 2:* Chemical shift is usually reported in "parts per million" or ppm, where the
35
27   numerator has unit Hz, and the denominator has unit MHz, like the spectrometer's
36
28   operating frequency.
37
29   *Note 3*: For historical reasons that predate Fourier-transform NMR, if a resonance
38
30   signal occurs at higher frequency than a reference signal, it is said to be downfield, and
39
31   if resonance occurs at lower frequency, the signal is upfield. Resonances downfield
40
32   from SiMe$_4$ have positive δ-values, and resonances upfield from SiMe$_4$ have negative
41
33   δ-values. These terms have been superseded, and deshielded and shielded are
42
34   preferred for downfield and upfield, respectively.
43
35   See [110].
44
36   See also *shielding*.
45
37   rev[3]
46
38   GB-revPOC
47
39
48
40   **chemical species**
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51
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40

Ensemble of chemically identical *molecular entities* that can explore the same set of molecular energy levels on the time scale of an experiment. The term is applied equally to a set of chemically identical atomic or molecular structural units in a solid array.

Note 1: For example, conformational *isomer*s 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.

Note 2: Except where the context requires otherwise, the term is taken to refer to a set of molecular entities containing isotopes in their natural abundance.

Note 3: The definition given is intended to embrace not only cases such as graphite and sodium chloride but also a surface oxide, where the basic structural units may not be capable of isolated existence.

Note 4: 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*.

GB[3]

chemically induced dynamic nuclear polarization (CIDNP)
Non-Boltzmann nuclear spin-state distribution produced in thermal or photochemical reactions, usually from *colligation* and diffusion or *disproportionation* of *radical pair*s, and detected by NMR spectroscopy as enhanced absorption or emission signals.
See [111,112].
revGB[3]

chemiexcitation
Generation, by a chemical reaction, of an electronically excited molecular entity from reactants in their ground electronic states.
See [9].
[3]

chemoselectivity
Feature of a chemical reagent that reacts preferentially with one of two or more different functional groups.

Note 1: A reagent has a high chemoselectivity if reaction occurs with only a limited number of different functional groups. For example, sodium tetrahydridoborate ($NaBH_4$) is a more chemoselective reducing agent than is lithium tetrahydridoaluminate ($LiAlH_4$). The concept has not been defined in more quantitative terms.

41

Note 2: The term is also applied to reacting molecules or intermediates that exhibit selectivity towards chemically different reagents.

Note 3: Usage of the term chemospecificity for 100 % chemoselectivity is discouraged.

See [113].

See also regioselectivity, stereoselectivity, stereospecificity.

GB[3]

chemospecificity

obsolete

See chemoselectivity.

GB[3]

chirality

Property of a structure that is not superimposable on its mirror image.

See [11,46].

GB[3]

chirality centre

chiral centre (superseded)

Atom with attached groups such that the arrangement is not superimposable on its mirror image.

Note: Often this is a tetrahedral atom with four different groups attached, such as CHBrClF, or C2 of $CH_3CHBrCH_2CH_3$, or the sulfur of $CH_3S(=O)Ph$, where the lone pair is considered as a fourth group.

See [11].

See also stereogenic centre.

GB[3]

chiral feature

Structural characteristic rendering a molecule chiral.

Examples: four different substituents on a carbon atom (chirality centre), conformational helix, chiral axis (as in allenes XCH=C=CHX).

chiral recognition

Attraction between molecules through noncovalent interactions that exhibit complementarity only between partners with specific chirality.

See also molecular recognition.

chromophore

42

1   Part (atom or group of atoms) of a *molecular entity* in which the electronic transition
2   responsible for a given spectral band is approximately localized.
3   *Note 1*: The term arose originally to refer to the groupings that are responsible for a
4   dye's colour.
5   *Note 2:* The electronic transition can often be assigned as involving n, π, π^*, σ, and/or
6   σ^* orbitals whose energy difference falls within the range of the visible or UV spectrum.
7   *Note 3*: The term has been extended to vibrational transitions in the infrared.
8   See [9,114,115].
9   GB[3]
10
11 **CIDNP**
12 Acronym for *chemically induced dynamic nuclear polarization*.
13   GB[3]
14
15 ***cine*-substitution**
16 *Substitution* reaction (generally *aromatic*) in which the entering group takes up a
17 position adjacent to that occupied by the *leaving group*.
18   *Example*:
19

20
21
22   See also *tele-substitution*.
23   GB[3]
24
25 **classical carbocation**
26 *Carbocation* whose electronic structure can be adequately described by two-electron-
27 two-centre bonds, i.e., synonymous with *carbenium ion*.
28
29 **clathrate**
30   See *host*, *inclusion compound*.
31   GB[3]
32
33 **coarctate**
34 *Feature of a *concerted* *transformation* in which the primary changes in bonding occur
35 within a cyclic array of atoms but in which two nonbonding *atomic orbital*s on an atom
36 interchange roles with two bonding orbitals.

43

1 *Example:* epoxidation with dimethydioxirane

2

3

4 *Note:* Because the atomic orbitals that interchange roles are orthogonal, such a
5 reaction does not proceed through a fully *conjugated* *transition state* and is thus not a
6 pericyclic reaction. It is therefore not governed by the rules that express *orbital*
7 *symmetry* restrictions applicable to pericyclic reactions.
8   See [116].
9   See also *pseudopericyclic.*

10

11 **colligation**
12 Formation of a covalent bond by combination or recombination of two *radical*s.
13   *Note*: This is the reverse of *unimolecular homolysis*.
14   *Example*:
15          $HO\cdot + H_3C\cdot \rightarrow CH_3OH$
16   GB[3]

17

18 **collision complex**
19 Ensemble formed by two reaction partners, where the distance between them is equal
20 to the sum of the van der Waals radii of neighbouring atoms.
21   See also *encounter complex.*
22   [3]GB

23

24 **common-ion effect (on rates)**
25 Reduction in the *rate* of certain reactions of a *substrate* RX in solution [by a path that
26 involves a *pre-equilibrium* with formation of R^+ (or R^-) ions as reaction intermediates]
27 caused by the addition to the reaction mixture of an electrolyte solute containing the
28 "common ion" X^- (or X^+).
29   *Example*: the rate of solvolysis of chlorodiphenylmethane in acetone-water is
30 reduced by the addition of salts of the common ion Cl^-, which causes a decrease in the
31 *steady-state* concentration of the diphenylmethyl cation:
32

33          $Ph_2CHCl \rightleftharpoons Ph_2CH^+ + Cl^-$ (free ions, not ion pairs)
34          $Ph_2CH^+ + 2\ OH_2 \rightarrow\ Ph_2CHOH + H_3O^+$

44

Note: This retardation due to a common ion should be distinguished from the acceleration due to a salt effect of all ions.

rev[3]

~~revGB-revPOC~~

compensation effect

Observation that a plot of $T\Delta_r S$ vs. $\Delta_r H$ (frequently $T\Delta^{\ddagger}S$ vs. $\Delta^{\ddagger}H$) for a series of reactions with a range of different substituents (or other unique variable such as solvent or dissolved salt), are straight lines of approximately unit slope, so that, e.g., the terms $\Delta^{\ddagger}H$ and $T\Delta^{\ddagger}S$ partially compensate, and $\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S$ shows less variation than $\Delta^{\ddagger}H$ or $T\Delta^{\ddagger}S$ separately.

Note: Frequently such $\Delta^{\ddagger}S$ vs. $\Delta^{\ddagger}H$ correlations are statistical artifacts, arising if entropy and enthalpy are extracted from the variation of an equilibrium constant or a *rate constant* with temperature, so that the slope and intercept of the van't Hoff plots are correlated. The problem is avoided if the equilibrium constant and the enthalpy are measured independently, for example by spectrophotometry and calorimetry, respectively.

See [117,118,119,120].

See also *isoequilibrium relationship, isokinetic relationship*.

rev[3]

~~revGB-revPOC~~

complex

Molecular entity formed by loose *association* involving two or more component molecular entities (ionic or uncharged), or the corresponding *chemical species*. The attraction between the components is often due to hydrogen-bonding or van der Waals attraction and is normally weaker than a covalent *bond*.

Note 1: The term has also been used with a variety of meanings in different contexts: it is therefore best avoided when a more explicit alternative is applicable, such as *adduct* when the association is a consequence of bond formation.

Note 2: In inorganic chemistry the term "coordination entity" is recommended instead of "complex" [29,121].

See also *activated complex*, *adduct*, *charge transfer complex*, *electron-donor-acceptor complex*, *encounter complex*, *inclusion complex*, σ-*adduct*, π-*adduct*, *transition state*.

~~GB~~[3]

composite reaction

45

Chemical reaction for which the expression for the rate of disappearance of a reactant (or rate of appearance of a product) involves *rate constant*s of more than a single *elementary reaction*.

Examples: "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 that form different products from a single set of reactants), and *stepwise reaction*s.

GB[3]

comproportionation

Any *chemical reaction* of the type A' + A" → 2 A

Example:

Pb + PbO$_2$ + 2 H$_2$SO$_4$ → 2 PbSO$_4$ + 2 H$_2$O (in a lead battery)

Note: Other stoichiometries are possible, depending on the *oxidation number*s of the species.

Reverse of *disproportionation*. The term "symproportionation" is also used.

See [122].

rev[3]

revGB-revPOC

concerted

Feature of a process in which two or more primitive changes occur within the same *elementary reaction*. Such changes will normally be "energetically coupled".

Note 1: 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.

Note 2: In a concerted process the primitive changes may be *synchronous* or asynchronous.

See also *bifunctional catalysis*, *potential-energy surface*.

GB[3]

condensation

Reaction (usually stepwise) in which two or more reactants (or remote reactive sites within the same *molecular entity*) yield a product with accompanying formation of water or some other small molecule, e.g., ammonia, ethanol, acetic acid, hydrogen sulfide.

Note 1: 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 dehydration of 3-

46

hydroxybutanal (aldol). The overall reaction in this example is known as the aldol condensation.

Note 2: The term is sometimes also applied to cases where the formation of water or other simple molecule does not occur, as in "benzoin condensation".

[3]

~~revGB~~

condensed formula

Linear representation of the structure of a *molecular entity* in which bonds are omitted.

Example: methyl 3-methylbutyl ether (isoamyl methyl ether, $(CH_3)_2CHCH_2CH_2OCH_3$, sometimes condensed further to $(CH_3)_2CH[CH_2]_2OCH_3$)

Note: This term is sometimes also called a *line formula*, because it can be written on a single line, but the line formula explicitly shows all bonds.

configuration (electronic)

Distribution of the electrons of an atom or a *molecular entity* over a set of one-electron wavefunctions called *orbital*s, according to the Pauli principle.

Note: 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

$$^3\Sigma_g^-, {}^1\Delta_g, \text{ and } {}^1\Sigma_g^+ \text{ multiplets}$$

See [8,9].

~~GB~~[3]

configuration (molecular)

Arrangement in space of the atoms of a *molecular entity* that distinguishes it from any other molecular entity having the same molecular formula and *connectivity* and that is not due to conformational differences (rotation about single bonds).

See [11].

[3]

conformations

Different spatial arrangements of a molecular entity that can be interconverted by rotation about one or more formally single bonds.

Note 1: Different conformations are often not considered to be stereoisomeric, because interconversion is rapid.

Note 2: Different or equivalent spatial arrangements of *ligands* about a central atom, such as those interconverted by pyramidal inversion (of amines) or Berry

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pseudorotation (as of PF$_5$) and other "polytopal rearrangements", are sometimes considered conformations, but they are properly described as *configuration*s.

See [11].

rev[3]

~~revGB~~

conformational isomers

conformers

conformer

Conformation of a *molecular entity* that corresponds to a minimum on the potential-energy surface of that molecular entity.

Note: The distinction between conformers and isomers is the height of the barrier for interconversion. Isomers are stable on macroscopic timescales because the barrier for interconversion is high, whereas a conformer cannot persist on a macroscopic timescale because the interconversion between conformations is achieved rapidly.

See [11].

conjugate acid

Brønsted acid BH$^+$ formed on protonation (hydronation) of the base B.

Note 1: B is called the conjugate base of the acid BH$^+$.

Note 2: 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, and so do NH$_4^+$ and its conjugate base NH$_3$.

rev~~GB~~[3]

conjugated system, conjugation

Molecular entity whose structure may be represented as a system of alternating multiple and single (or σ) bonds: e.g.,

CH$_2$=CH–CH=CH$_2$ or CH$_2$=CH–C$\equiv$N

Note: In such systems, conjugation is the interaction of one p-orbital with another p-orbital (or d-orbital) across an intervening σ bond, including the analogous interaction involving a p-orbital containing an unshared electron pair, e.g.,

R$_2$N̈−CH=CH$_2$

or the interaction across a double bond whose π system does not interact with the p orbitals of the conjugated system, as in

CH$_2$=C=C=CH$_2$

See also *cross-conjugation*, *delocalization*, *resonance*, *through-conjugation*.

48

1   ~~GB~~[3]
2

connectivity

Description of which atoms are bonded to which other atoms.

Note: Connectivity is often displayed in a *line formula* or other structure showing which atoms are bonded to which other atoms, but with minimal or no indication of *bond* multiplicity.

Example: The connectivity of propyne is specified by CH_3CCH.

revGB[3]

conrotatory

Stereochemical feature of an *electrocyclic reaction* in which the substituents at the interacting termini of the conjugated system rotate in the same sense (both clockwise or both counterclockwise).

See also *disrotatory*.

rev[3]

~~revGB-revPOC~~

conservation of orbital symmetry

An approach to understanding *pericyclic reaction*s that focuses on a symmetry element (e.g., a reflection plane) that is retained along a reaction pathway. If each of the singly or doubly occupied orbitals of the reactant(s) is of the same symmetry as a similarly occupied orbital of the product(s), that pathway is "allowed" by orbital symmetry conservation. If instead a singly or doubly occupied orbital of the reactant(s) is of the same symmetry as an unoccupied orbital of the product(s), and an unoccupied orbital of the reactant(s) is of the same symmetry as a singly or doubly occupied orbital of the product(s), that pathway is "forbidden" by orbital symmetry conservation.

Note 1: This principle permits the qualitative construction of correlation diagrams to show how molecular orbitals transform and how their energies change during chemical reactions.

Note 2: Considerations of orbital symmetry are frequently grossly simplified in that, for example, the π and π^* orbitals of a carbonyl group in an asymmetric molecule are treated as having the same topology (pattern of local nodal planes) as those of a symmetric molecule (e.g., $CH_2=O$), despite the absence of formal symmetry elements.

See [107,123].

See also *orbital symmetry*.

constitutional isomers

Species (or *molecular entities*) with the same atomic composition (*molecular formula*) but with different *connectivity*.

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1   *Note:* The term structural isomers is discouraged, because all isomers differ in
2 structure and because isomers may be constitutional, configurational, or
3 conformational.
4   See [11].
5

6 **contributing structure**
7 resonance form
8   rev[3]
9   revGB-revPOC
10

11 **coordinate covalent bond**
12 dative bond
13

14 **coordination**
15 Formation of a covalent *bond*, the two shared electrons of which come from only one
16 of the two partners linked by the bond, as in the reaction of a *Lewis acid* and a *Lewis*
17 *base* to form a *Lewis adduct*; alternatively, the bonding formed in this way.
18   *Note*: In the former sense, it is the reverse of *unimolecular heterolysis*.
19   See also *dative bond*, *π-adduct*.
20   rev[3]
21   revGB
22

23 **coordination number**
24 Number of other atoms directly linked to a specified atom in a *chemical species*
25 regardless of the number of electrons in the bonds linking them [29, Rule IR-10.2.5].
26 For example, the coordination number of carbon in methane or of phosphorus in
27 triphenylphosphane oxide (triphenylphosphine oxide) is four whereas the coordination
28 number of phosphor is five in phosphorus pentafluoride.
29   *Note*: The term is used in a different sense in the crystallographic description of ionic
30 crystals.
31   revGB[3]
32

33 **coronate**
34   See *crown ether*.
35   revGB[3]
36

37 **correlation analysis**
38 Use of empirical correlations relating one body of experimental data to another, with the
39 objective of finding quantitative relationships among the factors underlying the
40 phenomena involved. Correlation analysis in organic chemistry often uses linear Gibbs-

energy relations (formerly *linear free-energy relation*, LFER) for rates or equilibria of reactions, but the term also embraces similar analysis of physical (most commonly spectroscopic) properties and of biological activity.

See [124,125,126,127,128].

See also *linear free-energy relation*, *quantitative structure-activity relationship (QSAR)*.

GB[3]

coupling constant (spin-spin coupling constant)

J

(Unit: Hz)

Quantitative measure of nuclear spin-spin coupling in nuclear magnetic resonance spectroscopy.

Note: Spin-spin coupling constants have been correlated with atomic hybridization and with molecular conformations.

See [129,130,131].

revGB[3]

covalent bond

Stabilizing interaction associated with the sharing of electron pairs between two atomic centres of a molecular entity, leading to a characteristic internuclear distance.

See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.

See [8].

revGB[3]

Cox–Yates equation

Generalization of the *Bunnett-Olsen equation* of the form

$$\lg([SH^+])/[S]) - \lg\{[H^+]\} = m^*X + pK_{SH+}$$

where $[H^+]$ is the amount concentration of acid, X is the activity-coefficient ratio $\lg(\{\gamma_S\}\{\gamma_{H+}\}/\{\gamma_{SH+}\})$ for an arbitrary reference base, pK_{SH+} is the thermodynamic dissociation constant of SH^+, and m^* is an empirical parameter derived from linear regression of the left-hand side vs. X. Arguments in the lg functions should be unitless. Thus, the reduced quantities should be used: $\{[H^+]\}$ is $[H^+]$/units.

Note: The function X is called 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 $m^* = 1 - \phi$, where H_o is the Hammett *acidity function* and ϕ is the slope in the Bunnett-Olsen equation.

See [132,133,134].

51

See *Bunnett-Olsen equation*.
rev[3]
revGB

critical micellisation concentration *(cmc)*
critical micelle concentration
Relatively small range of concentrations separating the limit below which virtually no *micelle*s are detected and the limit above which virtually all additional surfactant molecules form micelles.

Note 1: Many physical properties of surfactant solutions, such as conductivity or light scattering, show an abrupt change at a particular concentration of the surfactant, which can be taken as the *cmc*.

Note 2: As values obtained using different properties are not quite identical, the method by which the *cmc* is determined should be clearly stated.

See [135].
See also *inverted micelle*.
rev[3]
revGB-revPOC

cross-conjugation
Phenomenon of three conjugated groups, two pairs of which exhibit conjugation but without *through-conjugation* of all three, as in 2-phenylallyl, benzoate anion, divinyl ether, or *m*-xylylene [1,3-$C_6H_4(CH_2)_2$].

See [64].
rev[3]
revGB-revPOC

crown ether
Molecular entity comprising a monocyclic *ligand* assembly that contains three or more *binding site*s held together by covalent bonds and capable of binding a *guest* in a central (or nearly central) position. The *adduct*s 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 –CR_2–CR_2O– (where R is most commonly H).

"18-crown-6"

52

1
2   See [136,137].
3   See also *host*.
4   rev[3]
5   revPOC
6

7   **cryptand**
8   *Molecular entity* comprising a cyclic or polycyclic assembly of *binding site*s that contains
9   three or more binding sites held together by *covalent bond*s, and which defines a
10   molecular cavity in such a way as to bind (and thus "hide" in the cavity) another
11   molecular entity, the *guest* (a cation, an anion or a neutral species), more strongly than
12   do the separate parts of the assembly (at the same total concentration of binding sites).
13   *Note 1*: The *adduct* thus formed is called a "cryptate". The term is usually restricted
14   to bicyclic or oligocyclic molecular entities.
15   *Example*:

16

17   *Note 2*: Corresponding monocyclic *ligand* assemblies (*crown ether*) are sometimes
18   included in this group, if they can be considered to define a cavity in which a guest can
19   hide. The terms "podand" and "spherand" are used for certain specific ligand
20   assemblies. Coplanar cyclic polydentate ligands, such as porphyrins, are not normally
21   regarded as cryptands.
22   See [138].
23   See also *host*. See also [139].
24   GB[3]
25

26   **curly arrows**
27   Symbols for depicting the flow of electrons in a chemical reaction or to generate
28   additional *resonance form*s.
29   *Note 1:* The tail of the curly arrow shows where an electron pair originates, and the
30   head of the curly arrow shows where the electron pair goes.
31   *Note 2:* Single-headed curly arrows are used to depict the flow of unpaired electrons.
32   *Examples:*
33

53

See *electron pushing*.

Curtin-Hammett principle

Statement that in a *chemical reaction* that yields one product (X) from one isomer (A')
and a different product (Y) from another 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 directly related
to the relative concentrations of the isomers in the *substrate*; it is controlled only by the
difference in standard Gibbs energies ($G^{\ddagger}_{A'} - G^{\ddagger}_{A''}$) of the respective *transition states*.

Note 1: The product composition is given by $[Y]/[X] = (k_Y k_1)/(k_{-1} k_X)$ or $K_c k_Y / k_X$, where
K_c is the equilibrium constant, $[A'']/[A']$, and where k_Y and k_X are the respective *rate
constant*s of their reactions; these parameters are usually unknown.

Note 2: The energy diagram below represents the transformation of rapidly
interconverting isomers A' and A" into products X and Y.

$$X \xleftarrow{\;k_X\;} A' \xrightleftharpoons[k_{-1}]{k_1} A'' \xrightarrow{\;k_Y\;} Y$$

$$k_1 \gg k_X \qquad\qquad k_{-1} \gg k_Y$$

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Note 3: A related concept is the Winstein-Holness equation for the overall rate of product formation in a system of rapidly interconverting isomers A' and A". The overall rate constant k is given by

$$k = x'k_X + x''k_Y$$

where x' and x'' are the respective mole fractions of the isomers at equilibrium [15]. However, since x' and x'' are simple functions of K_c, the apparent dependence of the overall rate on the relative concentrations of A' and A" disappears. The overall rate constant is the sum $k_X + K_c k_Y$, which is a function of the same quantities that determine the product ratio.

See [140]. See also [15,141,142].

rev~~GB~~[3]

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.

See [143,144].

~~GB~~[3]

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

See also *annulation*.

~~GB~~[3]

cycloaddition
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.

Note 1: The following two systems of notation have been used for the more detailed specification of cycloadditions, of which the second, more recent system (described under (2)) is preferred:

(1) An ($i+j+$...) cycloaddition is a reaction in which two or more molecules (or parts of the same molecule), respectively, provide units of i, j,... linearly connected atoms: these units become joined at their respective termini by new σ bonds so as to form a cycle containing ($i+j+$...) 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 of norbornadiene below is a (2+2+2)

55

cycloaddition. (Parentheses are used to indicate the numbers of atoms, but brackets are also used.)
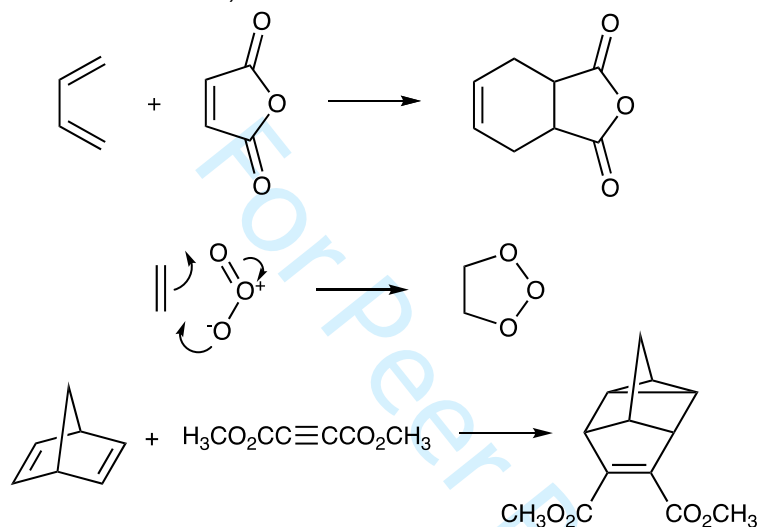
(2) The symbolism [*i*+*j*+...] for a cycloaddition identifies the numbers *i*, *j*,... of electrons in the interacting units that participate in the transformation of reactants to products. In this notation the reaction (a) and (b) of the preceding paragraph would both be described as [2+4] cycloadditions, 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 (with their usual significance) or n (for an orbital associated with a single atom), may be added as a subscript before the number. Thus the normal Diels-Alder reaction is a $[4_s+2_s]$ or $[_\pi 4_s + _\pi 2_s]$ cycloaddition, whilst the reaction

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1　would be a [14$_a$+2$_s$] or [$_\pi$14$_a$ + $_\pi$2$_s$] cycloaddition, leading to the stereoisomer shown,
2　with hydrogens *anti*. (Brackets are used to indicate the numbers of electrons, and
3　they are also used instead of parentheses to denote the numbers of atoms.)
4　　*Note 2*: Cycloadditions may be *pericyclic reaction*s or (non-*concerted*) *stepwise*
5　*reaction*s. The term "dipolar cycloaddition" is used for cycloadditions of 1,3-dipolar
6　compounds.
7　　See [107,145,146].
8　　See also *cheletropic reaction, ene reaction, pericyclic reaction*.
9　　rev~~GB~~[3]
10

11　**cycloelimination**
12　Reverse of *cycloaddition*. The term is preferred to the synonyms "cycloreversion",
13　"retro-addition", and "retrocycloaddition".
14　　~~GB~~[3]
15

16　**cycloreversion**
17　obsolete
18　　See *cycloelimination*.
19　　~~GB~~[3]
20

21　**dative bond**
22　obsolescent
23　*Coordination bond* formed between two chemical species, one of which serves as a
24　donor and the other as an acceptor of the electron pair that is shared in the bond.
25　　*Examples*: the N–B bond in H_3N^+–B^-H_3, the S–O bond in $(CH_3)_2S^+$–O^-.
26　　*Note 1*: A distinctive feature of dative bonds is that their minimum-energy rupture in
27　the gas phase or in inert solvent follows the heterolytic bond-cleavage path.
28　　*Note 2:* The term is obsolescent because the distinction between dative bonds and
29　ordinary covalent bonds is not useful, in that the precursors of the bond are irrelevant:
30　H_3N^+–B^-H_3 is the same molecule, with the same bonds, regardless of whether the
31　precursors are considered to have been $H_3N + BH_3$ or $H_3N^{\cdot+} + {}^-BH_3$.
32　　See [8].
33　　See *coordination*.
34　　rev[3]
35　　~~revGB~~
36

37　**degenerate chemical reaction**
38　　See *identity reaction*.
39　　~~GB~~[3]
40

57

degenerate rearrangement

Chemical reaction in which the product is indistinguishable (in the absence of isotopic labelling) from the reactant.

Note 1: The term includes both "degenerate *intramolecular* rearrangements" and reactions that involve *intermolecular* transfer of atoms or groups ("degenerate intermolecular reactions"): both are degenerate *isomerization*s.

Note 2: 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),

Note 3: Synonymous but less preferable terms are "automerization", "permutational isomerism", "isodynamic transformation", "topomerization".

See [147].

See also *fluxional*, *molecular rearrangement*, *narcissistic reaction*, *valence isomer*.

GB[3]

delocalization

Quantum-mechanical concept most usually applied in organic chemistry to describe the redistribution of π electrons in a *conjugated system*, where each link has a fractional double-bond character, or a non-integer *bond order*, rather than π electrons that are
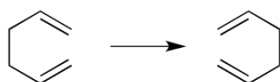
localized in double or triple bonds.

Note 1: There is a corresponding "delocalization energy", identifiable with the stabilization of the system relative to a hypothetical alternative in which formal (localized) single and double *bond*s 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).

Note 2: Delocalization in such species may be represented by partial bonds or by *resonance* (here symbolized by a two-headed arrow) between *resonance form*s.

58
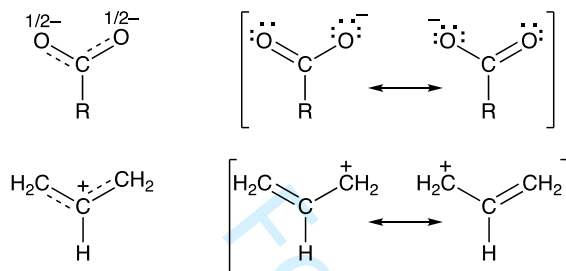
These examples also illustrate the concomitant delocalization of charge in ionic conjugated systems. Analogously, delocalization of the spin of an unpaired electron occurs in conjugated *radical*s.

Note 3: Delocalization is not limited to π electrons. *Hyperconjugation* is the delocalization of electrons of σ bonds.

~~GB~~[3]

dendrimer

Large molecule constructed from a central core with repetitive branching and multiple functional groups at the periphery.

See [148].

Example: (with 48 CH_2OH at the periphery)
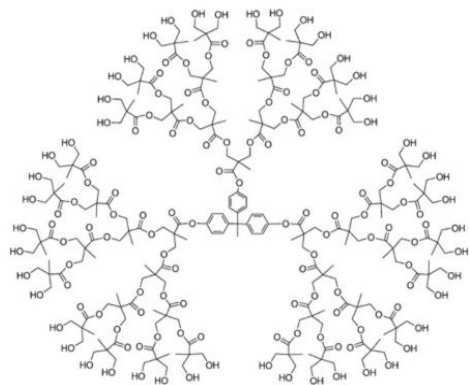
Note: The name comes from the Greek δενδρον (dendron), which translates to "tree". Synonymous terms include arborols and cascade molecules.

See [148,149,150,151,152].

deshielding

See *shielding*.

~~GB~~[3]

detachment

Reverse of *attachment*.

~~GB~~[3]

detailed balancing

Principle that 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 in a given finite time interval as will pass backward along each individual path.

Note 1: It then follows that the reaction path in the reverse direction must in every detail be the reverse of the reaction path in the forward direction (provided that the system is at equilibrium).

Note 2: The principle of detailed balancing is a consequence for macroscopic systems of the principle of *microscopic reversibility*.

~~GB~~[3]

diamagnetism

Property of substances having a negative magnetic susceptibility (χ), whereby they are repelled out of a magnetic field.

See also *paramagnetism*.

[3]

diastereoisomerism

Stereoisomerism other than *enantiomerism*.

See *diastereoisomers* [11].

~~GB~~[3]

diastereomeric excess (diastereoisomeric excess)

$x_1 - x_2$, where x_1 and x_2 (with $x_1 + x_2 = 1$) are the mole fractions of two *diastereoisomers* in a mixture, or the fractional yields of two *diastereoisomers* formed in a reaction.

Note: Frequently this term is abbreviated to d.e.

See *stereoselectivity*, *diastereoisomers*.

See [11].

diastereomeric ratio

60

1   x_1/x_2, where x_1 and x_2 are the mole fractions of two *diastereoisomers* in a mixture formed

2   in a reaction.

3   *Note:* Frequently this term is abbreviated to d.r.

4   See *stereoselectivity*, *diastereoisomers*.

5   See [11].

6

7   **diastereoisomers (diastereomers)**

8   Stereoisomers not related as mirror images of each other.

9   *Note*: Diastereoisomers are characterized by differences in physical properties, and

10 by differences in chemical behaviour toward chiral as well as achiral reagents.

11   See [11].

12

13 **diastereoselectivity**

14 Preferential formation in a chemical reaction of one *diastereoisomer* over another.

15   *Note*: This can be expressed quantitatively by the *diastereoisomeric excess* or by the

16 *diastereomeric ratio*, which is preferable because it is more closely related to a Gibbs-

17 energy difference.

18   See [11].

19   See *selectivity*.

20

21 **dielectric constant**

22 obsolete

23   See [12].

24   See *permittivity (relative)*.

25   revGB[3]

26

27 **dienophile**

28 Ene or yne component of a Diels-Alder reaction, including compounds with hetero-

29 double bonds and hetero-triple bonds.

30   See *cycloaddition*.

31   rev[3]

32   revGB-revPOC

33

34 **diffusion-controlled rate**

35 See *encounter-controlled rate*, *microscopic diffusion control*. Contrast *mixing control*.

36   GB[3]

37

38 **dimerization**

39 *Transformation* of a *molecular entity* A to give a molecular entity A_2.

40   *Examples*:

61

1    $2 CH_3 \cdot \rightarrow CH_3CH_3$
2    $2 CH_3COCH_3 \rightarrow (CH_3)_2C(OH)CH_2COCH_3$
3    $2 RCOOH \rightarrow (RCOOH)_2$
4   See also *association*.
5   ~~GB~~[3]
6

Dimroth-Reichardt E_T parameter

8   Quantitative measure of solvent polarity, based on the wavelength, λ_{max}, of the longest-
9   wavelength intramolecular charge-transfer absorption band of the *solvatochromic*
10   betaine dye 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-ium-1-yl)phenolate.

13   See [17,153,154,155].
14   See *solvent parameter*.
15   rev[3]
16   ~~revGB-revPOC~~
17

dipolar aprotic solvent

19   See *dipolar non-HBD solvent*.
20   rev[3]
21   ~~revGB-revPOC~~
22

dipolar non-HBD solvent (Non-hydrogen-bond donating solvent)

24   Solvent with a comparatively high relative *permittivity* ("dielectric constant"), greater
25   than ca. 15, and composed of molecules that have a sizable permanent dipole moment
26   and that, although it may contain hydrogen atoms, cannot donate suitably labile
27   hydrogen atoms to form strong solvent-solute hydrogen bonds.
28   *Examples*: dimethyl sulfoxide, acetonitrile, acetone, as contrasted with methanol and
29   *N*-methylformamide.
30   *Note 1*: The term "dipolar" refers to solvents whose molecules have a permanent
31   dipole moment, in contrast to solvents whose molecules have no permanent dipole
32   moment and should be termed "apolar" or "nonpolar".
33   *Note 2*: Non-HBD solvents are often called aprotic, but this term is misleading
34   because a proton can be removed by a sufficiently strong base. The aprotic nature of
35   a solvent molecule means that its hydrogens are in only covalent C–H bonds and not

62

1   in polar O–H$^{\delta+}$ or N–H$^{\delta+}$ bonds that can serve as hydrogen-bond donors. Use of
2   "aprotic" is therefore discouraged, unless the context makes the term unambiguous.
3   *Note 3*: It is recommended to classify solvents according to their capability to donate
4   or not donate, as well as to accept or not accept, hydrogen bonds to or from the solute,
5   as follows:
6   Hydrogen-bond donating solvents (short: HBD solvents), formerly protic solvents
7   Non-hydrogen-bond donating solvents (short: non-HBD solvents), formerly aprotic
8   solvents
9   Hydrogen-bond accepting solvents (short: HBA solvents)
10   Non-hydrogen-bond accepting solvents (short: non-HBA solvents)
11   See [156,157].
12

13 **dipole-dipole excitation transfer**
14   *Förster resonance-energy transfer (FRET)*
15   See [9].
16

17 **dipole-dipole interaction**
18 Intermolecular or intramolecular interaction between molecules or groups having a
19 permanent electric dipole moment. The strength of the interaction depends on the
20 distance and relative orientation of the dipoles.
21   *Note*: A dipole/dipole interaction is a simplification of the electrostatic interactions
22 between molecules that originate from asymmetries in the electron densities. Such
23 interactions can be described more correctly by the use of higher-order multipole
24 moments.
25   See also *van der Waals forces*.
26   rev[3]
27   revPOC
28

29 **dipole-induced dipole forces**
30   See *van der Waals forces*.
31   GB[3]
32

33 **diradical**
34 biradical
35 Even-electron *molecular entity* with two (possibly delocalized) radical centres that act
36 nearly independently of each other, e.g.,

63

Note 1: Species in which the two radical centres interact significantly are often referred to as "diradicaloids". If the two radical centres are located on the same atom, the species is more properly referred to by its generic name: carbene, nitrene, etc.

Note 2: The lowest-energy triplet state of a diradical 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). If the two radical centres interact significantly, the singlet state may be more stable. The states of those diradicals whose radical centres interact particularly weakly are most easily understood in terms of a pair of local doublets.

Note 3: Theoretical descriptions of low-energy states of diradicals display two unsaturated valences: the dominant valence-bond structures have two dots, the low-energy molecular orbital *configuration*s have only two electrons in two approximately nonbonding molecular orbitals, and two of the natural orbitals have occupancies close to one.

See [9,158,159,160,161,162,163].

See also *carbene*, *nitrene*.

GB[3]

dispersion forces

See *London forces*, *van der Waals forces*.

GB[3]

disproportionation

Any *chemical reaction* of the type A + A ⇋ A' + A", where A, A' and A" are different chemical species.

Examples:

2 $R_2COH\cdot$ (ketyl radical) → $R_2C=O$ + R_2CHOH

Cannizzaro reaction: 2 $ArCH=O$ → $ArCH_2OH$ + $ArCOOH$

Note 1: The reverse of disproportionation is called *comproportionation*.

Note 2: A special case of disproportionation (or "dismutation") is "radical disproportionation", exemplified by

$\cdot CH_2CH_3$ + $\cdot CH_2CH_3$ → $CH_2=CH_2$ + CH_3CH_3
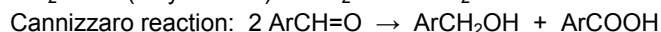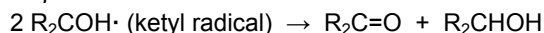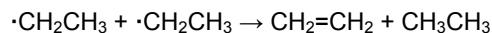
Note 3: A somewhat more restricted usage of the term prevails in inorganic chemistry, where A, A' and A" are of different oxidation states.

GB[3]

64

disrotatory
Stereochemical feature of an *electrocyclic reaction* in which the substituents at the interacting termini of the conjugated system rotate in opposite senses (one clockwise and the other counterclockwise).
　　See also *conrotatory*.
　　rev[3]
　　revGB-revPOC

dissociation
Separation of a *molecular entity* into two or more molecular entities (or any similar separation within a polyatomic molecular entity).
　　Example:
　　　$NH_4^+{}_{(aq)} \rightarrow H_3O^+ + NH_3$ or $CH_3COOH_{(aq)} \rightarrow H_3O^+ + CH_3CO_2^-$
　　Note 1: Although the separation of the constituents of an *ion pair* into free ions is a dissociation, the *ionization* that produces the ion pair is not a dissociation, because the ion pair is a single *molecular entity*.
　　Note 2: The reverse of dissociation is *association*.
　　rev[3]
　　revGB-revPOC

distonic ion
Radical ion in which charge and radical sites are separated.
　　Example: $\cdot CH_2CH_2OCH_2^+$
　　See [164,165].
　　rev[3]
　　revGB-revPOC

distortion interaction model (Activation Strain Model)
Method for analyzing activation energy as the sum of the energies to distort the reactants into the geometries they have in transition states plus the energy of interaction between the two distorted reactants.
　　See [166].

distribution ratio
partition ratio
Ratio of concentrations of a solute in a mixture of two immiscible phases at equilibrium.
　　See also *Hansch constant*.
　　See [167].

di-π-methane rearrangement

65

Photochemical reaction of a molecular entity with two π-systems separated by a saturated carbon, to form an ene-substituted cyclopropane.

Pattern:
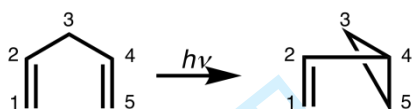
See [9,168].

donicity (also called donor number, DN, which is a misnomer)
Quantitative experimental measure of the Lewis basicity of a molecule B, expressed as the negative enthalpy of the formation of the 1:1 complex B·SbCl$_5$.
Note: donicity is often used as a measure of a solvent's basicity.
See also *acceptor parameter, Lewis basicity*.
See [63,169,170].

downfield
superseded but still widely used in NMR to mean deshielded.
See *chemical shift*, *shielding*.
rev[3]
revGB

driving force
(1) Negative of the Gibbs energy change ($\Delta_r G^0$) on going from the reactants to the products of a *chemical reaction* under standard conditions. Also called affinity.
(2) Qualitative term that relates the favorable thermodynamics of a reaction to a specific feature of molecular structure, such as the conversion of weaker bonds into stronger (CH$_3$–H + Br–Br → CH$_3$–Br + H–Br), neutralization of an acid (Claisen *condensation* of 2 CH$_3$COOEt + EtO$^-$ to CH$_3$COCH$^-$COOEt + EtOH), or increase of entropy (*cycloelimination* of cyclohexene to butadiene + ethylene).
Note 1: This term is a misnomer, because favorable thermodynamics is due to energy, not force.
Note 2: This term has also been used in connection with photoinduced electron transfer reactions, to indicate the negative of the estimated standard Gibbs energy change for the outer sphere electron transfer ($\Delta_{ET}G^0$) [9].
rev[3]
GB

dual substituent-parameter equation
Any equation that expresses substituent effects in terms of two parameters.

66

1   *Note*: In practice the term is used specifically for an equation for modeling the effects
2   of *meta*- and *para*-substituents X on chemical reactivity, spectroscopic properties, etc.
3   of a probe site in benzene or other aromatic system.
4        $P_X = \rho_I\,\sigma_I + \rho_R\,\sigma_R$
5   where P_X is the magnitude of the property for substituent X, expressed relative to the
6   property for X = H; σ_I and σ_R are inductive (or polar) and resonance substituent
7   constants, respectively, there being various scales for σ_R; ρ_I and ρ_R are the
8   corresponding regression coefficients.
9   See [171,172,173].
10   See also *extended Hammett equation, Yukawa-Tsuno equation*.
11   ~~GB~~[3]
12

13   **dynamic NMR**
14   NMR spectroscopy of samples undergoing chemical reactions.
15   *Note*: Customarily this does not apply to samples where the composition of the
16   sample, and thus its NMR spectrum, changes with time, but rather to samples at
17   equilibrium, without any net reaction. The occurrence of chemical reactions is
18   manifested by features of the NMR line-shape or by *magnetization transfer*.
19   See *chemical flux*.
20

21   **dyotropic rearrangement**
22   Process in which two σ bonds simultaneously migrate intramolecularly.
23   *Example*

24
25   See [174,175,176].
26   rev[3]
27   ~~revPOC~~
28

29   **educt**
30   deprecated: usage strongly discouraged
31   starting material, reactant
32   *Note*: This term should be avoided and replaced by reactant, because it means
33   "something that comes out", not "something that goes in".
34   rev~~GB~~[3]
35

36   **effective charge**, Z_{eff}

67

Net positive charge experienced by an electron in a polyelectronic atom, which is less than the full nuclear charge because of *shielding* by the other electrons.

~~rev~~[3]

~~revGB-revPOC~~

effective molarity (effective concentration)

Ratio of the first-order rate constant or equilibrium constant of an *intramolecular* reaction involving two functional groups within the same *molecular entity* to the second-order *rate constant* or equilibrium constant of an analogous *intermolecular* elementary reaction.

Note: This ratio has unit of concentration, mol dm^{-3} or mol L^{-1}, sometimes denoted by M.

See [177].

See also *intramolecular catalysis*.

~~GB~~[3]

eighteen-electron rule

Electron-counting rule that the number of nonbonding electrons at a metal plus the number of electrons in the metal-*ligand* bonds should be 18.

Note: The 18-electron rule in transition-metal chemistry is an analogue of the Lewis *octet rule*.

[3]

~~revGB-revPOC~~

electrocyclic reaction (electrocyclization)

Molecular rearrangement that involves the formation of a σ bond between the termini of a fully *conjugated* linear π-electron system (or a linear fragment of a π-electron system) and a decrease by one in the number of π bonds, or the reverse of that process.

Examples:
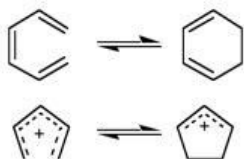
Note: The stereochemistry of such a process is termed "*conrotatory*" if the substituents at the interacting termini of the conjugated system both rotate in the same sense, as in

68
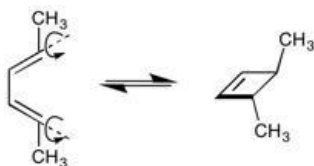
or "*disrotatory*" if one terminus rotates in a clockwise and the other in a counterclockwise sense, as in
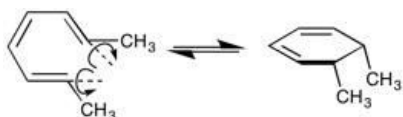
See also *pericyclic reaction*.
 [3]
revGB-revPOC

electrofuge
Leaving group that does not carry away the bonding electron pair.
   Examples: In the nitration of benzene by NO_2^+, H^+ is the electrofuge, and in an S_N1 reaction the carbocation is the electrofuge.
   Note 1: Electrofugality characterizes the relative rates of atoms or groups to depart without the bonding electron pair. Electrofugality depends on the nature of the reference reaction and is not the reverse of *electrophilicity* [178].
   Note 2: For electrofuges in S_N1 reactions see [179].
   See also *electrophile*, *nucleofuge*.
rev[3]
revGB-revPOC

electromeric effect
obsolete
rev[3]
revGB-revPOC

electron acceptor
Molecular entity to which an electron may be transferred.
   Examples: 1,4-dinitrobenzene,1,1'-dimethyl-4,4'-bipyridinium dication, benzophenone.
   Note 1: A group that accepts electron density from another group is not called an electron acceptor but an electron-withdrawing group.
   Note 2: A *Lewis acid* is not called an electron acceptor but an *electron-pair acceptor*.
revGB[3]

electron affinity
Energy released when an additional electron (without excess energy) attaches itself to a *molecular entity* (often electrically neutral but not necessarily).

69

Note 1: Equivalent to the minimum energy required to detach an electron from a singly charged negative ion.

Note 2: Measurement of electron affinities is possible only in the gas phase, but there are indirect methods for evaluating them from solution data, such as polarographic half-wave potentials or charge-transfer spectra.

See [8,180,181].
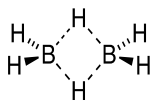
rev[3]

revGB

electron capture

Transfer of an electron to a *molecular entity*, resulting in a molecular entity of (algebraically) increased negative charge.

revGB

electron-deficient bond

Bond between adjacent atoms that is formed by fewer than two electrons.

Example:

Note: The B–H–B bonds are also called "two-electron three-centre bonds".

GB[3]

electron density

The electron density at a point with coordinates x,y,z in an atom or *molecular entity* is the product of the probability $P(x,y,z)$ (units: m^{-3}) of finding an electron at that point with the volume element $dx\ dy\ dz$ (units: m^3).

Note: For many purposes (e.g., X-ray scattering, forces on atoms) the system behaves as if the electrons were spread out into a continuous distribution, which is a manifestation of the wave-particle duality.

See also *atomic charge*, *charge density*.

rev[3]

electron donor

Molecular entity that can transfer an electron to another molecular entity, or to the corresponding *chemical species*.

Note 1: After the electron transfer the two entities may separate or remain associated.

70

Note 2: A group that donates electron density to another group is an electron-donating group, regardless of whether the donation is of σ or π electrons.

Note 3: A *Lewis base* is not called an electron donor, but an *electron-pair donor*.

See also *electron acceptor*.

rev[3]

~~revGB-revPOC~~

electron-donor-acceptor complex

obsolete

charge-transfer complex.

See also *adduct*, *coordination*.

electron-pair acceptor

Lewis acid.

~~GB~~[3]

electron-pair donor

Lewis base.

~~GB~~[3]

electron pushing

Method using *curly arrows* for showing the formal movement of an electron pair (from a lone pair or a σ or π bond) or of an unpaired electron, in order to generate additional *resonance form*s or to denote a *chemical reaction*.

Note 1: The electron movement may be *intramolecular* or *intermolecular*.

Note 2: When a single electron is transferred, a single-headed curly arrow or "fish-hook" is used, but the electron movement in the opposite direction is redundant and sometimes omitted.

Examples:

electron transfer

Transfer of an electron from one *molecular entity* to another, or between two localized sites in the same molecular entity.

71

1   See also *inner sphere (electron transfer)*, *Marcus equation*, *outer sphere (electron*
2   *transfer)*.
3   ~~GB~~[3]
4

5   **electron-transfer catalysis**
6   Process describing a sequence of reactions such as shown in equations (1)-(3), leading
7   from A to B, via species $A^{\cdot-}$ and $B^{\cdot-}$ that have an extra electron:
8         $A + e^- \rightarrow A^{\cdot-}$ (1)
9         $A^{\cdot-} \rightarrow B^{\cdot-}$ (2)
10        $B^{\cdot-} + A \rightarrow B + A^{\cdot-}$ (3)
11   *Note 1*: An analogous sequence involving radical cations ($A^{\cdot+}$, $B^{\cdot+}$) also occurs.
12   *Note 2*: The most notable example of electron-transfer catalysis is the $S_{RN}1$ (or
13    $T+D_N+A_N$) reaction of haloarenes with nucleophiles.
14   *Note 3*: The term has its origin in an analogy to acid-base catalysis, with the electron
15   instead of the proton. However, there is a difference between the two catalytic
16   mechanisms, since the electron is not a true catalyst, but rather behaves as the initiator
17   of a *chain reaction*. "Electron-transfer induced chain reaction" is a more appropriate
18   term for the mechanism described by equations (1)-(3).
19   See [182,183].
20   ~~GB~~[3]
21

22   **electronation**
23   obsolete
24   See *reduction*.
25   rev[3]
26   ~~revPOC~~
27

28   **electronegativity**
29   Measure of the power of an atom to attract electrons to itself.
30   *Note 1*: The concept has been quantified by a number of authors. The first, due to
31   Pauling, is based on *bond-dissociation energies*, E_d (units: eV), and is anchored by
32   assigning the electronegativity of hydrogen as $\chi_{r,H}$ = 2.1. For atoms A and B
33

34        $$\chi_{r,A} - \chi_{r,B} = \text{~~(eV)~~}^{\text{~~-1/2~~}}\sqrt{\{E_d(A–B)/eV − \tfrac{1}{2}\,[E_d(A–A) + E_d(B–B)]/eV\}}$$

35

36   where χ_r denotes the Pauling relative electronegativity; it is relative in the senses that
37   the values are ~~of dimensionless~~ dimension 1 and that only electronegativity differences
38   are defined on this empirical scale. See [12] section 2.5.

72

Note 2: Alternatively, the electronegativity of an element, according to the Mulliken scale, is the average of its atomic *ionization* energy and electron affinity. Other scales have been developed by Allred and Rochow, by Sanderson, and by Allen.

Note 3: Absolute electronegativity is property derived from density functional theory [8].

See [75,184,185,186,187,188,189,190].

rev[3]

revGB

electronic effects (of substituents)

Changes exerted by a substituent on a molecular property or molecular reactivity, often distinguished as *inductive* (through-bond polarization), through-space electrostatics (*field effect*), or *resonance*, but excluding *steric*.

Note 1: The obsolete terms mesomeric and electromeric are discouraged.

Note 2: Quantitative scales of substituent effects are available.

See [126,173,191].

See also *polar effect*.

rev[3]

revGB-revPOC

electrophile (n.), electrophilic (adj.)

Reagent that forms a *bond* to its reaction partner (the *nucleophile*) by accepting both bonding electrons from that partner.

Note 1: Electrophilic reagents are *Lewis acid*s.

Note 2: "Electrophilic catalysis" is catalysis by Lewis acids.

Note 3: The term "electrophilic" is also used to designate the apparent polar character of certain *radical*s, as inferred from their higher relative reactivities with reaction sites of higher electron density.

See also *electrophilicity*.

GB[3]

electrophilic substitution

Heterolytic reaction in which the entering group adds to a nucleophile and in which the leaving group, or *electrofuge*, relinquishes both electrons to its reaction partner, whereupon it becomes another potential electrophile.

Example (azo coupling)*:*

RN_2^+ (electrophile) + $H_2NC_6H_5$ (nucleophile) → p-$H_2NC_6H_4N$=NR + H^+ (electrofuge)

Note: It is arbitrary to emphasize the electrophile and ignore the feature that this is also a nucleophilic substitution, but the distinction depends on the electrophilic nature of the reactant that is considered to react with the *substrate*.

73

1   See also *substitution*.

2

3 **electrophilicity**

4 Relative reactivity of an electrophile toward a common *nucleophile*.

5   *Note*: The concept is related to *Lewis acid*ity. However, whereas Lewis acidity is

6 measured by relative equilibrium constants toward a common Lewis base,

7 electrophilicity is measured by relative *rate constant*s for reactions of different

8 electrophilic reagents towards a common nucleophilic *substrate*.

9   See [192,193,194].

10   See also *nucleophilicity*.

11 rev[3]

12 revGB-revPOC

13

14 **element effect**

15 Ratio of the *rate constant*s of two reactions that differ only in the identity of the element

16 in the *leaving group*.

17   *Example:* k_{Br}/k_{Cl} for the reaction of N_3^- (azide) with CH_3Br or CH_3Cl.

18 rev[3]

19 revGB

20

21 **elementary reaction**

22   Reaction for which no reaction intermediates have been detected or need to be

23 postulated in order to describe the chemical reaction on a molecular scale. An

24 elementary reaction is assumed to occur in a single step and to pass through only one

25 *transition state* or none.

26   See [13].

27   See also *composite reaction, stepwise reaction*.

28 revGB[3]

29

30 **elimination**

31 Reverse of an *addition reaction*.

32   *Note 1*: In an elimination two groups (called eliminands) are lost, most often from two

33 different centres (1,2-elimination (*β-elimination*) or 1,3-elimination, etc.) with

34 concomitant formation of an unsaturation (double bond, triple bond) in the molecule, or

35 formation of a ring.

36   *Note 2*: If the groups are lost from a single carbon or nitrogen centre (1,1-elimination,

37 *α-elimination*), the resulting product is a *carbene* or *nitrene*, respectively.

38 revGB[3]

39

40 **empirical formula**

74

1 List of the elements in a *chemical species*, with integer subscripts indicating the simplest
2 possible ratios of all elements.
3   *Note 1:* In organic chemistry C and H are listed first, then the other elements in
4 alphabetical order.
5   *Note 2:* This differs from the *molecular formula*, in which the subscripts indicate how
6 many of each element is included and which is an integer multiple of the empirical
7 formula. For example, the empirical formula of glucose is CH_2O while its molecular
8 formula is $C_6H_{12}O_6$.
9   *Note 3:* The empirical formula is the information provided by combustion analysis,
10 which has been largely superseded by mass spectrometry, which provides the
11 *molecular formula*.

12
13

14 **enantiomer**
15 One of a pair of stereoisomeric *molecular entities* that are non-superimposable mirror
16 images of each other.
17   See [11].
18   ~~GB~~[3]
19

20 **enantiomeric excess**
21 Absolute value of the difference between the mole fractions of two enantiomers:

23   $\underline{\Delta x}(\text{e.e.}) = |x_+ - x_-|$

24
25 where $x_+ + x_- = 1$.
26   *Note*: Enantiomeric excess can be evaluated experimentally from the observed
27 specific optical rotatory power $[\alpha]_{obs}$, relative to $[\alpha]_{max}$, the (maximum) specific optical
28 rotatory power of a pure enantiomer:

29
30 $\underline{\Delta x(\text{e.e.})}$
31   ~~e.e.~~ $= |[\alpha]_{obs}/[\alpha]_{max}|$

32
33 and also by chiral chromatography, NMR, and MS methods.
34   See [11].
35   rev[3]
36   ~~GB~~
37

38 **enantiomeric ratio**
39 mole fraction of one *enantiomer* in a mixture divided by the mole fraction of the other.
40

75

1   r(e.r.) = x_+/x_- or x_-/x_+

3 where $x_+ + x_- = 1$

4   See [11].

5   rev[3]

6   GB

enantioselectivity

    See *stereoselectivity*.

    GB[3]

encounter complex

Complex of *molecular entities* produced at an *encounter-controlled rate*, and which occurs as an intermediate in a reaction.

    Note 1: 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 for mechanisms involving *pre-association*.

    Note 2: The separation between the entities is small compared to the diameter of a solvent molecule.

    See also [9].

    rev[3]

    revGB-revPOC

encounter-controlled rate

Rate of reaction corresponding to the rate at which the reacting *molecular entities* encounter each other. This is also known as the "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 reacting molecular entities).

    Note: At 25 °C in most solvents, including water, a *bimolecular* reaction that proceeds at an encounter-controlled rate has a second-order *rate constant* of 10^9 to 10^{10} dm^3 mol^{-1} s^{-1}.

    See also *microscopic diffusion control*.

    GB[3]

ene reaction

Addition of a compound with a double bond and 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.

    Example, with propene as the ene and ethene as the enophile.
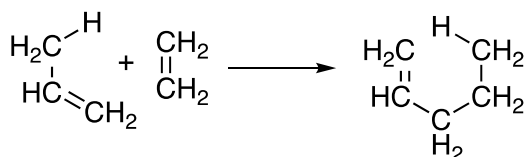
76

1　　*Note*: The reverse is a "retro-ene" reaction.

3　　~~GB~~[3]

5　　**energy of activation**

6　　E_a or E_A

7　　*Arrhenius energy of activation*

8　　activation energy

9　　(SI unit: kJ mol^{-1})

10　Operationally defined quantity expressing the dependence of a *rate constant* on

11　temperature according to

$$E_a(T) = -R\frac{\mathrm{d}\ln\{\frac{k(T)}{[k]}\}}{\mathrm{d}\left(\frac{1}{T}\right)}$$

15　as derived from the *Arrhenius equation*, $k(T) = A\exp(-E_A/RT)$, where A is the pre-

16　exponential factor and R the gas constant. As the argument of the ln function, k should

17　be divided by its units, i.e., by $[k]$.

18　　*Note 1:* According to collision theory, the pre-exponential factor A is the frequency of

19　collisions with the correct orientation for reaction and E_a (or E_0) is the threshold energy

20　that collisions must have for the reaction to occur.

21　　*Note 2:* The term Arrhenius activation energy is to be used only for the empirical

22　quantity as defined above. There are other empirical equations with different activation

23　energies, see [12].

24　　See [13].

25　　See also *enthalpy of activation*.

26　　rev[3]

27　　~~revGB~~

29　　**energy profile**

30　　See *Gibbs energy diagram*, *potential-energy profile*.

31　　~~GB~~[3]

33　　**enforced concerted mechanism**

34　Situation where a putative intermediate possesses a lifetime shorter than a bond

35　vibration, so that the steps become concerted.

36　　See [195,196,197].

37　　rev[3]

38　　~~revGB~~

77

1

enthalpy of activation (standard enthalpy of activation)

$\Delta^{\ddagger}H^{o}$

(SI unit: kJ mol^{-1})

Standard enthalpy difference between the *transition state* and the ground state of the reactants at the same temperature and pressure. It is related experimentally to the temperature dependence of the *rate coefficient k* according to equation (1) for first-order *rate constant*s:

$$\Delta^{\ddagger}H^{o} = -R \left\{ \frac{\partial \ln\left(\dfrac{k/_{\mathrm{s}^{-1}}}{T/\mathrm{K}}\right)}{\partial\left(\dfrac{1}{T}\right)} \right\}_{P} \tag{1}$$

and to equation (2) for second order rate coefficients

$$\Delta^{\ddagger}H^{o} = -R \left\{ \frac{\partial \ln\left(\dfrac{k/(\mathrm{mol\ dm}^3\ \mathrm{s}^{-1})}{T/\mathrm{K}}\right)}{\partial\left(\dfrac{1}{T}\right)} \right\}_{P} \tag{2}$$

This quantity can be obtained, along with the *entropy of activation* $\Delta^{\ddagger}S^{o}$, from the slope and intercept of the linear least-squares fit of rate coefficients k to the equation

$$\ln\left(\frac{k/_{\mathrm{s}^{-1}}}{T/\mathrm{K}}\right) = \Delta^{\ddagger}S^{o}/R - \Delta^{\ddagger}H^{o}/RT + \ln[\ (k_{\mathrm{B}}/\mathrm{J\ K}^{-1})/(h/\mathrm{J\ s})\ ]$$

for a first-order rate coefficient
and

$$\ln\left(\frac{k/(\mathrm{mol\ dm}^3\ \mathrm{s}^{-1})}{T/\mathrm{K}}\right) = \Delta^{\ddagger}S^{o}/R - \Delta^{\ddagger}H^{o}/R\ (1/T) + \ln[\ (k_{\mathrm{B}}/\mathrm{J\ K}^{-1})/(h/\mathrm{J\ s})\ ]$$

78

for a second-order rate coefficient where k_B is Boltzmann constant, h is Planck constant, and $k_B/h = 2.08366\ldots \times 10^{10}$ K^{-1} s^{-1}.

Note 1: An advantage of the least-squares fit is that it can also give error estimates for $\Delta^{\ddagger}H^{\circ}$ and $\Delta^{\ddagger}S^{\circ}$.

Note 2: It is also given by

$$\Delta^{\ddagger}H^{\circ} = RT^2(\partial \ln k/[k]/\partial T)_P - RT = E_a - RT$$

$$\Delta^{\ddagger}H^{\circ} = RT^2(\partial \ln\{k\}/\partial T)_P - RT$$

where E_a is the *energy of activation*, provided that the *rate coefficient*s for reactions other than first-order are expressed in temperature-independent concentration units (e.g., mol kg^{-1}, measured at a fixed temperature and pressure). The argument in a logarithmic function should be of dimension 1. Thus k is divided by its units, i.e., by [k], as in the alternative form, in terms of reduced variables.

See also *entropy of activation*, *Gibbs energy of activation*.

See [12,13].

rev[3]

~~revGB~~

entropy of activation, **(standard entropy of activation)**

$\Delta^{\ddagger}S^{\circ}$

(SI unit: J mol^{-1} K^{-1})

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

$$\Delta^{\ddagger}S^{\circ} = (\Delta^{\ddagger}H^{\circ} - \Delta^{\ddagger}G^{\circ})/T$$

provided that *rate coefficient*s for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3}, measured at fixed temperature and pressure). The numerical value of S depends on the standard state (and therefore on the concentration units selected).

Note 1: It can also be obtained from the intercept of the linear least-squares fit of rate coefficients k to the equation

$$\ln(k/[k]/T[T]) = \Delta^{\ddagger}S^{\circ}/R - \Delta^{\ddagger}H^{\circ}/R \,(1/T) + \ln(k_B/h),$$

$$\ln(\{k\}/\{T\}) = \Delta^{\ddagger}S^{\circ}/R - \Delta^{\ddagger}H^{\circ}/R \,(1/T) + \ln(k_B/h),$$

79

where $k_B/h = 2.08366… \times 10^{10}$ K^{-1} s^{-1}. k should be divided by its units, i.e., by $[k] = $ s^{-1} for first-order, and by $[k] = $ (s^{-1} mol^{-1} dm^3) for second-order rate coefficients and T should be divided by its units $[T] = $ K, as in the second equation, in terms of reduced variables.

Note 2: The information represented by the entropy of activation may alternatively be conveyed by the pre-exponential factor A, which reflects the fraction of collisions with the correct orientation for reaction (see *energy of activation*).

See [12,13].

rev[3]

revGB

epimer

Diastereoisomer that has the opposite *configuration* at only one of two or more tetrahedral *stereogenic centre*s in the respective *molecular entity*.

See [11].

GB[3]

epimerization

Interconversion of *epimer*s by reversal of the configuration at one of the *stereogenic centre*s.

See [11].

GB[3]

equilibrium, chemical

Situation in which reversible processes (processes that may be made to proceed in either the forward or reverse direction by the infinitesimal change of one variable) have reached a point where the rates in both directions are identical, so that the amount of each species no longer changes.

Note 1: In this situation the Gibbs energy, G, is a minimum. Also, the sum of the chemical potentials of the reactants equals that of the products, so that

$$\Delta_r G^o = -RT \ln K$$

where the thermodynamic equilibrium constant, K (of dimension 1), is the product of product activities divided by the product of reactant activities.

Note 2: In dilute solutions the numerical values of the thermodynamic activities may be approximated by the respective concentrations.

rev[3]

equilibrium control

See *thermodynamic control*.

GB[3]

80

E_T-value
See *Dimroth-Reichardt E_T parameter*, *Z-value*.
    ~~GB~~[3]

excess acidity
See *Bunnett-Olsen equations*, *Cox-Yates equation*.
    ~~GB~~[3]

excimer ("excited dimer")
Complex formed by the interaction of an *excited* molecular entity with another identical molecular entity in its ground state.
    Note: The complex is not stable in the ground state.
    See [9].
    See also *exciplex*.
    [3]

exciplex
Electronically excited *complex* of definite stoichiometry that is non-bonding in the ground state.
    Note: An exciplex is a complex formed by the noncovalent interaction of an excited *molecular entity* with the ground state of a different molecular entity, but an *excimer*, formed from two identical components, is often also considered to be an exciplex.
    See [9].
    See also *excimer*.
    ~~GB~~[3]

excited state
Condition of a system with energy higher than that of the ground state. This term is most commonly used to characterize a *molecular entity* in one of its electronically excited states, but may also refer to vibrational and/or rotational excitation in the electronic ground state.
    See [9].
    ~~GB~~[3]

EXSY (NMR exchange spectroscopy)
Two-dimensional NMR technique producing cross peaks corresponding to site-to site chemical exchange. The cross-peak amplitudes carry information about exchange rates.
    See [198].

81

extended Hammett equation
Multiparameter extension of the *Hammett equation* for the description of substituent effects.

Note 1: The major extensions using two parameters (*dual substituent-parameter equation*s) were devised for the separation of inductive and steric effects (*Taft equation*) or of inductive (or field) and resonance effects.

Note 2: Other parameters may be added (polarizability, hydrophobicity…) when additional substituent effects are operative.

See [191].

See also *Yukawa-Tsuno equation*.

[3]

revGB-revPOC

external return (external ion-pair recombination)
Recombination of free ions formed in an S_N1 reaction (as distinguished from ion-pair collapse).

See *ion-pair recombination*.

rev[3]

revGB-revPOC

extrusion
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, i.e.,

X–Y–Z → X–Z + Y

Example

Note 1: When Y is a metal, this process is called a reductive elimination.

Note 2: The reverse of an extrusion is called an *insertion*.

See also *cheletropic reaction*.

GB[3]

field effect

82

1   Experimentally observable substituent effect (on reaction rates, etc.) of *intramolecular*
2   electrostatic interaction between the centre of interest and a monopole or dipole, by
3   direct electric-field action through space rather than through bonds.
4   *Note 1*: The magnitude of the field effect depends on the monopole charge or dipole
5   moment, on the orientation of the dipole, on the distance between the centre of interest
6   and the monopole or dipole, and on the effective dielectric constant that reflects how
7   the intervening bonds are polarized.
8   *Note 2*: Although a theoretical distinction may be made between the field effect and
9   the *inductive effect* as models for the Coulomb interaction between a given site and a
10   remote monopole or dipole within the same entity, the experimental distinction between
11   the two effects has proved difficult, because the field effect and the inductive effect are
12   ordinarily influenced in the same direction by structural changes.
13   *Note 3:* The substituent acts through the electric field that it generates, and it is an
14   oversimplification to reduce that interaction to that of a monopole or dipole.
15   See also *electronic effect*, *inductive effect*, *polar effect*.
16   See [172,191,199,200].
17   rev[3]
18

19   **flash photolysis**
20   *Spectroscopic* or kinetic technique in which an *ultraviolet*, *visible*, or *infrared* radiation
21   pulse is used to produce transient species.
22   *Note 1*: Commonly, an intense pulse of short duration is used to produce a sufficient
23   concentration of transient species, suitable for spectroscopic observation. The most
24   common observation is of the absorption of the transient species (transient absorption
25   spectroscopy).
26   *Note 2*: If only photophysical processes are involved, a more appropriate term would
27   be "pulsed photoactivation". The term "flash photolysis" would be correct only if
28   chemical bonds are broken (the Greek "lysis" means dissolution or decomposition and
29   in general lysis is used to indicate breaking). However, historically, the name has been
30   used to describe the technique of pulsed excitation, independently of the process that
31   follows the excitation.
32   See [9].
33

34   **flash vacuum pyrolysis (FVP)**
35   Thermal reaction of a molecule by exposure to a short thermal shock at high
36   temperature, usually in the gas phase.
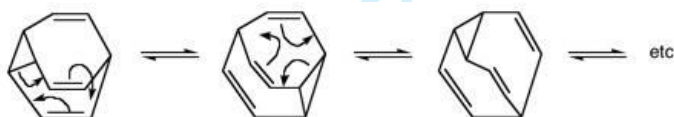37   *Example:*

83

1   See [201,202,203,204].
2   rev[3]
3   ~~revGB-revPOC~~
4

5   **fluxionality**
6   Property of a *chemical species* that undergoes rapid *degenerate rearrangement*s
7   (generally detectable by methods that allow the observation of the behaviour of
8   individual nuclei in a rearranged chemical species, e.g., NMR, X-ray).
9   *Example*: tricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (bullvalene), which has 1 209 600 (=
10   10!/3) interconvertible arrangements of the ten CH groups.
11

12
13   *Note 1*: Fluxionality differs from *resonance*, where no rearrangement of nuclear
14   positions occurs.
15   *Note 2*: The term is also used to designate positional change among *ligand*s of
16   complex compounds and organometallics. In these cases the change is not necessarily
17   degenerate.
18   See also *valence tautomerization*.
19   rev~~GB~~[3]
20

21   **force-field calculations**
22   See *molecular mechanics calculation*.
23   GB
24

25   **formal charge**
26   Quantity (omitted if zero) attached to each atom in a *Lewis structure* according to
27

28        $Z_{formal} = N_{valence} - N_{lonepairs} - \frac{1}{2} N_{bonds}$

29

30   *Examples*: $CH_2=N^+=N^-$, H_3O^+, $(CH_3)_2C=N\text{-}O^-$

31

32   *Note:* This formalism assumes that electrons in bonds are shared equally, regardless
33   of *electronegativity*.
34

35   **Förster resonance-energy transfer (FRET)**
36   dipole-dipole excitation transfer

84

1   Nonradiative mechanism for transfer of electronic excitation energy from one molecular
2   entity to another, distant one. It arises from the interaction between the *transition dipole*
3   *moment*s of the two entities.
4   See [9].
5
6   **fractionation factor, isotopic**
7   Ratio $[x_1(A)/x_2(A)]/[x_1(B)/x_2(B)]$, where x is the mole fraction of the isotope designated
8   by the subscript, when the two isotopes are equilibrated between two different *chemical*
9   *species* A and B (or between specific sites A and B in the same chemical species).
10   *Note 1*: The term is most commonly met in connection with deuterium solvent *isotope*
11   *effect*s, where the fractionation factor, symbolized by ϕ, expresses the ratio
12       $\phi = [x_D(\text{solute})/x_H(\text{solute})]/[x_D(\text{solvent})/x_H(\text{solvent})]$
13   for the exchangeable hydrogen atoms in the chemical species (or sites) concerned.
14   *Note 2*: The concept is also applicable to *transition states*.
15   See [2].
16   [3]
17
18   **fragmentation**
19   (1) *Heterolytic* or *homolytic* cleavage of a molecule into more than two fragments,
20   according to the general reaction (where a, b, c, d, and X are atoms or groups of atoms)
21
22   a–b–c–d–X $\rightarrow$ (a–b)$^+$ + c=d + X$^-$
23   or   a–b–c–d–X $\rightarrow$ (a–b)· + c=d + X
24   *Examples*:
25   Ph_3C–COOH + H$^+$ $\rightarrow$ Ph_3C^+ + C=O + H_2O
26   CH_3N=NCH_3 $\rightarrow$ CH_3· + N_2 + CH_3
27   See [205].
28
29   (2) Breakdown of a radical or radical ion into a closed-shell molecule or ion and a
30   smaller radical
31   *Examples*:
32       $(CH_3)_3C$–O· $\rightarrow$ $(CH_3)_2C$=O + H_3C·
33   [ArBr]·– $\rightarrow$ Ar· + Br$^-$ (solution)
34       $[(CH_3)_3C$–OH]·$^+$ $\rightarrow$ $(CH_3)_2C$=OH$^+$ + H_3C· (gas-phase, following *ionization*)
35   [3]
36   revGB-revPOC
37
38   **Franck-Condon Principle**
39   Approximation that an electronic transition is most likely to occur without change in
40   nuclear positions.

85

Note 1: The resulting state is called a Franck–Condon state, and the transition involved is called a vertical transition.

Note 2: As a consequence, the intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transition.

See [9].

GB

free energy

The thermodynamic function Gibbs energy (symbol *G*) or Helmholtz energy (symbol *A*) specifically defined as

$$G = G(P,T) = H - TS$$
$$\text{and} \quad A = A(V,T) = U - TS$$

where *H* is enthalpy, *U* is internal energy, and *S* is entropy. The possibility of spontaneous motion for a statistical distribution of an assembly of atoms (at absolute temperature *T* above 0 K) is governed by free energy and not by potential energy.

Note 1: The IUPAC recommendation is to use the specific terms Gibbs energy or Helmholtz energy whenever possible. However, it is useful to retain the generic term "free energy" for use in contexts where the distinction between (on the one hand) either Gibbs energy or Helmholtz energy and (on the other hand) potential energy is more important than the distinction between conditions either of constant pressure or of constant volume; e.g., in computational modelling to distinguish between results of simulations performed for ensembles under conditions of either constant *P* or constant *V* at finite *T* and calculations based purely on potential energy.

Note 2: Whereas motion of a single *molecular entity* is determined by the force acting upon it, which is obtained as the negative gradient of the potential energy, motion for an assembly of many molecular entities is determined by the mean force acting upon the statistical distribution, which is obtained as the negative gradient of the *potential of mean force*.

revGB

free radical

See *radical*.

GB[3]

frontier orbitals

Highest-energy Occupied Molecular Orbital (HOMO) and Lowest-energy Unoccupied Molecular Orbital (LUMO) of a *molecular entity*.

86

Note 1: These terms should be limited to doubly occupied orbitals, and not to a singly occupied molecular orbital (sometimes designated as a *SOMO*), because HOMO and LUMO are ambiguous for molecular orbitals that are half filled and thus only partly occupied or unoccupied.

Note 2: 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 theory of chemical behaviour.

Note 3: In some cases a *subjacent orbital* (*N*ext-to-*H*ighest *O*ccupied *M*olecular *O*rbital (NHOMO) or a *S*econd *L*owest *U*noccupied *M*olecular *O*rbital (SLUMO)) may affect reactivity.

See [8,206,207].

See also *SOMO*, *subjacent orbital*.

rev[3]

revGB-revPOC

frustrated Lewis acid-base pair

Acid and base for which *adduct* formation is prevented by *steric hindrance*.

See [208,209].

fullerene

Molecular entity composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube.

Note: Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes.

See [40,210].

functional group

Atom or group of atoms within *molecular entities* that are responsible for the characteristic *chemical reaction*s of those *molecular entities*. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule it is a part of. However, its relative reactivity can be modified by nearby *substituent*s.

rev[3]

revGB-revPOC

87

gas-phase acidity

Standard reaction Gibbs energy ($\Delta_r G^o$) change for the gas-phase reaction.

$$A–H \rightarrow A^- + H^+$$

Note 1: The symbol often found in the literature is $\Delta_{acid}G$ or GA.

Note 2: The corresponding enthalpy $\Delta_r H^o$ is often symbolized by $\Delta_{acid}H$ and called "enthalpy of acidity" or deprotonation enthalpy, abbreviated DPE.
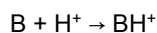
See [211,212].

rev[3]

revGB-revPOC

gas-phase basicity

Negative of the standard reaction Gibbs energy ($\Delta_r G^o$) change for the gas-phase reaction

$$B + H^+ \rightarrow BH^+$$

Note: An acronym commonly used in the literature is GB. The corresponding enthalpy $\Delta_r H^o$ is called *proton affinity*, PA, even though affinity properly refers to Gibbs energy. Moreover, such acronyms are not accepted by IUPAC.

See [213,214].

revGB[3]

Gaussian orbital

Function centred on an atom of the form $\phi(r) \propto x^i y^j z^k \exp(-\zeta r^2)$, used to approximate atomic orbitals in the LCAO-MO method.

See [8].

geminate pair

Pair of *molecular entities* in close proximity within a solvent cage and resulting from reaction (e.g., bond scission, electron transfer, group transfer) of a precursor.

Note: Because of the proximity the pair constitutes only a single kinetic entity.

See also *ion pair*, *radical pair*.

rev[3]

GB

geminate recombination

Recombination reaction of a *geminate pair*.

Example:

$$RN=NR \xrightarrow{\Delta} [R\cdot \ N_2 \ R\cdot]_{cage} \longrightarrow R\text{-}R \ + \ N_2$$

rev[3]

88

1　~~revGB-revPOC~~

2

3

general acid catalysis

Catalysis of a chemical reaction by *Brønsted acid*s (which may include the solvated hydrogen ion), where the rate of the catalysed part of the reaction is given by $\Sigma_{HA}k_{HA}[HA]$ multiplied by some function of *substrate* concentrations.

　Note 1: General acid catalysis can be experimentally distinguished from *specific catalysis* by hydrogen cations (*hydron*s) if the *rate of reaction* increases with buffer concentration at constant pH and ionic strength.

　Note 2: The acid catalysts HA are unchanged by the overall reaction. This requirement is sometimes relaxed, but the phenomenon is then properly called *pseudo-catalysis*.

　See also *catalysis*, *catalytic coefficient*, *intramolecular catalysis*, *pseudo-catalysis*, *specific catalysis*.

rev[3]

~~revGB-revPOC~~

general base catalysis

Catalysis of a *chemical reaction* by *Brønsted base*s (which may include the *lyate ion*), where the rate of the catalysed part of the reaction is given by $\Sigma_{B}k_{B}[B]$ multiplied by some function of *substrate* concentrations.

　See also *general acid catalysis*.

~~GB~~[3]

Gibbs energy diagram

Diagram showing the relative standard Gibbs energies of reactants, *transition state*s, reaction *intermediate*s, and products, in the same sequence as they occur in a *chemical reaction*.

　Note 1: The abscissa expresses the sequence of reactants, products, reaction intermediates, and transition states and is often an undefined "reaction coordinate" or only vaguely defined as a measure of progress along a reaction path. In some adaptations the abscissas are however explicitly defined as *bond order*s, Brønsted exponents, etc.
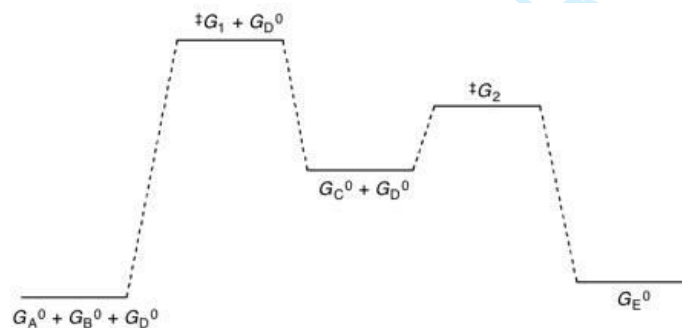
　Note 2: These points are often connected by a smooth curve (a "Gibbs energy profile", commonly referred to as a "free-energy profile", a terminology that is discouraged), but experimental observation can provide information on relative standard Gibbs energies only at the maxima and minima and not at the configurations between them.

89

1   *Note 3*: It should be noted that the use of standard Gibbs energies implies a common
2   standard state for all chemical species (usually 1 M for reactions in solution). Contrary
3   to statements in many textbooks, the highest point on a Gibbs energy diagram does not
4   automatically correspond to the transition state of the *rate-limiting step*. For example,
5   in a stepwise reaction consisting of two elementary reaction steps
6   (1)   A + B $\rightleftarrows$ C
7   (2)   C + D $\rightarrow$ E
8   one of the two transition states must (in general) have a higher standard Gibbs energy
9   than the other. Under experimental conditions where all species have the standard-
10   state concentration, then the *rate-limiting step* is that whose transition state is of highest
11   standard Gibbs energy. However, under (more usual) experimental conditions where
12   all species do not have the standard-state concentration, then the value of the
13   concentration of D determines which reaction step is rate-limiting. However, if the
14   particular concentrations of interest, which may vary, are chosen as the standard state,
15   then the rate-limiting step is indeed the one of highest Gibbs energy.
16

17   $G_A^0 + G_B^0 + G_D^0$
18
19   See also *potential energy profile*, *potential-energy surface*, *reaction coordinate*.
20   rev[3]
21   revGB-revPOC
22

23   **Gibbs energy of activation (standard free energy of activation)**
24   $\Delta^{\ddagger}G^\circ$
25   (SI unit: kJ mol^{-1})
26   Standard Gibbs energy difference between the *transition state* of an *elementary*
27   *reaction* and the ground state of the reactants for that step. It is calculated from the *rate*
28   *constant k* via the absolute rate equation:
29

30       $\Delta^{\ddagger}G^\circ = RT \, [\ln(\, (k_B/J \ K^{-1})/(h/J \ s) \,) - \ln(k/[k]/T/K)]$
31

90

$$\Delta^{\ddagger}G^{o} = RT\,[\ln(\{k_{B}\}/\{h\}) - \ln(\{k\}/\{T\})]$$

where k_{B} is Boltzmann's constant, $[k]$ are the units of k, and h Planck's constant. The values of the rate constants, and hence the Gibbs energies of activation, depend upon the choice of concentration units (or of the thermodynamic standard state).

Note 1: For a complex *stepwise reaction*, composed of many elementary reactions, $\Delta^{\ddagger}G^{o}$, the observed Gibbs energy of activation (activation free energy), can be calculated as $RT\,[\ln(k_{B}/J\ K^{-1})/(h/J\ s) - \ln(k'/[k']/T/K)]$, where k' is the observed rate constant, k' should be divided by its units, and T/K is the dimensionless absolute temperature, of dimension 1, since the argument of a logarithmic function should be of dimension 1, as expressed by the reduced variables in the second form of the equation.

Note 2: Both $\Delta^{\ddagger}G^{o}$ and k' are non-trivial functions of the rate constants and activation energies of the elementary steps.

See also *enthalpy of activation*, *entropy of activation*.

rev[3]

revGB-revPOC

graphene

Allotrope of carbon, whose structure is a one-atom-thick planar sheet of sp^2-bonded carbon atoms in a honeycomb (hexagonal) crystal lattice.

ground state

State of lowest Gibbs energy of a system [2].

Note: In *photochemistry* and quantum chemistry the lowest-energy state of a chemical entity (ground electronic state) is usually meant.

See [9].

See also *excited state*.

rev[3]

GB-revPOC

group

See *functional group*, *substituent*.

rev[3]

revGB-revPOC

Grunwald-Winstein equation

Linear Gibbs-energy relation (*Linear free-energy relation*)

$$\lg(k_{S}/k_{0}) = mY$$

91

expressing the dependence of the rate of solvolysis of a substrate on the ionizing power of the solvent, where the *rate constant* k_0 applies to the reference solvent (80:20 ethanol-water by volume) and k_S to the solvent S.

Note 1: The parameter m is characteristic of the substrate and is assigned the value unity for *tert*-butyl chloride (2-chloro-2-methylpropane). The value Y is intended to be a quantitative measure of the *ionizing power* of the solvent S.

Note 2: The equation was later extended [215] to the form

$$\lg(k_S/k_0) = mY + lN$$

where N is the *nucleophilicity* of the solvent and l a susceptibility parameter

Note 3: The equation has also been applied to reactions other than solvolysis.

Note 4: For the definition of other Y-scales, see [216,217,218,219].

See also *Dimroth-Reichardt E_T parameter*, *polarity*.

rev[3]

revGB-revPOC

guest

Organic or inorganic ion or molecule that occupies a cavity, cleft, or pocket within the molecular structure of a *host molecular entity* and forms a *complex* with it or that is trapped in a cavity within the crystal structure of a host, but with no covalent bond being formed.

See also *crown ether*, *cryptand*, *inclusion compound*.

GB[3]

half-life

$t_{1/2}$

(SI unit: s)

Time required for the concentration of a particular reacting *chemical species* to fall to one-half of its initial value.

Note 1: Half-life is independent of initial concentration only for a first-order process.

Note 2: For first-order reactions $t_{1/2} = \tau \ln2$, where τ is the *lifetime*.

See also *lifetime*.

rev[3]

revGB-revPOC

halochromism

Colour change that occurs on addition of *acid* or *base* to a solution of a compound as a result of chemical reaction, or on addition of a salt as a result of changing the solvent polarity.

92

1   See [220,221].
2   ~~GB~~[3]
3
4   **halogen bond**
5   *Association* between a Lewis-acidic halogen atom in a *molecular entity* and a Lewis-
6   basic region in another, or the same, molecular entity, which acts as an electron-pair
7   donor, such that the balance of forces of attraction and repulsion results in net
8   stabilization.
9   *Note 1*: Typical halogen-bond donors are I_2, Br_2, ICN, and IC≡CH.
10   *Note 2*: This is analogous to a *hydrogen bond*, in which the H is the acidic atom.
11   *Note 3:* The interaction provides a stabilization of a few kJ mol^{-1}.
12   See [222,223,224,225].
13
14
15   **Hammett equation (Hammett relation)**
16   Equation of the form
17
18       $\lg \{k_X\} = \rho\, \sigma_X + \lg \{k_0\}$
19   or $\lg \{K_X\} = \rho\, \sigma_X + \lg \{K_0\}$
20
21   expressing the influence of *meta* and *para* *substituent*s X on the reactivity of the
22   functional group Y in the benzene derivatives *m*- and *p*-XC_6H_4Y, where $\{k_X\}$ and $\{K_X\}$
23   are the numerical values of the rate or equilibrium constant, respectively, for the
24   reactions of *m*- and *p*-XC_6H_4Y, σ_X is the substituent constant characteristic of *m*- or *p*-
25   X, and ρ is the reaction constant characteristic of the given reaction of Y. The values $\lg$
26   $\{k_0\}$ and $\lg \{K_0\}$ are intercepts for graphical plots of $\lg \{k_X\}$ or $\lg \{K_X\}$, respectively, against
27   σ_X for all substituents X (including X = H, if present).
28   *Note* 1: It is very common in the literature to find either of these equations written
29   without the curly brackets denoting a reduced rate or equilibrium constant, i.e., *k* or *K*
30   divided by its unit, [*k*] or [*K*], respectively.
31   *Note* 2: The Hammett equation is most frequently used to obtain the value of ρ which,
32   as the slope of a graph or least-squares fit, is independent of the choice of units for k_X
33   or K_X. If the equation is used to estimate the unknown value of a rate or equilibrium
34   constant for an X-substituted compound based upon the known value of σ_X, the ordinate
35   must be multiplied by $[k_X]$ or $[K_X]$ in order to obtain the value with its appropriate units.
36   *Note 3:* The equation is often encountered in a form with k_H or K_H incorporated into
37   the logarithm on the left-hand side, where k_H or K_H corresponds to the reaction of parent
38   C_6H_5Y, with X = H;
39
40       $\lg(k_X/k_H) = \rho\, \sigma_X$

93

1 or $\lg(K_X/K_H) = \rho\,\sigma_X$

2

3 This form satisfies the requirement that arguments of the lg function must be of

4 dimension 1, but it would suggest a one-parameter linear least-squares fit, whereas lg

5 k_0, lg K_0, lg $k_0/[k_0]$ and lg $K_0/[K_0]$, in the other forms correctly represent the intercept in

6 a two-parameter linear least-squares fit of lg k, lg K, lg $k/[k]$, or lg $K/[K]$ vs. σ_X.

7   See [21,22,126,191,226].

8   See also *extended Hammett equation, Taft equation*, *Yukawa-Tsuno equation*, σ-

9 *constant*, ρ-*value*.

10 rev[3]

11 revGB

12

13

14

15

16 **Hammond postulate (Hammond-Leffler principle)**

17 Hypothesis that, when a *transition state* leading to a high-energy reaction *intermediate*

18 (or product) has nearly the same energy as that intermediate (or product), the two are

19 interconverted with only a small reorganization of molecular structure.

20   *Note 1:* Essentially the same idea is sometimes referred to as "Leffler's assumption",

21 namely, that the *transition state* bears a greater resemblance to the less stable species

22 (reactant or reaction intermediate/product). Many textbooks and physical organic

23 chemists, however, express the idea in Leffler's form (couched in terms of Gibbs

24 energies) but attribute it to Hammond (whose original conjecture concerns structure).

25   *Note 2:* As a corollary, it follows that a factor stabilizing a reaction *intermediate* will

26 also stabilize the *transition state* leading to that *intermediate*.

27   *Note 3*: If a factor stabilizes a reaction intermediate (or reactant or product), then the

28 position of the transition state along the *minimum-energy reaction path* (MERP) for that

29 elementary step moves away from that intermediate, as shown in the energy diagram

30 (a) below left, where the transition state moves from ‡ to ‡' when the species to the

31 right is stabilized. This behaviour is often called a Hammond effect and is simply a

32 consequence of adding a linear perturbation to the parabola.

33

94

Note 4: If a structure lying off the MERP is stabilized, then the position of the *transition state* moves toward that structure, as shown in the energy diagram (b) above right, where the transition state moves from ‡ to ‡'. This behaviour is often called anti-Hammond and arises because the transition state is a maximum along the MERP but a minimum perpendicular to it.

See [227,228,229,230].

See *Leffler's relation*, *More O'Ferrall – Jencks diagram*, *parallel effect*, *perpendicular effect*.

rev[3]

~~revGB-revPOC~~

Hansch constant

Measure of the contribution of a substituent to the *partition ratio* of a solute, defined as

$$\pi_X = \lg(P_X/P_H)$$

where P_X is the partition ratio for the compound with substituent X and P_H is the partition constant for the parent.

See [231,232].

rev[3]

~~revGB-revPOC~~

hapticity

Topological description for the number of contiguous atoms of a *ligand* that are bonded to a central metal atom.

Note: The hapticity is indicated as a superscript following the Greek letter η.

Example: $(C_5H_5)_2Fe$ (ferrocene) = bis(η^5-cyclopentadienyl)iron, where η^5 can be read as eta-five or pentahapto.

See [29].

95

hard acid, base
Lewis acid with an acceptor centre or *Lewis base* with a donor centre (e.g., an oxygen atom) of low *polarizability*.

Note 1: A high polarizability characterizes a soft acid or base.

Note 2: Whereas the definition above is qualitative, a theoretically consistent definition of hardness η, in eV, is as half the second derivative of the calculated energy E with respect to N, the number of electrons, at constant potential ν due to the nuclei.

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_\nu$$

Note 3: Other things being equal, complexes of hard acids with hard bases or of soft acids with soft bases have an added stabilization (sometimes called the HSAB rule). For limitations of the HSAB rule, see [36,233].

See [234,235,236].

rev[3]

~~revGB-revPOC~~

HBA solvent
Strongly or weakly basic solvent capable of acting as a *hydrogen-bond* acceptor (HBA) and forming strong intermolecular solute-solvent hydrogen bonds.

Note: A solvent that is not capable of acting as a hydrogen-bond acceptor is called a non-HBA solvent.

See [17].

HBD solvent (*Hydrogen-Bond* Donating solvent, also *dipolar HBD solvent* and *protic solvent*)
Solvent with a sizable permanent dipole moment that bears suitably acidic hydrogen atoms to form strong intermolecular solvent-solute hydrogen bonds.

Note: A solvent that is not capable of acting as hydrogen-bond donor is called a *non-HBD solvent* (formerly aprotic solvent).

See [17,155].

heat capacity of activation
$C_P{}^{\ddagger}$
(SI unit: J mol^{-1} K^{-1})
Temperature coefficient of $\Delta^{\ddagger}H$ (*enthalpy of activation*) or $\Delta^{\ddagger}S$ (*entropy of activation*) at constant pressure according to the equations:

$$C_P{}^{\ddagger} = (\partial\Delta^{\ddagger}H/\partial T)_P = T(\partial\Delta^{\ddagger}S/\partial T)_P$$

96

See [237].
rev[3]
revGB-revPOC

Henderson-Hasselbalch equation
Equation of the form

$$pH = pK_a - \lg([HA]/[A^-])$$

relating the pH of a buffer solution to the ratio [HA]/[A$^-$] and the dissociation constant of
the acid K_a.
See [238].
rev[3]
revGB-revPOC

heterobimetallic complex
Metal complex having two different metal atoms or ions.
rev[3]
revGB

heteroleptic
Characteristic of a transition metal or Main Group compound having more than one type
of *ligand*.
See also *homoleptic*.
GB[3]

heterolysis, heterolytic bond fission
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.,

A–B ⟶ A$^+$ + B$^-$
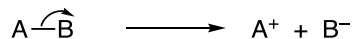
See also *heterolytic bond-dissociation energy*, *homolysis*.
GB[3]

heterolytic bond-dissociation energy
Energy required to break a given *bond* of a specific compound by *heterolysis*.
Note: For the *dissociation* of a neutral molecule AB in the gas phase into A$^+$ and B$^-$
the heterolytic *bond-dissociation energy* $D(A^+B^-)$ is the sum of the homolytic bond-

97

dissociation energy, D(A–B), and the adiabatic *ionization* energy of the radical A· minus the electron affinity of the radical B·.

~~GB~~[3]

high-throughput screening
Automated method to quickly assay large libraries of *chemical species* for the affinity of small organic molecules toward a target of interest.
Note: Currently more than 10^5 different compounds can be tested per day.
See [239].

highest occupied molecular orbital (HOMO)
Doubly filled molecular orbital of highest energy.
Note: Examination of the HOMO can predict whether an *electrocyclic reaction* is *conrotatory* or *disrotatory*.
See also *frontier orbitals*.

Hildebrand solubility parameter [symbol δ, derived unit: $Pa^{1/2}$ = $(kg\ m^{-1}\ s^{-2})^{1/2}$]
Ability of a solvent to dissolve a non-electrolyte, defined as the square root of the solvent's cohesive energy density (also called cohesive pressure, equal to the energy of vaporization divided by the solvent's molar volume and corresponding to the energy necessary to create a cavity in the solvent).
See [240].
rev[3]
~~revGB-revPOC~~

Hofmann rule
Observation that 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 is the predominant product.
Note: This orientation is observed in elimination reactions of quaternary ammonium salts and tertiary sulfonium (sulfanium) salts, and in certain other cases where there is steric hindrance.
See [241].
See also *Saytzeff rule*.
rev[3]
~~revGB-revPOC~~

HOMO
(1) Acronym for *Highest Occupied Molecular Orbital*.
See also *frontier orbitals*.

98

1   (2) Prefix (in lower case) used to indicate a higher homologue of a compound, as
2   homocysteine for $HSCH_2CH_2CH(NH_2)COOH$, the homologue of cysteine,
3     $HSCH_2CH(NH_2)COOH$.
4   rev[3]
5   GB
6

7 **homoaromatic**
8   Showing features of *aromaticity* despite a formal discontinuity in the overlap of a cyclic
9   array of p orbitals resulting from the presence of an sp^3-hybridized atom at one or
10   several positions within the cycle, in contrast to an *aromatic* molecule, where there is a
11   continuous overlap of p orbitals over a cyclic array.
12   *Note 1:* Homoaromaticity arises because p-orbital overlap can bridge an sp^3 centre.
13   *Note 2:* Pronounced homoaromaticity is not normally associated with neutral
14   molecules, but mainly with ionic species, e.g., the "homotropylium" cation, $C_8H_9^+$,

15

16   *Note 3:* In bis-, tris-, (etc.) homoaromatic species, two, three, (etc.) single sp^3 centres
17   separately interrupt the π-electron system.
18   GB[3]
19

20 **homodesmotic reaction**
21   Subclass of *isodesmic* reactions in which reactants and products contain not only the
22   same number of carbon atoms in each state of hybridization but also the same number
23   of each CH_n group joined to *n* hydrogen atoms.
24   *Examples:*
25

26   cyclo-$(CH_2)_3$ + 3 CH_3CH_3 $\rightleftarrows$ 3 $CH_3CH_2CH_3$ [$3CH_2$, $6CH_3$]
27   C_6H_6 (benzene) +   3 $CH_2=CH_2$ $\rightleftarrows$ 3 $CH_2=CH–CH=CH_2$ [$6CH$, $6CH_2$]
28

29   *Note:* The definition may be extended to molecules with heteroatoms.
30   See [8].
31   rev[3]
32   GB
33

34 **homoleptic**
35   Characteristic of a transition-metal or Main Group compound having only one type of
36   *ligand*, e.g., $Ta(CH_3)_5$
37   See also *heteroleptic*.

99

~~GB~~[3]

homolysis
Cleavage of a *bond* so that each of the molecular fragments between which the bond is broken retains one of the bonding electrons.

Note 1: 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:

$$\widehat{A \frown B} \quad \longrightarrow \quad A^{\cdot} + B^{\cdot}$$
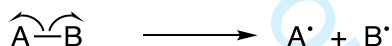
Note 2: Homolysis is the reverse of *colligation*.
See also *bond dissociation energy*, *heterolysis*.
~~GB~~[3]

host
Molecular entity that forms *complex*es (*adduct*s*) with organic or inorganic guests, or a chemical species that can accommodate guests within cavities of its crystal structure.

Examples include *cryptands* and *crown ethers* (where there are ion/dipole attractions between heteroatoms and cations), *hydrogen-bonded* molecules that form clathrates (e.g., hydroquinone or water), and host molecules of *inclusion compounds* (e.g., urea or thiourea), where *intermolecular* forces and *hydrophobic interaction*s bind the guest to the host molecule.
rev[3]
~~revGB-revPOC~~

Hückel molecular orbital (HMO) theory
Simplest molecular orbital theory of π-conjugated molecular systems. It uses the following approximations: π-electron approximation; LCAO representation of the π molecular orbitals; neglect of electron-electron and nuclear-nuclear repulsions. The diagonal elements of the effective Hamiltonian (Coulomb integrals) and the off-diagonal elements for directly bonded atoms (resonance integrals) are taken as empirical parameters, all overlap integrals being neglected**.**
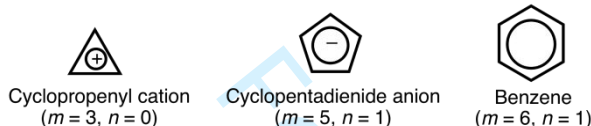See [8].
rev[3]
~~GB~~

Hückel (4n + 2) rule
Principle that monocyclic planar (or almost planar) systems of trigonally (or sometimes digonally) hybridized atoms that contain (4n + 2) π electrons (where n is an integer, generally 0 to 5) exhibit *aromatic* character.

100

Note 1: This rule is derived from *Hückel MO theory* calculations on planar monocyclic conjugated hydrocarbons $(CH)_m$ where integer m is at least 3, according to which $(4n + 2)$ electrons are contained in a closed-shell system.

Examples:

Cyclopropenyl cation ($m = 3$, $n = 0$)   Cyclopentadienide anion ($m = 5$, $n = 1$)   Benzene ($m = 6$, $n = 1$)

Note 2: Planar systems containing $4n$ π electrons (such as cyclobutadiene and cyclopentadienyl cation) are antiaromatic.

Note 3: Cyclooctatetraene, with 8 π electrons, is nonplanar and therefore neither aromatic nor antiaromatic but nonaromatic.

See [8].

See also *conjugation*, *Möbius aromaticity*.

rev[3]

~~revGB revPOC~~

hybrid orbital

Atomic orbital constructed as a linear combination of *atomic orbital*s on an atom.

Note 1: Hybrid orbitals are often used to describe the bonding in molecules containing tetrahedral (sp^3), trigonal (sp^2), and digonal (sp) atoms, whose σ bonds are constructed using 1:3, 1:2, or 1:1 combinations, respectively, of s and p atomic orbitals.

Note 2: Construction of hybrid orbitals can also include d orbitals, as on an octahedral atom, with d^2sp^3 hybridization.

Note 3: Integer ratios are not necessary, and the general hybrid orbital made from s and p orbitals can be designated as sp^λ.

~~GB~~

hydration

Addition of water or of the elements of water (i.e., H and OH) to a *molecular entity* or to a *chemical species*.

Example: hydration of ethene:

$$CH_2=CH_2 + H_2O \; \rightarrow \; CH_3CH_2OH$$

Note: In contrast to *aquation*, hydration, as in the incorporation of waters of crystallization into a protein or in the formation of a layer of water on a nonpolar surface, does not necessarily require bond formation.

See [48].

See also *aquation*.

rev[3]

101

1 revGB-revPOC
2
3

hydrogen bond
An attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.

Note 1: Both electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e., N, O, or F.

Note 2: A hydrogen bond is largely an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges.

Note 3: Hydrogen bonds may be *intermolecular* or *intramolecular*.

Note 4: With few exceptions, usually involving hydrogen fluoride and fluoride and other ions, the associated energies are less than 20-25 kJ mol^{-1}.

Note 5: Hydrogen bonds are important for many chemical structures, giving rise to the attraction between H_2O molecules in water and ice, between the strands of DNA, and between aminoacid residues in proteins.

See [242,243].

rev[3]
revGB-revPOC

hydrolysis
Solvolysis by water, generally involving the rupture of one or more bonds in the reactant and involvement of water as *nucleophile* or base.

Example: $CH_3C(=O)OCH_2CH_3 + H_2O \rightarrow CH_3C(=O)OH + CH_3CH_2OH$

rev[3]
revGB-revPOC

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 $^1H^+$, deuteron for $^2H^+$ and triton for $^3H^+$.

See [244].

GB[3]

hydronation
Attachment of the ion H^+ either in natural abundance or where it is not desired to distinguish between the isotopes.

hydrophilicity

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Capacity of a *molecular entity* or of a *substituent* to undergo stabilizing interactions with polar solvents, in particular with water and aqueous mixtures, to an extent greater than with a nonpolar solvent.

rev[3]

~~revGB~~

hydrophobic interaction

Tendency of *lipophilic* hydrocarbon-like groups in solutes to form *intermolecular* aggregates in an aqueous *medium*.
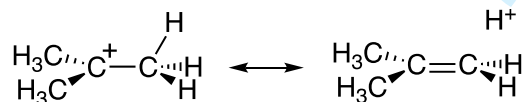
Note: The name arises from the attribution of the phenomenon to the apparent repulsion between water and hydrocarbons. However, the phenomenon is more properly attributed to the effect of the hydrocarbon-like groups to avoid disrupting the favorable water-water interactions.

~~GB~~[3]

hyperconjugation

Delocalization of electrons between σ bonds and a π network.

Note 1: The concept of hyperconjugation is often applied to *carbenium ion*s and *radical*s, where the interaction is between σ bonds and an unfilled or partially filled p or π orbital. *Resonance* illustrating this for the *tert*-butyl cation is:

Note 2: A distinction is made between positive hyperconjugation, as above, and negative hyperconjugation, where the interaction is between a filled σ or π orbital and adjacent antibonding σ* orbitals, as for example in the fluoroethyl anion (2-fluoroethan-1-ide).
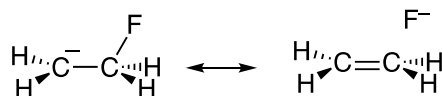
Note 3: Historically, conjugation involves only π bonds, and hyperconjugation is considered unusual in involving σ bonds.

See [245,246,247,248].

See also *σ*, *π*, *delocalization*.

rev[3]

~~revGB-revPOC~~

103

hypercoordinated

Feature of a main-group atom with a *coordination number* greater than four.

Example: the pentacoordinate carbon in the *carbonium ion* CH_5^+, where three C–H bonds may be regarded as two-electron bonds and the two electrons in the remaining CH_2 fragment are delocalized over three atoms. Likewise, both hydrogens in the CH_2 fragment are hypercoordinated.

See [2,8].

See also *agostic*.

rev[3]

rev GB-revPOC

hypervalency

Ability of an atom in a *molecular entity* to expand its valence shell beyond the limits of the Lewis octet rule.

Examples: PF_5, SO_3, iodine(III) compounds, and pentacoordinate carbocations (*carbonium ion*s).

Note: Hypervalent compounds are more common for the second- and subsequent-row elements in groups 15-18 of the periodic table. A proper description of the hypervalent bonding implies a transfer of electrons from the central (hypervalent) atom to the nonbonding molecular orbitals of the attached *ligand*s, which are usually more electronegative.

See [8].

See also *valence*.

rev[3]

GB

hypsochromic shift

Shift of a spectral band to higher frequency (shorter wavelength) upon substitution or change in medium.

Note: This is informally referred to as a blue shift and is opposite to a *bathochromic shift* ("red shift"), but these historical terms are discouraged because they apply only to visible transitions.

See [9].

rev[3]

GB

identity reaction

Chemical reaction whose products are chemically identical with the reactants

Examples:

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(i)   bimolecular exchange reaction of CH_3I with I^-
(ii) proton transfer between NH_4^+ and NH_3
(iii) electron transfer between manganate(VI) MnO_4^{2-} and permanganate MnO_4^-.
See also *degenerate rearrangement*.
rev[3]
revGB

imbalance
Feature that reaction parameters characterizing different bond-forming or bond-breaking processes in the same reaction change to different extents as the *transition state* is approached (along some arbitrarily defined reaction path).
Note: Imbalance is common in reactions such as elimination, addition, and other complex reactions that involve proton (*hydron*) transfer.
Example: the nitroalkane anomaly, where the Brønsted β exponent for hydron removal is smaller than the Brønsted α for the nitroalkane as acid, because of imbalance between the extent of bond breaking and the extent of resonance delocalization in the transition state.
See [249].
See also *Brønsted relation*, *synchronization (principle of nonperfect synchronization)*, *synchronous*.
rev[3]
GB

inclusion compound (inclusion complex)
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.
Note: 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".
See [40].
GB[3]

induction period
Initial slow phase of a *chemical reaction* whose rate later accelerates.
Note: Induction periods are often observed with radical reactions, but they may also occur in other reactions, such as those where a steady-state concentration of the reactants is not established immediately.
See [13].

105

GB[3]

inductive effect

Experimentally observable effect (on rates of reaction, etc.) of a *substituent* through transmission of charge through a chain of atoms by electrostatics.

Note: Although 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 monopole 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"), because the inductive effect and the field effect are ordinarily influenced in the same direction by structural changes.

See [171,172,250].

See also *field effect*, *polar effect*.

rev[3]

revGB-revPOC

inert

Stable and *unreactive* under specified conditions.

GB[3]

inhibition

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 or 1,4-benzoquinone can act as an inhibitor in many chain reactions involving *radical*s as intermediates by virtue of its ability to act as a *scavenger* toward those radicals.

Note: If the rate of a reaction in the absence of inhibitor is v_o and that in the presence of a certain amount of inhibitor is v, the degree of inhibition (i) is given by

$$i = (v_o - v)/v_o$$

See also *mechanism-based inhibition*.

GB[3]

initiation

Reaction or process generating *radical*s (or some other reactive reaction *intermediate*s) which then induce a *chain reaction* or catalytic cycle.

Example: In the chlorination of alkanes by a radical mechanism the initiation step may be the *dissociation* of molecular chlorine.

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1 rev[3]
2 ~~revGB-revPOC~~
3
4 **inner-sphere (electron transfer)**
5 Feature of an electron transfer between two metal centres that in the transition state
6 share a *ligand* or atom in their coordination shells.
7 *Note*: The definition has been extended to any situation in which the interaction
8 between the electron-donor and electron-acceptor centres in the *transition state* is
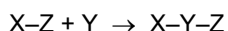9 significant (>20 kJ mol^{-1}).
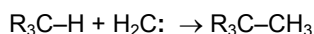10 See [9].
11 See also *outer-sphere electron transfer*.
12 ~~GB~~[3]
13
14 **insertion**
15 *Chemical reaction* or *transformation* of the general type
16
17 $$X-Z + Y \rightarrow X-Y-Z$$
18
19 in which the connecting atom or *group* Y replaces the bond joining the parts X and Z of
20 the reactant XZ.
21 *Example*: *carbene* insertion reaction
22
23 $$R_3C-H + H_2C\colon \rightarrow R_3C-CH_3$$
24
25 *Note*: The reverse of an insertion is called an *extrusion*.
26 ~~GB~~[3]
27
28 **intermediate (reactive intermediate)**
29 *Molecular entity* in a stepwise chemical reaction with a *lifetime* appreciably longer than
30 a molecular vibration (corresponding to a local potential energy minimum of depth
31 greater than *RT*, and thus distinguished from a *transition state*) that is formed (directly
32 or indirectly) from the reactants and reacts further to give (directly or indirectly) the
33 products of a chemical reaction.
34 See also *elementary reaction*, *reaction step*, *stepwise reaction*.
35 ~~GB~~[3]
36
37 **intermolecular**
38 (1) Descriptive of any process that involves a transfer (of atoms, *group*s, electrons, etc.)
39 or interactions between two or more *molecular entities*.
40 (2) Relating to a comparison between different molecular entities.

107

See also *intramolecular*.

~~GB~~[3]

internal return

See *ion-pair recombination*.

rev[3]

~~revGB~~

intramolecular

(1) Descriptive of any process that involves a transfer (of atoms, *group*s, electrons, etc.) or interactions between different parts of the same *molecular entity*.

(2) Relating to a comparison between different groups within the same molecular entity.

See also *intermolecular*.

~~GB~~[3]

intramolecular catalysis

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.

Note 1: The use of the term should be restricted to cases for which analogous intermolecular catalysis by a *chemical species* bearing that catalytic group is observable.

Note 2: 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.

See also *effective molarity*, *neighbouring group participation*.

~~GB~~[3]

intrinsic barrier, $\Delta^{\ddagger}G_0$

Gibbs energy of activation in the limiting case where $\Delta_r G^o = 0$, i.e., when the effect of thermodynamic driving force is eliminated, as in an identity reaction, $X^* + AX \rightarrow X^*A + X$, where A may be an atom, ion, or group of atoms or ions, and where the *equilibrium* constant K is equal to 1.

Note: According to the *Marcus equation*, originally developed for outer-sphere electron transfer reactions, the intrinsic barrier is related to λ, the *reorganization energy* of the reaction, by the equation

$$\Delta^{\ddagger}G^o = \lambda/4$$

108

1 For a non-identity reaction, Y + AX → YA + X, the intrinsic barrier $\Delta^{\ddagger}G^{o}$(Y,X) is estimated
2 as ½[$\Delta^{\ddagger}G$(X,X) + $\Delta^{\ddagger}G$(Y,Y)], where the latter two terms are the Gibbs energies of
3 activation of the identity reactions X* + AX → X*A + X and Y* + AY → Y*A + Y,
4 respectively.
5   See [251,252,253,254].
6   rev[3]
7   revGB-revPOC
8
9 **intrinsic reaction coordinate (IRC)**
10 Minimum-energy path leading from the saddle point (corresponding to the *transition*
11 *structure*) on the *potential-energy surface* for an *elementary reaction*, obtained by
12 tracing the steepest descent in mass-weighted coordinates in both directions.
13   *Note*: The IRC is mathematically well defined, in contrast to the (generally) vague
14 *reaction coordinate*. Strictly, the IRC is a specific case of a *minimum-energy reaction*
15 *path*, and its numerical value at any point along this path is usually taken to be zero at
16 the saddle point, positive in the direction of the products, and negative in the direction
17 of the reactants.
18   See [8,255].
19   rev[3]
20   revGB
21
22 **inverted micelle (reverse micelle)**
23 Association colloid formed reversibly from surfactants in non-polar solvents, leading to
24 aggregates in which the polar *group*s of the surfactants are concentrated in the interior
25 and the *lipophilic* groups extend toward and into the non-polar solvent.
26   *Note:* Such association is often of the type
27   Monomer ⇌ Dimer ⇌ Trimer ⇌ ⋯ ⇌ *n*-mer
28 and a *critical micelle concentration* is consequently not observed.
29   GB[3]
30
31 **ion pair**
32 Pair of oppositely charged ions held together by coulomb attraction without formation
33 of a *covalent bond*.
34   *Note 1:* Experimentally, an ion pair behaves as one unit in determining conductivity,
35 kinetic behaviour, osmotic properties, etc.
36   *Note 2:* Following Bjerrum, oppositely charged ions with their centres closer together
37 than a distance
38

39
$$d = \frac{Z_{+}Z_{-}e^{2}}{4\pi\varepsilon_{0}\varepsilon_{r}k_{B}T}$$

109

are considered to constitute an ion pair. Here Z_+ and Z_- are the charge numbers of the ions, e is the elementary charge, ε_0 is the vacuum permittivity, ε_r is the relative *permittivity* ("dielectric constant") of the medium, k_B is Boltzmann's constant, and T is the absolute temperature. This is the distance at which the Coulomb energy equals the thermal energy, and $e^2/(4\pi\varepsilon_0 k_B)$ is approximately equal to 1.671×10^{-5} m K^{-1}.

Note 3: An ion pair, the constituent ions of which are in direct contact (and not separated by intervening solvent or by other neutral molecule) is designated as a "tight ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of R$^+$ and X$^-$ is symbolically represented as R$^+$X$^-$.

Note 4: 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 R$^+$||X$^-$. The components 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.

Note 5: A further conceptual distinction has sometimes been made between two types of loose ion pairs. In "solvent-shared ion pairs" for which 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.

See [256].

See also *common-ion effect*, *dissociation*, *ion-pair return*, *special salt effect*.

~~GB~~[3]

ion-pair recombination (formerly **ion-pair return**)
Recombination of a pair of ions R$^+$ and X$^-$ formed from *ionization* of RX.

Note: Ion-pair recombination can be distinguished as external or internal, depending on whether the ion pair did or did not undergo dissociation to free ions.

See *ion pair*.

rev[3]

~~revGB-revPOC~~

ionic liquid (ionic solvent, molten salt)
Liquid that consists exclusively or almost exclusively of equivalent amounts of oppositely charged ions.

Note 1: In practice the ions are monocations and monoanions.

110

Note 2: Ionic liquids that are liquid at or around room temperature are called room-temperature ionic liquids (RTILs).

Note 3: The term *ionic liquid* has been often restricted to those water-free liquids that have melting points (or glass-transition temperatures) below 100 °C, following a definition given by Walden [257], who prepared the first ionic liquid, ethylammonium nitrate, $CH_3CH_2NH_3^+ NO_3^-$, mp. 13-14 °C, for conductivity measurements.

Note 4: The terminology for ionic liquids is not yet settled, as stated by Welton [258]. Room-temperature ionic liquid, non-aqueous ionic liquid, molten salt, liquid organic salt, and fused salt are often synonymous.

See [259,260,261].

ionic strength

I

(In concentration basis, I_c, SI unit: mol m^{-3}, more commonly mol dm^{-3} or mol L^{-1}, in molality basis, I_m, SI unit: mol kg^{-1})

In concentration basis: $I_c = 0.5 \ \Sigma_i c_i Z_i^2$, in which c_i is the concentration of a fully dissociated electrolyte in solution and Z_i the charge number of ionic species i.

In molality basis: $I_m = 0.5 \ \Sigma_i m_i Z_i^2$, in which m_i is the molality of a fully dissociated electrolyte in solution and Z_i the charge number of ionic species i.
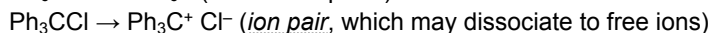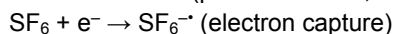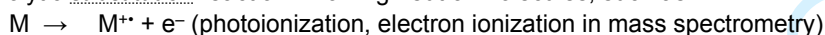
rev[3]

~~revPOC~~

ionization

Generation of one or more ions.

Note 1: This may occur, e.g., by loss or gain of an electron from a neutral *molecular entity*, by the *unimolecular heterolysis* of that entity into two or more ions, or by a heterolytic *substitution* reaction involving neutral molecules, such as

$M \rightarrow M^{+\bullet} + e^-$ (photoionization, electron ionization in mass spectrometry)

$SF_6 + e^- \rightarrow SF_6^{-\bullet}$ (electron capture)

$Ph_3CCl \rightarrow Ph_3C^+ Cl^-$ (*ion pair*, which may dissociate to free ions)

$CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3CO_2^-$ (*dissociation*)

Note 2: In mass spectrometry ions may be generated by several methods, including electron ionization, photoionization, laser desorption, chemical ionization, and electrospray ionization.

Note 3: Loss of an electron from a singly, doubly, etc. charged cation is called second, third, etc. ionization.

See also *dissociation*, *ionization energy*.

rev[3]

~~revGB-revPOC~~

111

1 **ionization energy**

2 E_i

3 (SI unit J)

4 Minimum energy required to remove an electron from an isolated *molecular entity* (in

5 its vibrational ground state) in the gaseous phase.

6   *Note 1:* If the resulting molecular entity is in its vibrational ground state, the energy

7 is the "adiabatic ionization energy".

8   *Note 2:* If the molecular entity produced possesses the vibrational energy determined

9 by the *Franck-Condon principle* (according to which the electron ejection takes place

10 without an accompanying change in molecular geometry), the energy is the "vertical

11 ionization energy".

12   *Note 3:* The name ionization energy is preferred to the somewhat misleading earlier

13 name "ionization potential".

14   See also *ionization*.

15   ~~GB~~[3]

16

17 **ionizing power**

18 Tendency of a particular solvent to promote *ionization* of a solute.

19   *Note*: The term has been used in both kinetic and thermodynamic contexts.

20   See also *Dimroth-Reichardt E_T parameter*, *Grunwald-Winstein equation*, *Z-value*.
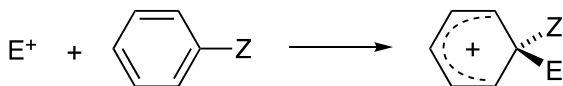
21   ~~GB~~[3]

22

23 ***ipso* attack**

24 Attachment of an entering group to a position in an aromatic compound already carrying

25 a *substituent* group other than hydrogen.

26   *Note:* The entering group may displace that substituent group or may itself be

27 expelled or migrate to a different position in a subsequent step. The term "*ipso*-

28 substitution" is not used, since it is synonymous with substitution.

29   *Example:*

30

31 where E^+ is an *electrophile* and Z is a substituent other than hydrogen.

32   See [262].

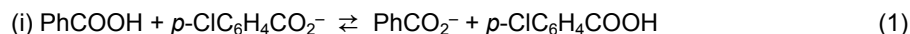33   See also *cine-substitution*, *tele-substitution*.

34   ~~GB~~[3]

35

36 **isentropic**

37   See *isoentropic*.

38

112

isodesmic

Property of a reaction (actual or hypothetical) in which the types of bonds that are made in forming the products are the same as those that are broken in the reactants.

Examples:

(i) $PhCOOH + p\text{-}ClC_6H_4CO_2^- \rightleftarrows PhCO_2^- + p\text{-}ClC_6H_4COOH$ (1)

(ii) $2\ CH_3F \rightleftarrows CH_2F_2 + CH_4$ (2)

Note 1: Such processes have advantages for theoretical treatment.

Note 2: The *Hammett equation* as applied to equilibria, as in (1), succeeds because it deals with isodesmic processes.

Note 3: For the use of isodesmic processes in quantum chemistry, see [263].

See [8].

See also *homodesmotic.*

rev[3]

revGB

isoelectronic

Having the same number of valence electrons and the same structure, i.e., number and *connectivity* of atoms, but differing in some or all of the elements involved.

Examples:

(i) CO, N_2, and NO^+

(ii) $CH_2=C=O$ and $CH_2=N^+=N^-$
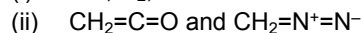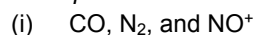
GB[3]

isoentropic

Isentropic

Property of a reaction series in which the individual reactions have the same standard entropy or *entropy of activation*.

GB[3]

isoequilibrium relationship

Feature of a series of related substrates or of a single *substrate* under a series of reaction conditions whereby the enthalpies and entropies of reaction can be correlated by the equation

$$\Delta_r H - \beta\,\Delta_r S = \text{constant}$$

Note: The parameter β is called the isoequilibrium temperature.

See [264,265].

See also *compensation effect*, *isokinetic relationship.*

113

1   ~~GB~~[3]

2

3   **isokinetic relationship**

4   Feature of a series of related substrates or of a single _substrate_ under a series of
5   reaction conditions whereby the _enthalpies of activation_ and _entropies of activation_ can
6   be correlated by the equation

7        $\Delta^{\ddagger}H - \beta\,\Delta^{\ddagger}S$ = constant

8   _Note 1:_ The parameter β is called the isokinetic temperature. At this temperature all
9   members of the series react at the same rate.

10   _Note 2:_ Isokinetic relationships as established by direct correlation of $\Delta^{\ddagger}H$ with $\Delta^{\ddagger}S$
11   are often spurious, and the calculated value of β is meaningless, because errors in $\Delta^{\ddagger}H$
12   lead to compensating errors in $\Delta^{\ddagger}S$. Satisfactory methods of establishing such
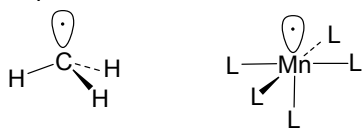13   relationships have been devised.

14   See [264,265].

15   See also _compensation effect_, _isoequilibrium relationship_, _isoselective relationship_.

16   ~~GB~~[3]

17

18   **isolobal**

19   Feature of two molecular fragments for which the number, symmetry properties,
20   approximate energy, shape of the _frontier orbitals_, and number of electrons in them are
21   similar.

22   _Example:_

23

24   See also _isoelectronic_.

25   rev[3]

26   ~~revGB-revPOC~~

27

28   **isomer**

29   One of several species (or _molecular entities_) all of which have the same atomic
30   composition (molecular formula) but differ in their connectivity or stereochemistry and
31   hence have different physical and/or chemical properties.

32   _Note:_ Conformational isomers that interconvert by rapid rotation about single bonds
33   and configurations that interconvert by rapid pyramidal inversion are often not
34   considered as separate isomers.

35   rev[3]

36   ~~revGB-revPOC~~

37

114

isomerization
Chemical reaction in which the product is an *isomer* of the reactant.
    See also *molecular rearrangement*.
    rev[3]
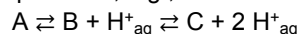   revGB-revPOC

isosbestic point
Wavelength (or frequency) at which two or more components in a mixture have the same molar absorption coefficients.
    Note 1: 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, as in an acid-base indicator equilibrium.
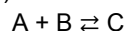   *Note 2:* The effect may also appear (c) in the spectra of a set of solutions of two or more non-interacting components having the same total concentration.
    Note 3: In all these examples, A (and/or B) may be either a single *chemical species* or a mixture of chemical species present in invariant proportion.
    Note 4: If absorption spectra of the types considered above intersect not at one or more isosbestic points but over a progressively changing range of wavelengths, this is prima facie evidence (a) for the formation of a reaction *intermediate* in substantial concentration (A → C → B) or (b) for the involvement of a third absorbing species in the equilibrium, e.g.,
        $A \rightleftarrows B + H^+_{aq} \rightleftarrows C + 2 H^+_{aq}$
or (c) for some interaction of A and B, e.g.,
        $A + B \rightleftarrows C$
    Note 5: Isobestic is a misspelling and is discouraged.
    rev[3]
    revGB-revPOC

isoselective relationship
Relationship analogous to the *isokinetic relationship*, but applied to *selectivity* data of reactions.
    Note: At the isoselective temperature, the selectivities of the series of reactions following the relationship are identical, within experimental error.
    See [266].
    See also *isoequilibrium relationship*, *isokinetic relationship*.
    GB[3]

115

isotope effect
Relative difference between, or the ratio of, the *rate ~~constants~~ coefficients* or *equilibrium* constants of two reactions that differ only in the isotopic composition of one or more of their otherwise chemically identical components.

Note: The ratio k_l/k_h of rate constants (or K_l/K_h of equilibrium constants) for "light" and "heavy" reactions is most often used in studies of chemical reaction mechanisms. However, the opposite ratios are frequently used in environmental chemistry and geochemistry; i.e., k_h/k_l or K_h/K_l. Furthermore the relative difference $k_h/k_l - 1$ or $K_h/K_l - 1$ (often expressed as the percentage deviation of the ratio from unity) is commonly used to quantify isotopic fractionation.

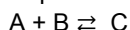See *kinetic isotope effect*, *equilibrium isotope effect*.
rev[3]
~~revGB~~

isotope effect, equilibrium
isotope effect, thermodynamic
Effect of isotopic substitution on an *equilibrium* constant

Note 1: For example, the effect of isotopic substitution in reactant A that participates in the equilibrium:

$$A + B \rightleftarrows C$$

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 also be expressed as the equilibrium constant for the isotopic exchange reaction:

$$A_l + C_h \rightleftarrows A_h + C_l$$
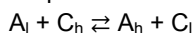
in which reactants such as B that are not isotopically substituted do not appear.

Note 2: The *potential-energy surface*s of isotopic molecules are identical to a high degree of approximation, so thermodynamic isotope effects can arise only from the effect of isotopic mass on the nuclear motions of the reactants and products, and can be expressed quantitatively in terms of nuclear partition functions:

$$K_l/K_h = [Q^l(C)/Q^h(C)]/ [Q^l(A)/Q^h(A)]$$

Note 3: Although the nuclear partition function is a product of the translational, rotational, and vibrational partition functions, the isotope effect is usually 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.

See [267].
See also *fractionation factor*.

116

1   rev[3]
2   revGB
3
4   **isotope effect, heavy-atom**
5   *Isotope effect* due to isotopes other than those of hydrogen.
6   GB[3]
7
8   **isotope effect, intramolecular**
9   *Kinetic isotope effect* observed when a single substrate, in which the isotopic atoms
10 occupy equivalent reactive positions, reacts to produce a non-statistical distribution of
11 *isotopologue* products.
12
13   *Example*: $PhCH_2D + Br\cdot \rightarrow BrH + PhCHD\cdot$ vs. $BrD + PhCH_2\cdot$
14
15 The intramolecular isotope effect k_H/k_D can be measured from the D content of product
16 ($PhCH_2Br + PhCHDBr$), which is experimentally much easier than measuring the
17 intermolecular isotope effect k_H/k_D from the separate rates of reaction of $PhCH_3$ and
18 $PhCD_3$.
19   rev[3]
20   revGB-revPOC
21
22 **isotope effect, inverse**
23 *Kinetic isotope effect* in which $k_l/k_h < 1$, i.e., the heavier substrate reacts more rapidly
24 than the lighter one, as opposed to the more usual "normal" *isotope effect*, in which k_l/k_h
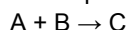25 > 1.
26   *Note:* The isotope effect will be "normal" when the vibrational frequency differences
27 between the isotopic *transition state*s are smaller than in the reactants. Conversely, an
28 inverse isotope effect can be taken as evidence for an increase in the force constants
29 on passing from the reactant to the *transition state*.
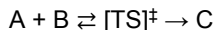30   GB[3]
31
32 **isotope effect, kinetic**
33 Effect of isotopic substitution on a *rate constant*.
34   For example in the reaction
35          $A + B \rightarrow C$
36   the effect of isotopic substitution in reactant A is expressed as the ratio of *rate
37 constant*s k_l/k_h, where the superscripts l and h represent reactions in which the
38 molecules A contain the light and heavy isotopes, respectively.
39   *Note 1:* Within the framework of transition-state theory, where the reaction is
40 rewritten as

117

$$A + B \rightleftarrows [TS]^{\ddagger} \rightarrow C$$

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 (see *thermodynamic (equilibrium) isotope effect*).

Note 2: Isotope effects like the above, involving a direct or indirect comparison of the rates of reaction of *isotopologue*s, are called "intermolecular", in contrast to intramolecular isotope effects (see *intramolecular isotope effect*), in which a single substrate reacts to produce a non-statistical distribution of isotopologue product molecules.

See [267,268].

~~GB~~[3]

isotope effect, primary

Kinetic isotope effect attributable to isotopic substitution of an atom to which a bond is made or broken in the *rate-limiting step* or in a *pre-equilibrium* step of a reaction.

Note: 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*.

See also *secondary isotope effect*.

~~GB~~[3]

isotope effect, secondary

Kinetic isotope effect that is attributable to isotopic substitution of an atom to which bonds are neither made nor broken in the *rate-limiting step* or in a *pre-equilibrium* step of a specified reaction.

Note 1: The corresponding isotope effect on the equilibrium constant of such a reaction is called a secondary *equilibrium isotope effect*.

Note 2: Secondary isotope effects can be classified as α, β, etc., where the label denotes the position of isotopic substitution relative to the reaction centre.

Note 3: Although secondary isotope effects have been discussed in terms of conventional electronic effects, e.g., induction, *hyperconjugation*, *hybridization*, such an effect is not electronic but vibrational in origin.

See [269].

See also *steric isotope effect*.

rev[3]

~~revGB~~

isotope effect, solvent

118

Kinetic or equilibrium isotope effect resulting from change in the isotopic composition of the solvent.

See also *kinetic isotope effect*, *equilibrium isotope effect*.

GB[3]

isotope effect, steric

Secondary isotope effect attributed to the different vibrational amplitudes of *isotopologue*s.

Note 1: 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.

Note 2: Ultimately the steric isotope effect arises from changes in vibrational frequencies and zero-point energies, as normally do other isotope effects.

rev[3]

revGB

isotope effect, thermodynamic

See isotope effect, equilibrium.

GB[3]

isotope exchange

Chemical reaction in which the reactant and product *chemical species* are chemically identical but have different isotopic composition.

Note: 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,
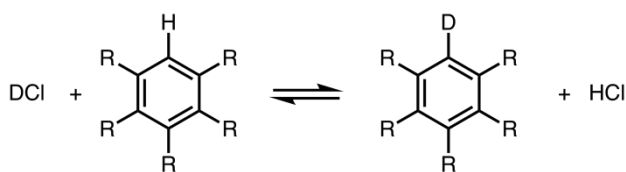
GB[3]

isotopic perturbation, method of

Measurement of the NMR shift difference due to the *isotope effect* on a fast (degenerate) *equilibrium* between two species that are equivalent except for isotopic substitution.

Note: This method can distinguish a rapidly equilibrating mixture with time-averaged symmetry from a single structure with higher symmetry.
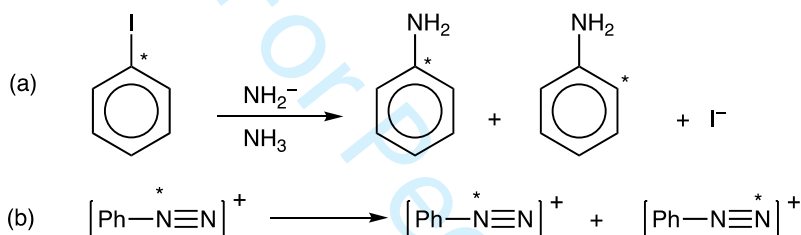
119

See [270,271,272,273].

GB[3]

isotopic scrambling

Achievement of, or the process of achieving, a redistribution of isotopes within a specified set of atoms in a *chemical species* or group of chemical species.

Examples

(where * denotes the position of an isotopically different atom.)

See also *fractionation factor*.

GB[3]

isotopologues

Molecular entities that differ only in isotopic composition (number of isotopic substitutions), e.g., CH_4, CH_3D, CH_2D_2,

Note: These are isotopic homologues. It is a misnomer to call them *isotopomers*, because they are not isomers with the same atoms.

rev[3]

revGB

isotopomers

Isomers having the same number of each isotopic atom but differing in their positions. The term is a contraction of "isotopic isomer".

Note: Isotopomers can be either constitutional isomers (e.g., $CH_2DCH=O$ and $CH_3CD=O$) or isotopic stereoisomers (e.g., (R)- and (S)-CH_3CHDOH or (Z)- and (E)-$CH_3CH=CHD$).

See [11].

GB[3]

Kamlet-Taft solvent parameters

Quantitative measure of solvent *polarity*, based on the solvent's hydrogen-bond donor, hydrogen-bond acceptor, dipolarity/*polarizability*, and cohesive-pressure properties.

See [274,275,276,277,278,279].

120

1 See *solvent parameter*.
2 rev[3]
3 revGB-revPOC
4

Kaptein-Closs rules
5
6 Rules used to predict the sign of *chemically induced dynamic nuclear polarization*
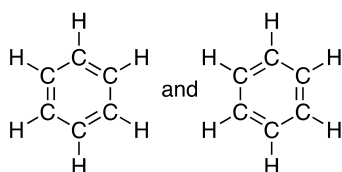7 (CIDNP) effects.
8 See [280,281,282].
9 GB
10

Kekulé structure
11
12 Representation of a *molecular entity* (usually *aromatic*) with fixed alternating single and
13 double bonds, in which interactions between multiple bonds are ignored.
14 *Example:* For benzene the Kekulé structures are

15
16 *Note:* The distinction among *Lewis structure*, *Kekulé structure*, and *line formula* is
17 now not generally observed, nor is the restriction to aromatic molecular entities.
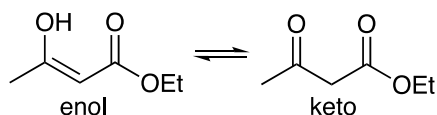18 See also *non-Kekulé structure*.
19 rev[3]
20 revGB-revPOC
21

keto-enol tautomerization
22
23 Interconversion of ketone and enol *tautomers* by hydron migration, accelerated by acid
24 or base catalysis.
25 *Example*:

26
27 See also *tautomerization*.
28

kinetic ambiguity
29
30 deprecated
31 See *kinetic equivalence*.

121

1 ~~GB~~
2

kinetic control (of product composition)
Conditions (including reaction times) that lead to reaction products in a proportion
governed by the relative rates of the parallel (forward) reactions by which those
products are formed, rather than by the *equilibrium* constants.
  See also *thermodynamic control*.
~~GB~~[3]

kinetic electrolyte effect
kinetic ionic-strength effect
General effect of an added electrolyte (i.e., other than, or in addition to, that due to its
possible involvement as a reactant or catalyst) on the *rate constant* of a reaction in
solution.
  Note 1: 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. 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 actions can sometimes 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. At higher concentrations the effect of an added electrolyte does not
necessarily involve a new reaction path, but merely the breakdown of the Debye-Hückel
law, whereby ionic activity coefficients vary with the ion.
  Note 2: Kinetic electrolyte effects are also called kinetic salt effects.
  Note 3: 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 is the secondary electrolyte effect on the
concentration of hydrogen ion (acting as catalyst) produced from the *ionization* of a
weak acid in a buffer solution. To eliminate the complication of kinetic electrolyte effects
in buffer solutions, it is advisable to maintain constant ionic strength.
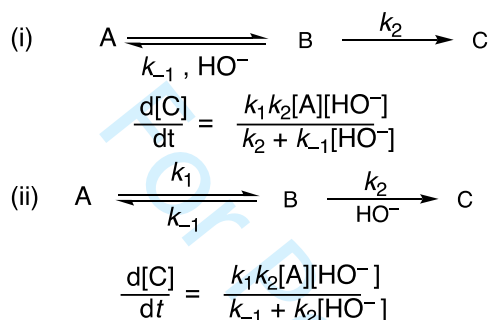 See [283].
  See also *common-ion effect*, *order of reaction*.
~~GB~~[3]

kinetic equivalence

122

1 Property of two reaction schemes that imply the same *rate law*.

2   *Example*: Schemes (i) and (ii) for the formation of C from A under conditions that B

3 does not accumulate as a reaction *intermediate*:

(i) $A \underset{k_{-1},\ HO^-}{\overset{}{\rightleftharpoons}} B \xrightarrow{k_2} C$

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][HO^-]}{k_2 + k_{-1}[HO^-]}$$

(ii) $A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow[HO^-]{k_2} C$

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][HO^-]}{k_{-1} + k_2[HO^-]}$$

16 Both equations for d[C]/dt are of the form

$$\frac{d[C]}{dt} = \frac{r\,[A][HO^-]}{1 + s[HO^-]}$$

18 where r and s are constants (sometimes called *rate coefficients*). The equations are

19 identical in their dependence on concentrations and do not distinguish whether HO^-

20 catalyses the formation of B and its reversion to A, or is involved only in its further

21 transformation to C. The two schemes are therefore kinetically equivalent.

22   GB[3]

Koppel-Palm solvent parameters

26 Quantitative measure of solvent *polarity*, based on the solvent's *permittivity*, refractive

27 index, *basicity* or *nucleophilicity*, and *acidity* or *electrophilicity*.

28   See [284].

29   See *solvent parameter*.

30   rev[3]

31   revGB

Kosower *Z* value

34   See *Z-value*.

35   GB[3]

labile

38 Property of a *chemical species* that is relatively *unstable* and *transient* or reactive.

123

1   *Note:* This term must not be used without explanation of the intended meaning.

2   See also *inert*, *persistent*, *reactivity*, *unreactive*.

3   GB[3]

4

5 **Laurence solvent parameters**

6 Quantitative measures of solvent *polarity*, based on the solvent's dispersion/induction

7 interactions, electrostatic interactions between permanent multipoles, solute Lewis

8 base/solvent Lewis acid interactions, and solute HBD/solvent HBA interactions.

9   See [285].

10

11 **least nuclear motion, principle of** (hypothesis of least motion)

12 Hypothesis that, for given reactants, the reactions involving the smallest change in

13 nuclear positions will have the lowest *energy of activation*.

14   *Note:* The basis for this hypothesis is that the energy of a structural deformation

15 leading toward reaction is proportional to the sum of the squares of the changes in

16 nuclear positions, which holds only for small deformations and is therefore not always
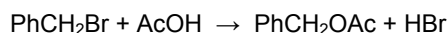
17 valid.

18   See [8,286].

19   rev[3]

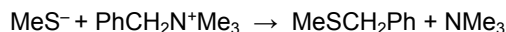20   revGB

21

22 **leaving group**

23 Species (charged or uncharged) that carries away the bonding electron pair when it

24 becomes detached from another fragment in the residual part of the *substrate*.

25   *Example 1*: In the heterolytic *solvolysis* of (bromomethyl)benzene (benzyl bromide)

26 in acetic acid

27

28       $PhCH_2Br + AcOH \rightarrow PhCH_2OAc + HBr$

29

30 the leaving group is Br^-.

31   *Example 2*: In the reaction

32

33       $MeS^- + PhCH_2N^+Me_3 \rightarrow MeSCH_2Ph + NMe_3$

34

35 the leaving group is NMe_3.

36   *Note:* The historical term "leaving group" is ambiguous, because in the heterolysis of

37 R–X, both R^+ and X^- are fragments that leave from each other. For that reason, X^- (as

38 well as Br^- and NMe_3 in examples 1 and 2) can unambiguously be called nucleofuges,

39 whereas R^+ is an electrofuge.

40   See also *electrofuge*, *entering group*, *nucleofuge*.

41   rev[3]

124

1 ~~revGB-revPOC~~

2

3 **Leffler's relation**

4 Leffler's assumption

5 In a series of elementary reactions the changes in Gibbs activation energies are often

6 found to be proportional to the changes in Gibbs energies for the overall reaction.

7

8 $$\delta \, \Delta^{\ddagger}G = \alpha \, \Delta_r G^0$$

9

10 This relation was interpreted in terms of the simple assumption that a small change in

11 any transition-state property $P_{\ddagger}$ is a linear combination of changes in reactant- and

12 product-state properties, P_R and P_P.

13

14 $$\delta P_{\ddagger} = \alpha \, \delta P_P + (1 - \alpha) \, \delta P_R$$

15

16 Within the limits of this assumption, the parameter α is an approximate measure of the

17 fractional displacement of the transition state along the *minimum-energy reaction path*

18 from reactants to products.

19   See [109].

20   *Note:* There are many exceptions to the validity of Leffler's assumption that α is a

21 measure of the position of the transition state.

22   See [287].

23   See *Hammond postulate*.

24 rev[3]

25 ~~revGB-revPOC~~

26

27 **left-to-right convention**

28 Arrangement of the structural formulae of the reactants so that the bonds to be made

29 or broken form a linear array in which the *electron pushing* proceeds from left to right.

30   See [288].

31 ~~GB~~[3]

32

33 **levelling effect**

34 Tendency of a solvent to make all *Brønsted acid*s whose *acidity* exceeds a certain value

35 appear equally acidic.

36   *Note 1:* This phenomenon is due to the complete transfer of a hydron to a Brønsted-

37 basic solvent from a dissolved acid stronger than the *conjugate acid* of the solvent. The

38 only acid present to any significant extent in all such solutions is the *lyonium ion*.

125

Note 2: 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.

Note 3: A corresponding levelling effect applies to strong bases in *protogenic* solvents.

~~GB~~[3]

Lewis acid

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.

Example:

Me_3B (Lewis acid) + $:NH_3$ (Lewis base) $\rightarrow$ $Me_3B^-\!-\!N^+H_3$ (Lewis adduct)

See also *coordination*.

~~GB~~[3]

Lewis acidity

Thermodynamic tendency of a substrate to act as a *Lewis acid*.

Note 1: This property is defined quantitatively by the *equilibrium* constant or Gibbs energy for *Lewis adduct* formation of a series of Lewis acids with a common reference *Lewis base*.

Note 2. An alternative measure of Lewis acidity in the gas phase is the enthalpy of *Lewis adduct* formation for that Lewis acid with a common reference *Lewis base*.

See also *electrophilicity*, *Lewis basicity*.

rev[3]

~~revGB~~

Lewis adduct

Adduct formed between a *Lewis acid* and a *Lewis base*.

~~GB~~[3]

Lewis base

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*.

~~GB~~[3]

Lewis basicity

126

1 Thermodynamic tendency of a substance to act as a *Lewis base*.

2   *Note 1:* This property is defined quantitatively by the equilibrium constant or Gibbs
3 energy of *Lewis adduct* formation for that Lewis base with a common reference *Lewis*
4 *acid*.

5   *Note 2:* An alternative measure of Lewis *basicity* in the gas phase is the enthalpy of
6 *Lewis adduct* formation for that Lewis base with a common reference *Lewis acid*.

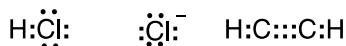7   See also *donicity*, *Lewis acidity*, *nucleophilicity*, *proton affinity*.

8   rev[3]
9   revGB

10

11 **Lewis structure**

12 electron-dot structure, Lewis formula

13 Representation of molecular structure in which (a) nonbonded valence electrons are
14 shown as dots placed adjacent to the atoms with which they are associated and in
15 which (b) a pair of bonding valence electrons in a *covalent bond* is shown as two dots
16 between the bonded atoms, and in which (c) formal charges (e.g., +, −, 2+) are attached
17 to atoms to indicate the difference between the nuclear charge (atomic number) and
18 the total number of electrons associated with that atom, on the formal basis that bonding
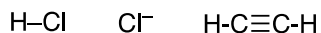19 electrons are shared equally between atoms they join.

20   *Examples*:

$$H:\overset{..}{\underset{..}{Cl}}: \qquad :\overset{..}{\underset{..}{Cl}}:^{-} \qquad H:C:::C:H$$

21

22   *Note 1:* A double bond is represented by two pairs of dots, and a triple bond by three
23 pairs, as in the last example above.

24   *Note 2:* Bonding pairs of electrons are usually denoted by lines, representing
25 covalent bonds, as in *line formula*s, rather than as a pair of dots, and the lone pairs are
26 sometimes omitted.

27   *Examples*:

$$H–Cl \qquad Cl^{-} \qquad H-C≡C-H$$

28

29   *Note 3:* The distinction among Lewis structure, *Kekulé structure*, and *line formula* is
30 now not generally observed.

31   rev[3]
32   revGB

33

34 **lifetime (mean lifetime)**

35 τ

36 Time needed for the concentration of a *chemical species* that decays in a first-order
37 process to decrease to 1/e of its original value. i.e., $c(t = \tau) = c(t = 0)/e$.

127

1   *Note 1:* Statistically, it represents the mean life expectancy of the species.

2   *Note 2:* Mathematically: $\tau = 1/k = 1/(\Sigma_i k_i)$ where k_i is the first-order *rate constant* for

3 the *i*-th decay process of the species.

4   *Note 3:* Lifetime is sometimes applied to processes that are not first-order. However,

5 in such cases the lifetime depends on the initial concentration of the entity or of a

6 *quencher* and, therefore, only an initial lifetime can be defined. In this case, it should be

7 called *decay time*.

8   See [9].

9   See also *chemical relaxation*, *half-life*, *rate of reaction*.

10   ~~GB~~[3]

11

12 **ligand**

13 Atom or *group* bound to a central atom in a polyatomic *molecular entity* (if it is possible

14 to indicate such a central atom).

15   See [29].

16   *Note 1:*The term is generally used in connection with metallic central atoms.

17   *Note 2:* In biochemistry a part of a polyatomic *molecular entity* may be considered

18 central, and atoms, groups, or molecules bound to that part are considered ligands.
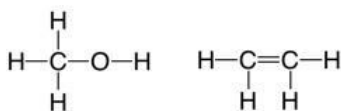
19   See [289], p. 335.

20   ~~GB~~[3]

21

22 **line formula**

23 Two-dimensional representation of *molecular entities* in which atoms are shown joined

24 by lines representing single bonds (or multiple lines for multiple bonds), without any

25 indication or implication concerning the spatial direction of bonds.

26   *Examples:* methanol, ethene

27

28   See also *condensed formula, Kekulé formula, Lewis formula, skeletal formula.*

29   rev[3]

30   ~~revGB-revPOC~~

31

32 **linear free-energy relation**

33 linear Gibbs-energy relation

34   ~~GB~~[3]

35

36 **linear Gibbs-energy relation**

37 linear free-energy relation (LFER)

128

1   Linear correlation between the logarithm of a *rate constant* or *equilibrium* constant for
2   a series of reactions and the logarithm of the rate constant or equilibrium constant for a
3   related series of reactions.
4   Typical examples of such relations are the *Brønsted relation* and the *Hammett*
5   *equation* (see also *σ-value*).
6   *Note:* The name arises because the logarithm of the value of an equilibrium constant
7   (at constant temperature and pressure) is proportional to a standard Gibbs energy (free
8   energy) change, and the logarithm of the value of a rate constant is a linear function of
9   the Gibbs energy (free energy) of activation.
10   GB[3]
11

linear solvation-energy relationship (LSER)
13 Application of *solvent parameter*s in the form of a single- or multi-parameter equation
14 expressing the solvent effect on a given property: e.g., *rate of reaction*, *equilibrium*
15 constant, spectroscopic shift.
16   *Note:* The solvent effect may be estimated as a linear combination of elementary
17 effects on a given property P, relative to the property P_0 in the reference solvent:
18

19      $P - P_0 = a\,A + b\,B + p\,DP\ldots$
20

21 where A, B, DP, etc. are acidity, basicity, dipolarity, etc. parameters, and a, b, p… are
22 the sensitivity of the property to each effect.
23   See *Catalán solvent parameters*, *Dimroth-Reichardt E_T parameter*, *Kamlet-Taft*
24 *solvent parameters*, *Koppel-Palm solvent parameters*, *Laurence solvent parameters*,
25 *Z-value*.
26   rev[3]
27   revGB
28

line-shape analysis
30 Method for determination of *rate constant*s for dynamic chemical exchange from the
31 shapes of spectroscopic signals, most often used in nuclear magnetic resonance
32 spectroscopy.
33   GB[3]
34

Lineweaver-Burk plot
36   See *Michaelis-Menten kinetics*.
37   GB[3]
38

lipophilic

129

Feature of *molecular entities* (or parts of molecular entities) that have a tendency to dissolve in fat-like solvents (e.g., hydrocarbons).

See also *hydrophilic*, *hydrophobic interaction*.

rev[3]

~~GB~~

London forces

dispersion forces

Attractive forces between molecules due to their mutual *polarizability*.

Note: London forces are the principal components of the forces between nonpolar molecules.

See [290].

See also *van der Waals forces*.

~~GB~~[3]

lone (electron) pair (nonbonding electron pair)

Two spin-paired electrons localized in the valence shell on a single atom.

Note: In structural formulas lone pairs should be designated as two dots.

See also *Lewis structure*.

rev[3]

~~GB~~

LUMO

Acronym for Lowest Unoccupied Molecular Orbital

See *frontier orbitals*.

rev[3]

~~GB~~

lyate ion

Anion produced by *hydron* (proton, deuteron, triton) removal from a solvent molecule.

Example: the hydroxide ion is the lyate ion of water.

~~GB~~[3]

lyonium ion

Cation produced by *hydronation* (protonation, deuteronation, tritonation) of a solvent molecule.

Example: $CH_3OH_2^+$ is the lyonium ion of methanol.

See also *onium ion*.

~~GB~~[3]

130

macroscopic diffusion control
See *mixing control*.
~~GB~~[3]

magnetic equivalence
Property of nuclei that have the same resonance frequency in nuclear magnetic resonance spectroscopy and also identical spin-spin interactions with each nucleus of a neighbouring group.
Note 1: The spin-spin interaction between magnetically equivalent nuclei is not manifested in the spectrum, and has no effect on the multiplicity of the respective NMR signals.
Note 2: Magnetically equivalent nuclei are necessarily chemically equivalent, but the reverse is not necessarily true.
~~GB~~[3]

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.
Note: 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*.
~~GB~~[3]

Marcus equation
General expression that correlates the *Gibbs energy of activation* ($\Delta^{\ddagger}G$) with the Gibbs energy of the reaction ($\Delta_r G^{\circ}$)

$$\Delta^{\ddagger}G \ = \ (\lambda/4)(1 + \Delta_r G^{\circ}/\lambda)^2 \ = \ \Delta^{\ddagger}G_o \ + \ {}^1/_2\, \Delta_r G^{\circ} \ + \ (\Delta_r G^{\circ})^2/(16\, \Delta^{\ddagger}G_o)$$

where λ is the *reorganization energy* and $\Delta^{\ddagger}G_o$ is the *intrinsic barrier*, with $\lambda = 4\Delta^{\ddagger}G_o$.
Note: Originally developed for outer-sphere electron transfer reactions, the Marcus equation applies to many atom- and group-transfer reactions. The Marcus equation captures earlier ideas that reaction thermodynamics can influence reaction barriers: e.g., the *Brønsted relation* (1926), the *Bell-Evans-Polanyi principle* (1936-38), *Leffler's relation* (1953), and the *Hammond postulate* (1955) [227]. It also implies that changes in intrinsic barriers may dominate over changes of reaction Gibbs energies and thus

131

account for the fact that reaction rates may not be controlled by the relative thermodynamic stabilities of the products.

See [291,292,293,294,295,296].

rev[3]

Markovnikov (Markownikoff) rule

Statement of the common mechanistic observation that in electrophilic addition reactions the more electropositive atom (or part) of a polar molecule becomes attached to the carbon bearing more hydrogens.

Note 1: This rule was originally formulated by Markownikoff (Markovnikov) as "In the addition of hydrogen halides to [unsaturated] hydrocarbons, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms".

Note 2: This rule can be rationalized as the addition of the more electropositive atom (or part) of the polar molecule to the end of the multiple bond that would result in the more stable *carbenium* ion (regardless of whether the carbenium ion is a stable *intermediate* or a transient structure along the *minimum-energy reaction path*).

Note 3: Addition in the opposite sense, as in radical addition reactions, is commonly called anti-Markovnikov addition.
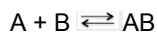
See [297].

GB[3]

mass action, law of

Statement that the velocity of a reaction depends on the active mass, i.e., the concentrations of the reactants.

Example: for an association reaction (1) and its reverse (2)

$$A + B \quad \rightarrow \quad AB \qquad (1)$$
$$AB \quad \rightarrow \quad A + B \qquad (2)$$

the forward velocity is $v_1 = k_1 [A][B]$, with k_1 the *rate constant* for the association reaction. For the dissociation reaction 2 the velocity is $v_2 = k_2 [AB]$. This is valid only for *elementary reactions*. Furthermore, the law of mass action states that, when a reversible chemical reaction reaches *equilibrium* at a given temperature, the forward rate is the same as the backward rate. Therefore, the concentrations of the chemicals involved bear a constant relation to each other, described by the equilibrium constant, i.e., for

$$A + B \rightleftharpoons AB$$

132

1　in equilibrium, $v_1 = k_1$ [A][B] $= v_2 = k_2$ [AB] and one form of the equilibrium constant for
2　the above chemical reaction is the ratio

3

4　　　$$K_c = \frac{[AB]}{[A][B]} = \frac{k_1}{k_2}$$

5

6　　*Note*: First recognized in 1864 as the kinetic law of mass action by Guldberg and
7　Waage, who first introduced the concept of dynamic equilibrium, but incorrectly
8　assumed that the rates could be deduced from the stoichiometric equation [298]. Only
9　after the work of Horstmann [299] and van't Hoff [300] a mathematical derivation of the
10　reaction rates considering the *order of the reaction* involved was correctly made.
11　　See also [301,302,303].
12　rev[3]
13　revGB-revPOC
14

15　**matrix isolation**
16　Technique for preparation of a reactive or unstable species by dilution in an inert solid
17　matrix (argon, nitrogen, etc.), usually condensed on a window or in an optical cell at low
18　temperature, to preserve its structure for identification by spectroscopic or other means.
19　　See [304].
20　GB[3]
21

22　**Mayr-Patz equation**
23　*Rate constant*s for the reactions of sp^2-hybridized *electrophile*s with *nucleophile*s can
24　be expressed by the correlation

25

26　　　lg $[k/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})] = s_N(E + N)$,

27

28　where E is the nucleophile-independent *electrophilicity* parameter, N is the electrophile-
29　independent *nucleophilicity* parameter, and s_N is the electrophile-independent
30　nucleophile-specific susceptibility parameter.
31　　*Note 1:* This equation is equivalent to the conventional *linear Gibbs energy
32　relationship* lg $k = Nu + s_N E$, where $Nu = s_N N$. The use of N is preferred, because it
33　provides an approximate ranking of relative reactivities of nucleophiles.
34　　*Note 2:* The correlation should not be applied to reactions with bulky electrophiles,
35　where steric effects cannot be neglected. Because of the way of parametrization, the
36　correlation is applicable only if one or both reaction centres are carbon.
37　　*Note 3:* As the E parameters of the reference electrophiles are defined as solvent-
38　independent, all solvent effects are shifted into the parameters N and s_N.
39　　*Note 4:* The equation transforms into the *Ritchie equation* for $s_N = 1$.

133

Note 5: Applications to S_N2-type reactions are possible if an electrophile-specific susceptibility parameter is introduced.

See [305,306,307,308].

See also *Ritchie equation, Swain-Scott equation*.

The Mayr scale is available at http://www.cup.lmu.de/oc/mayr/DBintro.htm

mechanism

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 *intermediate*s, products, and *transition state*s.

Note 1: 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.

Note 2: Inferences concerning the electronic motions that dynamically interconvert successive species along the *reaction path* (as represented by curved arrows, for example) are often included in the description of a mechanism.

rev[3]

revGB-revPOC

mechanism-based inhibition (suicide inhibition)

Irreversible *inhibition* of an enzyme by formation of covalent bond(s) between the enzyme and the inhibitor, which is a substrate analogue that is converted by the enzyme into a species that reacts with the enzyme.
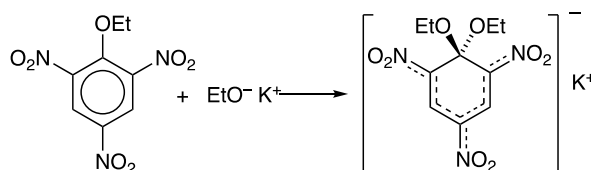
rev[3]

revGB-revPOC

medium

Phase (and composition of the phase) in which *chemical species* and their reactions are studied.

GB[3]

**Meisenheimer adduct** (Jackson-Meisenheimer adduct)

Lewis adduct formed in nucleophilic aromatic substitution from a *nucleophile* (*Lewis base*) and an *aromatic* or heteroaromatic compound,

134

Note 1: In cases where the substrate lacks electron-withdrawing groups, and depending also on the nucleophile, the Meisenheimer adduct is not a minimum on the *potential-energy surface* but a *transition state*.

See [309,310,311,312].

Note 2: Analogous cationic adducts, such as
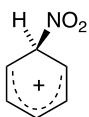
which are *intermediate*s in *electrophilic* aromatic *substitution* reactions, are instead called Wheland intermediates or *σ-adduct*s (or the discouraged term σ-complexes).

See [313,314].

rev[3]

~~revGB-revPOC~~

melting point (corrected/uncorrected)

Temperature at which liquid and solid phases coexist in equilibrium, as measured with a thermometer whose reading was corrected (or not) for the emergent stem that is in ambient air.

Note: In current usage the qualification often means that the thermometer was/(was not) calibrated or that its accuracy was/(was not verified). This usage is inappropriate and should be abandoned.

~~GB~~[3]

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 assigned to the fragments.

See [315,316].

~~GB~~[3]

mesomerism, mesomeric structure

obsolete

Resonance, *resonance form*

rev[3]

~~revGB~~

mesophase

135

1 Phase of a liquid crystalline compound between the crystalline and the isotropic liquid
2 phase.
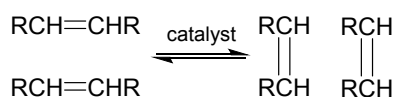3   See [317].
4   difGB[3]
5

6 **metastable (chemical species)**
7 deprecated
8 *Transient (chemical species).*
9   GB[3]
10

11 **metathesis**
12 Process formally involving the redistribution of fragments between similar *chemical*
13 *species* so that the bonds to those fragments in the products are identical (or closely
14 similar) to those in the reactants.
15   *Example*:

$$RCH\!=\!CHR \quad \xrightarrow{\text{catalyst}} \quad \begin{matrix} RCH \\ \| \\ RCH \end{matrix} \quad \begin{matrix} RCH \\ \| \\ RCH \end{matrix}$$

$$RCH\!=\!CHR$$

16
17   *Note:* The term has its origin in inorganic chemistry, with a different meaning, but that
18 older usage is not applicable in physical organic chemistry.
19   GB[3]
20

21 **micellar catalysis**
22 Acceleration of a *chemical reaction* in solution by the addition of a surfactant at a
23 concentration higher than its *critical micelle concentration* so that the reaction can
24 proceed in the environment of surfactant aggregates (*micelles*).
25   *Note 1:* Rate enhancements may be due to a higher concentration of the reactants
26 in that environment, or to a more favourable orientation and solvation of the species, or
27 to enhanced *rate constant*s in the micellar pseudophase of the surfactant aggregate.
28   *Note 2:* Micelle formation can also lead to a decreased reaction rate.
29   See [318].
30   See also *catalyst*.
31   GB[3]
32

33 **micelle**
34 Aggregate of 1- to 1000-nm diameter formed by surfactants in solution, which exists in
35 equilibrium with the molecules or ions from which it is formed.
36   See [135].
37   See also *inverted micelle*.

136

1 rev[3]
2 ~~revGB-revPOC~~
3
4 **Michaelis-Menten kinetics**
5 Appearance of saturation behavior in the dependence of the initial _rate of reaction_ v_0
6 on the initial concentration $[S]_0$ of a _substrate_ when it is present in large excess over
7 the concentration of an enzyme or other _catalyst_ (or reagent) E, following the equation,
8
9      $v_0 = V_{max} [S]_0 /(K_M + [S]_0)$,
10
11 where v_0 is the observed initial rate, V_{max} is its limiting value at substrate saturation (i.e.,
12 when $[S]_0 \gg K_M$, so that all enzyme is bound to substrate), and K_M is the substrate
13 concentration at which $v_0 = V_{max}/2$.
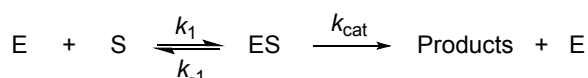14   _Note 1:_ Empirical definition, applying to any reaction that follows an equation of this
15 general form.
16   _Note 2:_ Often only initial rates are measured, at low conversion, so that $[S]_0$ can be
17 considered as time-independent but varied from run to run.
18   _Note 3:_ The parameters V_{max} and K_M (the Michaelis constant) can be evaluated from
19 slope and intercept of a linear plot of $1/v_0$ against $1/[S]_0$ (Lineweaver-Burk plot) or from
20 slope and intercept of a linear plot of $[S]_0/v_0$ against $[S]_0$ (Eadie-Hofstee plot), but a
21 nonlinear fit, which is readily performed with modern software, is preferable.
22   _Note 4:_ This equation is also applicable to the condition where E is present in large
23 excess, in which case [E] appears in the equation instead of $[S]_0$.
24   _Note 5:_ The term has been used to describe reactions that proceed according to the
25 scheme

$$E \; + \; S \; \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \; ES \; \xrightarrow{k_{cat}} \; \text{Products} \; + \; E$$

26
27
28 in which case $K_M = (k_{-1} + k_{cat})/k_1$ (Briggs-Haldane conditions). It has more usually been
29 applied only to the special case in which $k_{-1} \gg k_{cat}$ and $K_M = k_{-1}/k_1$; in this case K_M is a
30 true dissociation constant (Michaelis-Menten conditions).
31   See [319,320].
32 ~~GB~~[3]
33
34 **microscopic diffusion control (encounter control)**
35 Observable consequence of the limitation that the rate of a bimolecular _chemical_
36 _reaction_ in a homogeneous medium cannot exceed the rate of encounter of the reacting
37 _molecular entities_.
38   _Note:_ The maximum _rate constant_ is usually in the range 10^9 to 10^{10} dm^3 mol^{-1} s^{-1} in
39 common solvents at room temperature.

137

See also *mixing control*.
rev[3]
revGB

microscopic reversibility, principle of
In a reversible reaction the *mechanism* in one direction is exactly the reverse of the mechanism in the other direction.
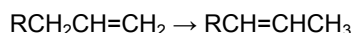See also *chemical reaction*, *detailed balancing*.
revGB[3]

migration
Transfer (usually *intramolecular*) of an atom or *group* during the course of a *molecular rearrangement*.
Example (of a hydrogen migration):

$$RCH_2CH=CH_2 \rightarrow RCH=CHCH_3$$

rev[3]
revGB

migratory aptitude
Tendency of a *group* to participate in a *molecular rearrangement*, relative to that of another group, often in the same molecule.
Example: In the Baeyer-Villiger rearrangement of $PhCOCH_3$, via *intermediate* $PhC(OH)(OOCOAr)CH_3$, the major product is CH_3COOPh, by phenyl migration, rather than $PhCOOCH_3$.
Note: 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.
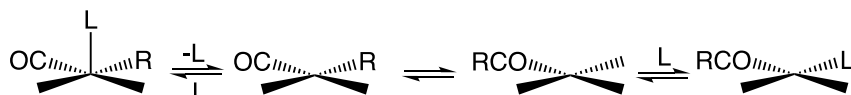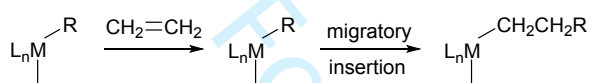rev[3]
revGB

migratory insertion
Reaction that involves the *migration* of a *group* to another position on a metal centre, with insertion of that group into the bond between the metal and the group that is in that other position.
*Example*s:
CO insertion

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Ziegler-Natta reaction

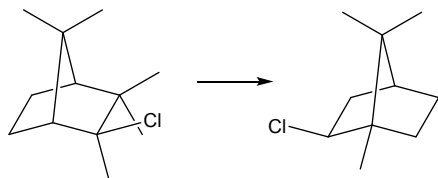*Note:* On repetition of the reaction the substituent alternates between the two positions.

rev[3]

~~revGB~~

minimum structural change, principle of

Principle that a *chemical reaction* is expected to occur with a minimum of bond changes or with a minimum redistribution of electrons (although more complex reaction cascades are also possible).

Example:

where the transfer of Cl is accompanied by migration of only one carbon, rather than a more extensive *molecular rearrangement* involving *migration* of three methyls.

See [286].

See also *least nuclear motion, principle of.*

rev[3]

~~revGB~~

minimum-energy reaction path (MERP)

Path of steepest-descent from a saddle point on a *potential-energy surface* in each direction towards adjacent energy minima; equivalent to the energetically easiest route from reactants to products.

See *intrinsic reaction coordinate.*

See [8].

139

1 GB
2

3 **mixing control**
4 Experimental limitation of the rate of reaction in solution by the rate of mixing of
5 solutions of the two reactants.
6 *Note 1:* Mixing control can occur even when the reaction *rate constant* is several
7 orders of magnitude less than that for an encounter-controlled reaction.
8 *Note 2:* Analogous (and more important) effects of the limitation of reaction rates by
9 the rate of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas)
10 systems.
11 See [321].
12 See also *microscopic diffusion control*, *stopped flow*.
13 GB[3]
14
15
16

17 **Möbius aromaticity**
18 Feature of a monocyclic array of π orbitals in which there is a single out-of-phase
19 overlap (or, more generally, an odd number of out-of-phase overlaps), whereby the
20 pattern of aromatic character is opposite to Hückel systems; with $4n$ π electrons it is
21 stabilized (aromatic), whereas with $4n + 2$ it is destabilized (antiaromatic).
22 *Note 1:* The name is derived from the topological analogy of such an arrangement of
23 orbitals to a Möbius strip.
24 *Note 2:* The concept has been applied to transition states of pericyclic reactions.*Note*
25 *3:* In the electronically excited state $4n + 2$ Möbius π-electron systems are stabilized,
26 and 4n systems are destabilized.
27 *Note 4:* A few examples of ground-state Möbius π systems are known [322,323].
28 See [324,325].
29 See also *aromatic*, *Hückel (4n + 2) rule*.
30 rev[3]
31 revGB
32

33 **molecular entity**
34 Any constitutionally or isotopically distinct atom, *molecule*, ion, *ion pair*, *radical*, *radical*
35 *ion*, *complex*, *conformer*, etc., identifiable as a separately distinguishable entity.
36 *Note 1:* Molecular entity is used in this glossary as a general term for singular entities,
37 irrespective of their nature, while *chemical species* stands for sets or ensembles of
38 molecular entities. Note that the name of a substance may refer to the molecular entity
39 or to the chemical species, e.g., methane, may mean either a single molecule of CH_4

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(molecular entity) or an ensemble of such species, specified or not (chemical species), participating in a reaction.

Note 2: 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 may be necessary to distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the molecule.

GB[3]

molecular formula
List of the elements in a *chemical species* or *molecular entity*, with subscripts indicating how many atoms of each element are included.

Note: In organic chemistry C and H are listed first, then the other elements in alphabetical order.

See [29].

See also *empirical formula*.

molecular mechanics (MM**)** (empirical force-field calculation)
Computational method intended to give estimates of structures and energies for molecules.

Note: Even though such calculations can be made with either classical or quantum mechanics (or both), the term molecular mechanics is widely understood as a classical mechanics method that does not explicitly describe the electronic structure of the molecular entities. It is based on the assumption of preferred bond lengths and angles, deviations from which lead to strain, and the existence of torsional interactions and attractive and repulsive *van der Waals* and Coulombic forces between non-bonded atoms, all of which are parametrized to fit experimental properties such as energies or structures. In contrast, in the quantum mechanical implementation no such assumptions/parameters are needed.

See [8,326].

rev[3]

revGB

molecular metal
Non-metallic material whose properties, such as conductivity, resemble those of metals, usually following oxidative doping.

Example: polyacetylene following oxidative doping with iodine.

GB[3]

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1 **molecular orbital**
2 One-electron *wavefunction* describing a single electron moving in the field provided by
3 the nuclei and all other electrons of a *molecular entity* of more than one atom.
4   *Note 1:* Molecular orbitals describing valence electrons are often delocalized over
5 several atoms of a molecule. They are conveniently expressed as linear combinations
6 of *atomic orbital*s. They can be described as two-centre, multi-centre, etc. in terms of
7 the number of nuclei (or "centres") encompassed.
8   *Note 2:* For molecules with a plane of symmetry, a molecular orbital can be classed
9 as sigma (σ) or pi (π), depending on whether the orbital is symmetric or antisymmetric
10 with respect to reflection in that plane.
11   See *atomic orbital*, *orbital*.
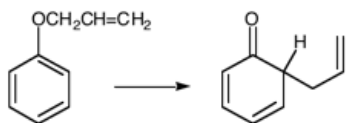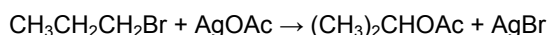12   See [8].
13 rev[3]
14 revGB
15

16 **molecular rearrangement**
17 Reaction of a *molecular entity* that involves a change of *connectivity*.
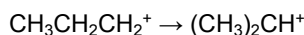18   *Note 1*: The simplest type of rearrangement is an *intramolecular* reaction in which
19 the product is isomeric with the reactant (intramolecular *isomerization*). An example is
20 the first step of the Claisen rearrangement.
21

22
23   *Note 2*: The definition of molecular rearrangements includes reactions in which there
24 is a *migration* of an atom or bond (unexpected on the basis of the principle of *minimum*
25 *structural change*), as in the reaction
26
27 $CH_3CH_2CH_2Br + AgOAc \rightarrow (CH_3)_2CHOAc + AgBr$
28
29 where the rearrangement step can formally be represented as the "1,2-shift" of hydride
30 between adjacent carbon atoms in a carbocation
31
32      $CH_3CH_2CH_2^+ \rightarrow (CH_3)_2CH^+$
33
34   *Note 3*: Such migrations also occur in *radical*s, e.g.,
35
36      $PhC(CH_3)_2–CH_2\cdot \rightarrow \cdot C(CH_3)_2CH_2Ph$ (neophyl rearrangement)

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Note 4: The definition also includes reactions in which an entering group takes up a different position from the *leaving group*, with accompanying *bond* migration, such as in the "allylic rearrangement":

$$(CH_3)_2C=CHCH_2Br + HO^- \rightarrow (CH_3)_2C(OH)CH=CH_2 + Br^-$$
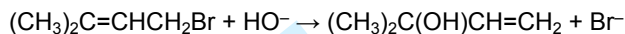
Note 5: A distinction can be made between intramolecular rearrangements (or "true" molecular rearrangements) and *intermolecular* rearrangements (or apparent rearrangements). In the former case the atoms and groups that are common to a reactant and a product never separate into independent fragments during the rearrangement stage, whereas in an intermolecular rearrangement a migrating *group* becomes completely free from the parent molecule and is re-attached to a different position in a subsequent step, as in the Orton reaction:

$$C_6H_5N(Cl)COCH_3 + HCl \rightarrow C_6H_5NHCOCH_3 + Cl_2$$
$$\rightarrow o\text{- and } p\text{-}ClC_6H_4NHCOCH_3 + HCl$$
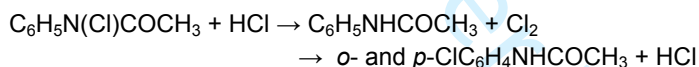
See [327].

rev[3]

~~revGB~~

molecular recognition

Attraction between specific molecules through noncovalent interactions that often exhibit electrostatic and stereochemical complementarity between the partners

Note: The partners are usually designated as *host* and *guest*, where the host recognizes and binds the guest with high selectivity over other molecules of similar size and shape.

molecularity

Number of reactant *molecular entities* that are involved in the "microscopic chemical event" constituting an *elementary reaction*.

Note 1: 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.

Note 2: A reaction with a molecularity of one is called "*unimolecular*", one with a molecularity of two "bimolecular", and of three "termolecular".

See also *chemical reaction*, *order of reaction*.

~~GB~~[3]

molecule

143

1 An electrically neutral entity consisting of more than one atom.

2 *Note:* Rigorously, a molecule must correspond to a depression on the *potential-*
3 *energy surface* that is deep enough to confine at least one vibrational state.

4 See also *molecular entity*.

5 ~~GB~~[3]

6

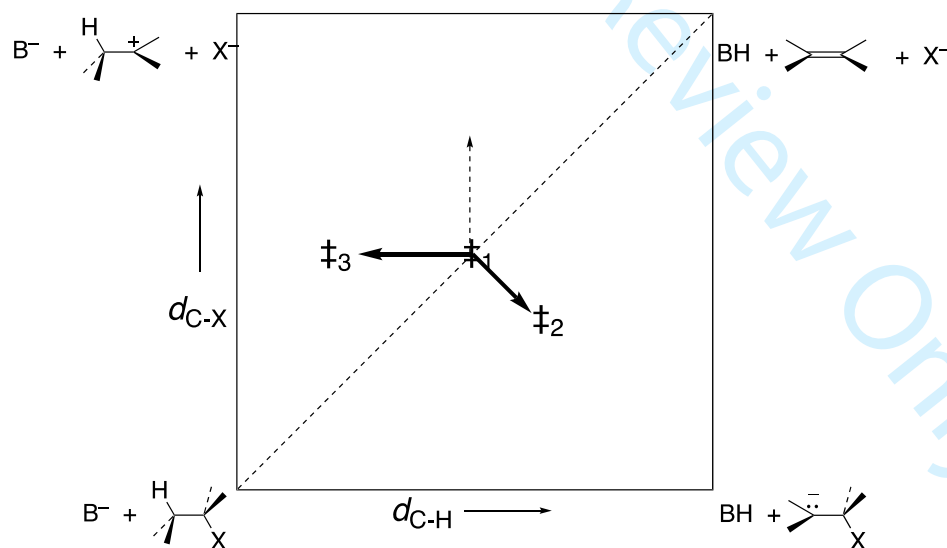## 7 More O'Ferrall - Jencks diagram

8 Conceptual visualization of the *potential-energy surface* for a reacting system, as a
9 function of two coordinates, usually bond lengths or bond orders.

10 *Note 1:* The diagram is useful for analyzing structural effects on transition-state
11 geometry and energy.

12 *Note 2:* According to the *Hammond postulate*, stabilization of the products relative to
13 the reactants (an effect parallel to the *minimum-energy reaction path*, MERP) shifts the
14 transition state away from the product geometry, whereas destabilization of the
15 products shifts the *transition state* towards the product geometry. As first noted by
16 Thornton, stabilization of a structure located off the assumed MERP in a direction
17 perpendicular to it shifts the transition state toward that more stabilized geometry (a
18 *perpendicular effect*); destabilization shifts the transition state in the opposite direction.

19

22 *Figure*. More O'Ferrall-Jencks diagram for *β-elimination* reaction, with reactants,
23 products, and possible *intermediate*s at the four corners.

144

1   *Case 1*: In a concerted *elimination* the transition state ($\ddagger_1$) is a saddle point near the
2   centre of the diagram, and the assumed MERP follows close to the diagonal.
3   *Case 2*: If the *carbanion* intermediate is stabilized, the transition state shifts toward
4   that *intermediate*, to a transition state ($\ddagger_2$) in which the C–H bond is more extensively
5   broken and the C–X bond is more intact. Conversely, if the *carbocation* intermediate is
6   stabilized, the transition state shifts towards the top-left corner of the Figure, with less
7   C–H bond breaking and more C–X bond making
8   *Case 3*: If leaving group X$^-$ is stabilised, energy decreases along the dotted vertical
9   arrow. It follows that in the resulting transition state ($\ddagger_3$) the C–H bond is more intact but
10   there is little change in the C–X bond, the shift of the transition state is the resultant of
11   a parallel (Hammond) component away from the top-right corner and a perpendicular
12   (anti-Hammond) component towards the top-left corner, yielding a transition state ($\ddagger_3$)
13   with less C–H bond breaking but approximately no change in the extent of C–X bond
14   making.
15   See [229,328,329,330,331].
16   See also *Hammond Postulate*, *anti-Hammond effect*.
17   rev[3]
18   revGB
19
20   **Morse potential**
21   $V(r)$
22   (unit J)
23   Empirical function relating the potential energy of a molecule to the interatomic distance
24   r accounting for the anharmonicity of bond stretching:
25
26       $$V(r) \ = \ D_e\{1 - \exp[-a(r-r_e)]\}^2$$
27
28   where D_e is the *bond-dissociation energy*, r_e is the equilibrium bond length, and a is a
29   parameter characteristic of a given molecule.
30   See [8].
31   GB
32
33   **mu**
34   μ
35   (1) Symbol used to designate (as a prefix) a ligand that bridges two or more atoms.
36   *Note*: If there are more than two atoms being bridged, μ carries a subscript to denote
37   the number of atoms bridged.
38   (2) Symbol used to designate dipole moment as well as many other terms in physics
39   and physical chemistry.
40

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multi-centre bond

Bond in which an electron pair is shared among three or more atomic centres.

   Note 1: This may be needed when the representation of a *molecular entity* solely by localized two-electron two-centre *bonds* is unsatisfactory, or when there are not enough electrons to allow one electron pair shared between two adjacent atoms.

   Note 2: This is restricted to σ bonds and does not apply to species with delocalized π electrons.

   Examples include the three-centre bonds in diborane B_2H_6 and in *bridged carbocation*s.

   rev[3]

   revGB-revPOC

multident

multidentate

   See *ambident*.

   GB[3]

nanomaterial

Substance whose particles are in the size range of 1 to 100 nm.

   Note: This may have chemical properties different from those of the corresponding bulk material.

narcissistic reaction

Chemical reaction that can be described as the *automerization or* enantiomerization of a reactant into its mirror image (regardless of whether the reactant is *chiral*).

   Examples are cited under *degenerate rearrangement* and *fluxional*.
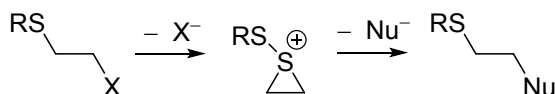
   See [332].

   rev[3]

   revGB-revPOC

neighbouring-group participation

Direct interaction of the reaction centre (usually, but not necessarily, an incipient *carbenium-ion* centre) with a lone pair of electrons of an atom or with the electrons of a σ or π bond contained within the parent molecule but not *conjugated* with the reaction centre.

   Example:

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Note 1: A distinction is sometimes made between n, σ, and π participation.

Note 2: The neighbouring group serves as a *nucleophile*, as in S_N2 reactions, except that the nucleophile is *intramolecular*, so that this step is *unimolecular*.

Note 3: A rate increase due to neighbouring-group participation is known as anchimeric assistance.

Note 4: Synartetic acceleration is the name given to the special case of participation by electrons on a substituent attached to a β-carbon, relative to the *leaving group* attached to the α-carbon, as in the example above. This term is deprecated.

See also *intramolecular catalysis*, *multi-centre bond*.

rev[3]

revGB

NHOMO

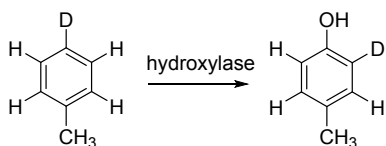Next-to-highest occupied *molecular orbital*.

See *subjacent orbital*.

rev[3]

GB

NIH shift

Intramolecular hydrogen *migration* that can be observed in enzymatic and chemical hydroxylations of *aromatic* rings, as evidenced by appropriate deuterium labelling, as in

Note 1: In enzymatic reactions the NIH shift is thought to derive from the rearrangement of arene oxide *intermediate*s, but other pathways have been suggested.

Note 2: NIH stands for National Institutes of Health, where the shift was discovered.

See [333].

GB[3]

nitrene

Generic name for the species HN and substitution derivatives thereof, containing an electrically neutral univalent nitrogen atom with four nonbonding electrons.

Note 1: Two nonbonding electrons may have antiparallel spins (singlet state) or parallel spins (triplet state).

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Note 2: The name is the strict analogue to *carbene* and, as a generic name, it is preferred to a number of alternative proposed (imene, imine radical, aminylene, azene, azylene, azacarbene, imin, imidogen).

See [97,334].

~~GB~~[3]

no-bond resonance

double-bond-no-bond resonance

Inclusion of one or more contributing structures that lack the σ bond of another contributing structure.

Example:
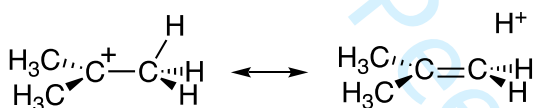
See *hyperconjugation*.

rev[3]

~~GB~~

nonclassical carbocation

Carbocation that has delocalized (bridged) bonding σ electrons.

See [89,335].

rev[3]

~~revGB~~

non-Kekulé structure

Compound with unpaired electrons for which no *Lewis structure*s are possible with all bonding electrons paired in single or double bonds.

Examples:

Note: For the second example ("trimethylenemethane") the *isomer* shown (valence tautomer methylidenecyclopropane) is a *Kekulé structure*.

See [336].

~~diffGB~~

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nucleofuge

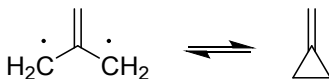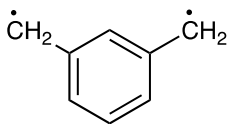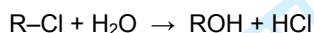*Leaving group* that carries away the bonding electron pair in a *nucleophilic substitution* reaction.

Example: In the *hydrolysis* of a chloroalkane, Cl⁻ is the nucleofuge.

R–Cl + H₂O → ROH + HCl

Note 1: Nucleofugality, commonly called leaving-group ability, characterizes the relative rates of atoms or groups to depart with the bonding electron pair from a reference substrate. Nucleofugality depends on the nature of the reference reaction and is not the reverse of *nucleophilicity*.

Note 2: Protofugality is a special type of nucleofugality, characterizing the relative rates of proton transfer from a series of *Brønsted acid*s H–X to a common *Brønsted base*.

See [194].

See also *electrofuge*, *nucleophile*.

rev[3]

revGB

nucleophile (n.), nucleophilic (adj.)

Reactant that forms a bond to its reaction partner (the *electrophile*) by donating both of its bonding electrons.

Note 1: A "*nucleophilic substitution* reaction" is a heterolytic reaction in which the reagent supplying the entering group acts as a nucleophile.

Example:

MeO⁻ (nucleophile) + EtCl → MeOEt + Cl⁻ (*nucleofuge*)
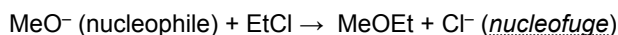
Note 2: Nucleophilic reagents are *Lewis base*s.

Note 3: The term "nucleophilic" is also used to designate the apparent polar character of certain *radical*s, as inferred from their higher relative reactivity with reaction sites of lower electron density.

See also *nucleophilicity, order of reaction*.

GB[3]

nucleophilic catalysis

Catalysis by a *Lewis base*, involving conversion of a substrate with low *electrophilicity* into an *intermediate* with higher electrophilicity.

Example 1: hydrolysis of acetic anhydride in aqueous solution, catalysed by 4-(dimethylamino)pyridine

149

1    $Me_2NC_5H_4N + (CH_3CO)_2O \rightarrow (Me_2NC_5H_4NCOCH_3)^+ + CH_3CO_2^-$
2   then $(Me_2NC_5H_4COCH_3)^+ + H_2O \rightarrow Me_2NC_5H_4N + CH_3CO_2H + H^+_{aq}$
3
4   *Example 2:* S_N2 reaction of CH_3CH_2Cl with HO^-, catalyzed by I^-:
5
6    $CH_3CH_2Cl + I^- \rightarrow Cl^- + CH_3CH_2I$, then $CH_3CH_2I + HO^- \rightarrow CH_3CH_2OH + I^-$
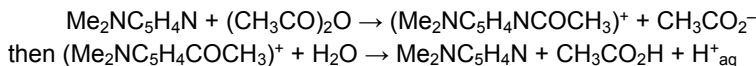7
8   See also *nucleophilicity*.
9   rev[3]
10   revGB-revPOC
11
12   **nucleophilic substitution**
13   Heterolytic reaction in which an entering group adds to the electrophilic part of the
14   substrate and in which the leaving group, or *nucleofuge*, retains both electrons of the
15   bond that is broken, whereupon it becomes another potential *nucleophile*.
16   *Example*:
17
18   CH_3Br (substrate) + HO^- (nucleophile) $\rightarrow CH_3OH + Br^-$ (nucleofuge)
19
20   *Note 1:* It is arbitrary to emphasize the nucleophile and ignore the feature that this is
21   also an electrophilic substitution, but the distinction depends on the nucleophilic nature
22   of the reactant that is considered to react with the *substrate*.
23   *Note 2:* Nucleophilic substitution reactions are designated as S_N1 or S_N2, depending
24   on whether they are unimolecular or bimolecular, respectively. Mechanistically, these
25   correspond to two-step and one-step processes, respectively. S_N1 reactions follow first-
26   order kinetics but S_N2 reactions do not always follow second-order kinetics.
27   See *order of reaction*, *rate coefficient.*
28
29
30   **nucleophilicity**
31   Relative reactivity of a *nucleophile* toward a common *electrophile*.
32   *Note 1*: The concept is related to *Lewis basicity*. However, whereas the Lewis
33   basicity of a base B: is measured by its *equilibrium* constant for *adduct* formation with
34   a common acid A, the nucleophilicity of a *Lewis base* B: is measured by the *rate
35   coefficient* for reaction with a common *substrate* A–Z, often involving formation of a
36   bond to carbon.
37   *Note 2: Protophilicity* is a special case of nucleophilicity, describing the relative rates
38   of reactions of a series of Lewis bases B: with a common *Brønsted acid* H–Z. The term
39   "protophilicity" is preferred over the alternative term "kinetic basicity" because *basicity*

150

refers to equilibrium constants, whereas "philicity" (like "fugality") refers to *rate constant*s.

See [192,193,307].

See also *Brønsted basicity*, *electrophilicity*, *Lewis basicity*, *Mayr-Patz equation*, *Ritchie equation*, *Swain-Scott equation*.

rev[3]

revGB

n-σ* delocalization (n-σ* no-bond resonance)

Delocalization of a lone pair (*n*) into an antibonding σ-orbital (σ*).

See also *anomeric effect*, *hyperconjugation*, *resonance*.

GB[3]

octanol-water partition ratio (K_{OW}):

Equilibrium concentration of a substance in octan-1-ol divided by its equilibrium concentration in water.

Note: This is a measure of the *lipophilicity* of a substance. It is used in pharmacological studies and in the assessment of environmental fate and transport of organic chemicals.

See [337,338].

See also *partition ratio*.

octet rule

Electron-counting rule that the number of lone-pair electrons on a first-row atom plus the number of electron pairs in that atom's bonds should be 8.

onium ion

(1) Cation derived by addition of a *hydron* to a mononuclear parent hydride of the nitrogen, chalcogen, and halogen family, e.g., H_4N^+ ammonium ion.

(2) Derivative formed by substitution of the above parent ions by univalent groups, e.g., $(CH_3)_2SH^+$ dimethylsulfonium (dimethylsulfanium), $(CH_3CH_2)_4N^+$ tetraethylammonium.

See [97].

See also *carbenium ion*, *carbonium ion*.

rev[3]

revGB

optical yield

Ratio of the optical purity of the product to that of the *chiral* precursor or reactant.

Note 1: This should not be confused with *enantiomeric excess*.

Note 2: The optical yield is not related to the chemical yield of the reaction.

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1 See [11].
2 See *stereoselectivity*.
3 ~~GB~~[3]
4

orbital (atomic or molecular)
Wavefunction depending on the spatial coordinates of only one electron.
Note: An orbital is often illustrated by sketching contours, often very approximate, on which the wavefunction has a constant value or by indicating schematically the envelope of the region of space in which there is an arbitrarily fixed high probability (say 95 %) of finding the electron occupying that region, and affixing also the algebraic sign (+ or −) of the wavefunction in each part of that region, or suggesting the sign by shading.
Examples:

1s   2p$_z$ sp^3 hybrid   bonding MO
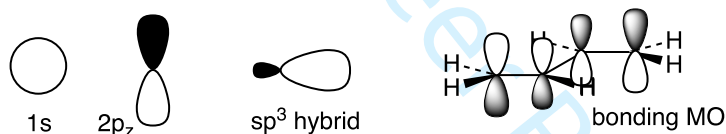
See *atomic orbital*, *molecular orbital*.
See [8].
rev[3]
~~revGB-revPOC~~

orbital steering
Concept expressing the principle that the energetically favourable stereochemistry of approach of two reacting species is governed by the most favourable overlap of their appropriate *orbital*s.
rev[3]
~~revGB-revPOC~~

orbital symmetry
Behaviour of an *atomic orbital* or *molecular orbital* under molecular symmetry operations, such that under reflection in a symmetry plane or rotation by 180º around a symmetry axis the phase of the orbital is either unchanged (symmetric) or changes sign (antisymmetric), whereby positive and negative lobes are interchanged.
Examples:
(1) The orbital of an idealized single bond is σ, with cylindrical symmetry.

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1   (2) A p-orbital or π-bond orbital has π symmetry, i.e., it is antisymmetric with respect
2   to reflection in a plane passing through the atomic centres with which it is associated.
3   (3) The *HOMO* of 1,3-butadiene (illustrated below by its component atomic orbitals)
4   is antisymmetric with respect to 180º rotation about an axis through the C2–C3 bond
5   and perpendicular to the molecular plane.
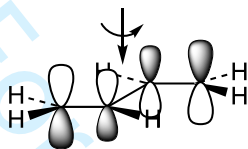
12   See [107,123].
13   See also *conservation of orbital symmetry*, *sigma*, *pi*.
14   rev[3]
15   revGB-revPOC

order of reaction

18   Exponent α, independent of concentration and time, in the differential rate equation
19   (*rate law*) relating the macroscopic (observed, empirical, or phenomenological) rate of
20   reaction v to c_A the concentration of one of the chemical species present, as defined by

$$\alpha = \left(\frac{\partial \ln \{v\}}{\partial \ln \{c_A\}} \right)_{[B],\dots}$$

23   The argument in the ln function should be of dimension 1. Thus, reduced quantities
24   should be used, i.e., the quantity divided by its unit, $\{v\} = v/(\text{mol dm}^{-3} \text{ s}^{-1})$ and $\{c_A\} =$
25    $c_A/(\text{mol dm}^{-3})$.

26   *Note 1:* A rate equation can often be expressed in the form $v = k [A]^{\alpha}[B]^{\beta}\dots$,
27   describing the dependence of the rate of reaction on the concentrations [A], [B],...,
28   where exponents α, β, ... are independent of concentration and time and k is
29   independent of [A], [B], ... In this case the reaction is said to be of order α with respect
30   to A, of order β with respect to B,..., and of (total or overall) order $n = \alpha + \beta +\dots$. The
31   exponents α, β,... sometimes called "partial orders of reaction", can be positive or
32   negative, integral, or rational nonintegral numbers.

33   *Note 2:* For an *elementary reaction* a partial order of reaction is the same as the
34   stoichiometric number. The overall order is then the same as the *molecularity*. For
35   stepwise reactions there is no general connection between stoichiometric numbers and
36   partial orders. Such reactions may have more complex rate laws, so that an apparent
37   order of reaction may vary with the concentrations of the *chemical species* involved and

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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.

Note 3: In a *stepwise reaction*, orders of reaction may in principle be assigned to the elementary steps.

Note 4: For chemical rate processes occurring in systems for which concentration changes are not measurable, as in the case of a dynamic equilibrium $aA \rightleftarrows pP$, and if a *chemical flux* ϕ_{-A} is found experimentally (e.g., by NMR *line-shape analysis*) to be related to the concentration of A and to concentrations of other species B, ..., by the equation

$$\phi_{-A} = k[A]^{\alpha}[B]^{\beta} \ldots$$

then the reaction is of order α with respect to A... and of total (or overall) order $(=\alpha + \beta + \ldots)$.

Note 5: If the overall rate of reaction is given by

$$v = k[A]^{\alpha}[B]^{\beta}$$

but [B] remains constant in any particular sample (but can vary from sample to sample), then the order of the reaction in A will be α, and the rate of disappearance of A can be expressed in the form

$$v_A = k_{obs}[A]^{\alpha}$$

The proportionality factor k_{obs} is called the "observed rate coefficient" and is related to the *rate constant k* by

$$k_{obs} = k[B]^{\beta}$$

Note 6: For the frequent case where $\alpha = 1$, k_{obs} is often referred to as a "pseudo-first-order rate coefficient".

See [13].

See also *kinetic equivalence*, *rate coefficient*, *rate constant*.

rev[3]

~~revGB-revPOC~~

organocatalysis

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Catalysis by small organic molecules, as distinguished from catalysis by (transition) metals or enzymes.

Note 1: Frequently used organocatalysts are secondary amines (covalent catalysis by generation of enamines or of iminium ions as *reactive intermediates*) and thioureas (hydrogen-bonding catalysis).

*Note 2*: Organocatalysts are often employed for *enantioselectivity*.

Note 3: The mechanisms employed by organocatalysts are examples of *general acid catalysis*, *general base catalysis*, *nucleophilic catalysis*, *specific acid catalysis*, *specific base catalysis*.

See [339,340,341,342].

outer-sphere electron transfer

Feature of an *electron transfer* between redox centres not sharing a common atom or group.

Example:

$$MnO_4^- + Mn*O_4^{2-} \rightleftarrows MnO_4^{2-} + Mn*O_4^-$$
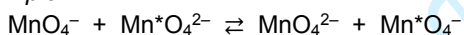
Note 1: In the *transition state* the interaction between the relevant electronic orbitals of the two centres is weak (below 20 kJ mol^{-1}), and the electron(s) must tunnel through space.

Note 2: If instead the donor and the acceptor exhibit a strong electronic coupling, often through a *ligand* that bridges both, the reaction is described as *inner-sphere electron transfer*.

Note 3: These two terms derive from studies of metal complexes, and for organic reactions the terms "nonbonded' and 'bonded" electron transfer are often used.

See [9,182,343].

rev[3]

~~GB~~

oxidation

(1) Removal of one or more electrons from a *molecular entity*.

(2) Increase in the *oxidation number* of an atom within a *substrate*, see [344].

(3) Gain of oxygen and/or loss of hydrogen by an organic substrate.

Note 1: All oxidations meet criterion (2) and many meet criterion (3), but this is not always easy to demonstrate. Alternatively, an oxidation can be described as the *transformation* of an organic substrate by removal of one or more electrons from the substrate, often accompanied by gain or loss of water, *hydrons*, and/or hydroxide, or by *nucleophilic* substitution, or by *molecular rearrangement*.

Note 2: 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 organic chemistry

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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

$$CH_4 - 2e^- - H^+ + HO^- = CH_3OH \qquad \text{(oxidation)},$$

followed by

$$CH_3OH + HCl \qquad = CH_3Cl + H_2O \quad \text{(neither oxidation nor reduction)}$$
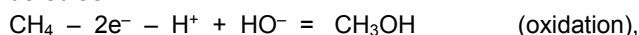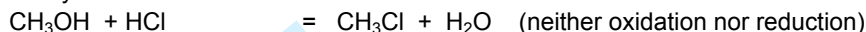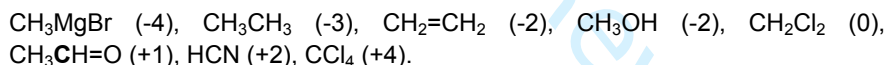
rev[3]
revGB-revPOC

oxidation number
oxidation state
Number assigned to a carbon atom in a *covalent* organic compound according to

$$N_{Ox} = N_X + N_O + N_N - N_H - N_M$$

where N_X, N_O, N_N, N_H, and N_M are the numbers of bonds to halogen, oxygen (or sulfur), nitrogen, hydrogen, and a metal, respectively.
   Examples:

   CH_3MgBr (-4), CH_3CH_3 (-3), $CH_2=CH_2$ (-2), CH_3OH (-2), CH_2Cl_2 (0), $CH_3\mathbf{C}H=O$ (+1), HCN (+2), CCl_4 (+4).

   Note 1: This assignment is based on the convention that each attached atom more electronegative than carbon contributes +1, while each atom less electronegative (including H) contributes -1, and an attached carbon contributes zero.
   Note 2: Oxidation numbers are not significant in themselves, but changes in oxidation number are useful for recognizing whether a reaction is an oxidation or a reduction or neither.
   Note 3: A different system is used for transition-metal species [345].
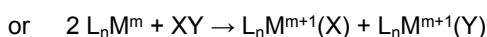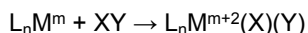   See also *electronegativity*, *oxidation*.
   rev[3]
   diffGB

oxidative addition
Insertion of the 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.,
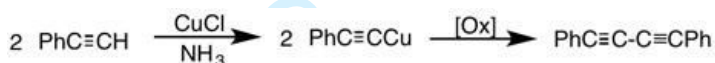
$$L_nM^m + XY \rightarrow L_nM^{m+2}(X)(Y)$$

or $2 L_nM^m + XY \rightarrow L_nM^{m+1}(X) + L_nM^{m+1}(Y)$

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1 rev[3]
2 ~~revGB-revPOC~~
3

4 **oxidative coupling**
5 Coupling of two *molecular entities* through an oxidative process, usually catalysed by a
6 transition-metal compound.
7   *Example* (where the oxidant can be O_2 or Cu(II) or others):
8

$$2\ PhC\equiv CH \xrightarrow[NH_3]{CuCl} 2\ PhC\equiv CCu \xrightarrow{[Ox]} PhC\equiv C\text{-}C\equiv CPh$$

9
10 rev[3]
11 ~~revGB-revPOC~~
12

13 **parallel effect**
14 Change of the position of the *transition state* upon stabilization or destabilization of a
15 structure (or structures) along the assumed *minimum-energy reaction path*.
16   See *Hammond postulate*, *More O'Ferrall - Jencks diagram*.
17

18 **parallel reaction**
19   See *composite reaction*.
20 ~~GB~~[3]
21

22 **paramagnetism**
23 Property of substances having a magnetic susceptibility greater than 0, whereby they
24 are drawn into a magnetic field.
25   See also *diamagnetism*.
26 ~~GB~~[3]
27

28 **partial rate factor** p_f^Z, m_f^Z
29 *Rate constant* for substitution at one specific site in an *aromatic* compound divided by
30 the rate constant for substitution at one position in benzene.
31   *Note 1:* The partial rate factor p_f^Z for para-substitution in a monosubstituted benzene
32 C_6H_5Z is related to the rate constants $k(C_6H_5Z)$ and $k(C_6H_6)$ for the total reactions (i.e.,
33 at all positions) of C_6H_5Z and benzene, respectively, and f_{para} (the fraction of para-
34 substitution in the total product formed from C_6H_5Z, usually expressed as a percentage)
35 by the relation
36

37 $$p_f^Z = \frac{6k(C_6H_5Z)}{k(C_6H_6)}\, f_{para}$$

38

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Similarly for meta-substitution:

$$m_f^Z = \frac{6k(C_6H_5Z)}{2k(C_6H_6)} f_{meta}$$

The symbols f_p^Z, f_m^Z, f_o^Z are also in use.

Note 2: The term applies also to the *ipso* position, and it can be extended to other substituted *substrate*s undergoing parallel reactions at different sites with the same reagent according to the same *rate law*.

See [262,346,347].

See also *selectivity*.

rev[3]

~~revGB-revPOC~~

partition ratio (partition constant, distribution ratio) *P*

Concentration of a substance in one phase divided by its concentration in another phase, at equilibrium.

Example, for an aqueous/organic system the partition ratio (or distribution ratio *D*) is given by

$P = c_{org}(A)/c_{aq}(A)$

Note 1: The most common way of applying *P* in *correlation analysis* or *quantitative structure-activity relationships* is as lg *P*.

Note 2: The parameter *P* is extensively used as an indicator of the capacity of a molecular entity to cross biological membranes by passive diffusion.

Note 3: The term *partition coefficient* is in common usage in toxicology but is not recommended for use in chemistry and should not be used as a synonym for partition constant, partition ratio, or distribution ratio.

See [167,232].

See also *Hansch constant, octanol-water partition ratio*.

~~diffGB~~

pericyclic reaction

Chemical reaction in which *concerted* reorganization of bonding takes place throughout a cyclic array of continuously bonded atoms.

Note 1: It may be viewed as a reaction proceeding through a fully *conjugated* cyclic transition state.

Note 2: The term embraces a variety of processes, including *cycloaddition*, *cheletropic reaction*, *electrocyclic reaction* and *sigmatropic rearrangement*, etc. (provided they are *concerted*).

See also *pseudopericyclic*.

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1 ~~GB~~[3]

2

3 **permittivity, relative** ε_r

4 dielectric constant (obsolete)

5 Measure of the reduction of the magnitude of the potential energy of interaction between

6 two charges on going from vacuum to a condensed medium, expressed as the ratio of

7 the former to the latter.

8   *Note*: The term dielectric constant is obsolete. Moreover, the dielectric constant is

9 not a constant since it depends on frequency.

10   See [12].

11   ~~GB~~

12

13 **perpendicular effect**

14 Change of the position of the transition state upon stabilization or destabilization of a

15 structure (or structures) that lies off the assumed *minimum-energy reaction path*.

16   See *anti-Hammond effect*, *Hammond postulate*, *More O'Ferrall - Jencks diagram*.

17   rev[3]

18   ~~revGB-revPOC~~

19

20 **persistence**

21 Characteristic of a *molecular entity* that has an appreciable *lifetime* (minutes or

22 nanoseconds or other, depending on context).

23   *Note 1*: Dilute solution or inert solvent may be required for persistence.

24   *Note 2*: Persistence is a kinetic or reactivity property, whereas, in contrast, stability

25 (being *stable*) is a thermodynamic property.

26   See [348].

27   See also *transient*.

28   rev[3]

29   ~~revGB-revPOC~~

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31 **pH-rate profile**

32 Plot of observed *rate coefficient*, or more usually the decadic logarithm of its numerical

33 value, against solution pH, other variables being kept constant.
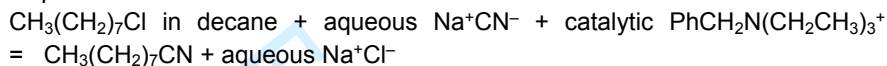
34   ~~GB~~[3]

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36 **phase-transfer catalysis**

37 Enhancement of the rate of a reaction between *chemical species* located in different

38 phases (immiscible liquids or solid and liquid) by addition of a small quantity of an agent

39 (called the phase-transfer *catalyst*) that extracts one of the reactants, most commonly

40 an anion, into the other phase so that reaction can proceed.

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Note 1: These catalysts are often *onium ion*s (e.g., tetraalkylammonium ions) or complexes of inorganic cations (e.g., as *crown ether* complexes).

Note 2: The catalyst cation is not consumed in the reaction although an anion exchange does occur.

Example:

$CH_3(CH_2)_7Cl$ in decane + aqueous Na^+CN^- + catalytic $PhCH_2N(CH_2CH_3)_3^+$

= $CH_3(CH_2)_7CN$ + aqueous Na^+Cl^-

rev[3]

~~revGB revPOC~~

phenonium ion

See *bridged carbocation*.

~~GB~~[3]

photochromism

Reversible transformation of a *molecular entity* between two forms, A and B, having different absorption spectra, induced in one or both directions by absorption of electromagnetic radiation.

Note 1: The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (photochromism of type T) or photochemically (photochromism of type P).

Note 2: The spectral change is typically, but not necessarily, of visible colour.

Note 3: An important parameter is the number of cycles that a photochromic system can undergo.

See [9].

~~GB~~

photolysis

Bond cleavage induced by ultraviolet, visible, or infrared radiation.
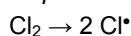
Example:

$Cl_2 \rightarrow 2\ Cl^\bullet$

Note: The term is used incorrectly to describe irradiation of a sample without any bond cleavage, although in the term "flash photolysis" this usage is accepted.

See [9].

~~GB~~[3]

photostationary state

160

Steady state reached by a chemical system undergoing photochemical reaction, such that the rates of formation and disappearance are equal for each of the transient *molecular entities* formed.

   See [9].

   GB

pi-adduct

   See *π-adduct*.

pi-bond

   See *σ, π*.

polar aprotic solvent

   See *dipolar non-HBD solvent*.

   GB[3]

polar effect

All the interactions whereby a *substituent* on a reactant molecule RY modifies the electrostatic forces operating at the reaction centre Y, relative to the reference standard R_oY.

   Note 1: These forces may be governed by charge separations arising from differences in the *electronegativity* of atoms (leading to the presence of dipoles), by the presence of monopoles, or by electron *delocalization*.

   Note 2: It is distinguished from a *steric effect*.

   Note 3: Sometimes, however, the term polar effect is taken to refer to the influence, other than steric, that non-conjugated substituents exert on reaction rates or equilibria, thus excluding effects of electron delocalization between a substituent and the molecular framework to which it is attached.

   See also *electronic effects (of substituents)*, *field effect*, *inductive effect*.

   GB[3]

polar solvent

Liquid composed of molecules with a significant dipole moment, capable of dissolving ions or other molecules with significant dipole moments.

   See *polarity*.

   rev[3]

   revGB

polarity (of a bond**)**

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1 Characteristic of a bond between atoms of different *electronegativity*, such that the
2 electrons in that bond are not shared equally.
3
4 **polarity (**of a solvent**)**
5 Overall solvation capability (solvation power) of a solvent toward solutes, which
6 depends on the action of all possible intermolecular interactions between solute ions or
7 molecules and solvent molecules, excluding interactions leading to definite chemical
8 alterations of the ions or molecules of the solute.
9   *Note:* Quantitative measures of solvent polarity include relative *permittivity* (dielectric
10 constant) and various spectroscopic parameters.
11   See [17].
12   See *solvent parameter*.
13   rev[3]
14   revGB-revPOC
15
16 **polarizability**
17 α
18 (SI unit: C m^2 V^{-1})
19 electric polarizability
20 Induced dipole moment, $\mu_{induced}$, divided by applied electric field strength $\boldsymbol{E}$
21    $\alpha = \mu_{induced}/\boldsymbol{E}$
22   *Note 1*: The polarizability represents the ease of distortion of the electron cloud of a
23 *molecular entity* by an electric field (such as that due to the proximity of a charged
24 species).
25   *Note 2*: Polarizability is more often expressed as polarizability volume, with unit cm^3,
26 where ε_0 is the *permittivity* of vacuum:
27

28    $$\alpha/\text{cm}^3 = \frac{10^6}{4\pi\varepsilon_0}\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}E}$$

29
30   *Note 3*: In general, polarizability is a tensor that depends on direction, for example,
31 depending on whether the electric field is along a bond or perpendicular to it, and the
32 induced dipole may not even be along the direction of the electric field. However, in
33 ordinary usage the term refers to the mean polarizability, the average over three
34 rectilinear axes of the molecule.
35   rev[3]
36   revGB-revPOC
37
38 **polydent**
39 polydentate

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1   See *ambident*.
2   ~~GB~~[3]
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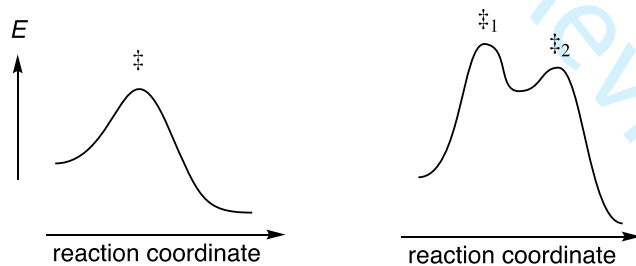4   **potential-energy profile**
5   Curve describing the variation of the potential energy of a system of atoms as a function
6   of a single coordinate.
7   *Note 1*: For an *elementary reaction* the relevant coordinate is the *reaction coordinate*,
8   which is a measure of progress along the *minimum-energy reaction path* (MERP) from
9   a saddle point on a *potential-energy surface* in each direction toward adjacent energy
10   minima. For a stepwise reaction it is the succession of reaction coordinates for the
11   successive individual reaction steps. For a reaction involving a *bifurcation* each branch
12   requires a different reaction coordinate and has its own profile.
13   *Note 2*: A profile constructed as a function of an arbitrary internal coordinate (for
14   example, a bond distance) is not guaranteed to pass through a saddle point on the
15   corresponding potential-energy surface; in order to do so, it must be smooth,
16   continuous, and follow the path of lowest energy connecting the reactant and product
17   energy minima.
18   *Examples:* (one-step reaction, two-step reaction)
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21
22   See [349].
23   See also *Gibbs energy diagram*, *potential-energy surface*.
24   rev[3]
25   ~~revGB-rev POC~~
26
27   **potential-energy surface** (**PES**)
28   Surface describing the variation within the *Born-Oppenheimer approximation* of the
29   potential energy of a system of atoms as a function of a set of internal coordinates.
30   *Note 1*: A minimum on a PES is characterized by positive curvature in all directions
31   and corresponds to a structure that is stable with respect to small displacements away
32   from its equilibrium geometry; for this structure (a reactant, *intermediate* or product) all
33   vibrational frequencies are real. A saddle point is characterized by positive curvature in

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all directions except for one with negative curvature and corresponds to a transition structure, for which one vibrational frequency is imaginary. A local maximum is characterized by negative curvatures in two (or more) directions and has two (or more) imaginary frequencies; it is sometimes called a second-order (or higher-order) saddle point.

Note 2: It is usual to select only two coordinates in order to represent the surface, with potential energy as the third dimension, or alternatively as a two-dimensional contour map. For example, a PES for a simple reacting triatomic system A–B + C → A + B–C, could be constructed using the A⋯B and B⋯C distances as two internal coordinates; the third independent coordinate could be the ABC angle or the A⋯C distance, and its value could either be kept fixed or else be relaxed to minimize the energy at each point on the (A⋯B, B⋯C) surface.

Note 3: The path of steepest-descent from a saddle point in each direction towards adjacent energy minima defines a *minimum-energy reaction path* (MERP) that is equivalent to the energetically easiest route from reactants to products. The change in potential energy along this path across the PES defines a *potential-energy profile* for the *elementary reaction*. Progress along this path is measured by the value of the *reaction coordinate*.

Note 4: In general there is neither a unique set of internal coordinates nor a unique choice of two coordinates with which to construct a PES of reduced dimensionality. Consequently there is no guarantee of a smooth and continuous PES containing a saddle point connecting reactant and product minima.

See [8,73,350,351].

See: *bifurcation*, *minimum-energy reaction path*, *potential-energy profile*, *reaction coordinate*, *transition structure*.

rev[3]

revGB-revPOC

potential of mean force (PMF)

Free energy as a function of a set of coordinates, the negative gradient of which gives the average force acting on that configuration averaged over all other coordinates and momenta within a statistical distribution. If the averaging is performed within a canonical ensemble (constant volume, temperature, and number of particles) the PMF is equivalent to the Helmholtz energy, but if it is performed within an isobaric-isothermal ensemble (constant pressure, temperature, and number of particles) the PMF is equivalent to the Gibbs energy.

Note 1: Commonly, the PMF acting upon a selected geometric variable and averaged over the coordinates and momenta of all other geometric variables is evaluated for a succession of constrained values of the selected variable, thereby generating (generically) a *free-energy* profile with respect to the selected *reaction coordinate* (e.g.,

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a bond distance or angle, or a combination of internal coordinates); specifically this is either a Helmholtz-energy or a Gibbs-energy profile, depending upon the choice of ensemble for the statistical averaging within a computational simulation.

Note 2: Selection of two geometric variables as reaction coordinates allows a free-energy surface to be computed as a two-dimensional PMF.

Note 3: Molecular simulations often yield Helmholtz energies, not Gibbs energies, but for condensed phases the difference is usually neglected.

See: *free energy*, *reaction coordinate*.

pre-association

Step on the *reaction path* of some *stepwise reaction*s in which the *molecular entity* C forms an encounter pair or *encounter complex* with A prior to the reaction of A to form product.

Example:

Note 1: 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.

Specific example (aminolysis of phenyl acetate)*:*

Note 2: Pre-association is important when B is too short-lived to permit B and C to come together by diffusion. In the specific example, T$^{\pm}$ would dissociate faster than general acid HA can diffuse to it. Experimentally, the Brønsted α is > 0, which is inconsistent with *rate-limiting* diffusion and *hydron* transfer.

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1 See [352].
2 See also *Brønsted relation*, *microscopic diffusion control*, *spectator mechanism*.
3 ~~rev~~[3]
4 ~~revGB-revPOC~~
5

precursor complex
7 See *encounter complex*.
8 ~~revGB-revPOC~~[3]
9

pre-equilibrium
11 prior equilibrium
12 Rapid reversible step preceding the *rate-limiting step* in a *stepwise reaction*.
13 *Example:*

16 See also *kinetic equivalence*, *steady state*.
17 ~~GB~~[3]
18

pre-exponential factor
20 See *energy of activation*, *entropy of activation*.
21 ~~GB~~[3]
22

principle of nonperfect synchronization
24 Consideration applicable to reactions in which there is a lack of synchronization
25 between bond formation or bond rupture and other changes that affect the stability of
26 products and reactants, such as *resonance*, *solvation*, electrostatic, *hydrogen bonding*
27 and *polarizability* effects.
28 *Note*: The principle states that a product-stabilizing factor whose development lags
29 behind bond changes at the *transition state*, or a reactant-stabilizing factor whose loss
30 is ahead of bond changes at the transition state, increases the *intrinsic barrier* and
31 decreases the *rate constant* of a reaction. For a product-stabilizing factor whose
32 development is ahead of bond changes, or a reactant-stabilizing factor whose loss lags
33 behind bond changes, the opposite relations hold. The reverse effects are observable
34 for factors that destabilize a reactant or product.
35 See [108].
36 See also *imbalance*, *synchronous*.
37 ~~revGB~~
38

166

prior equilibrium
See *pre-equilibrium*.
~~GB~~[3]

product-determining step
Step of a *stepwise reaction* in which the product distribution is determined.
Note: The product-determining step may be identical to, or may occur later than, the *rate-determining step* in the reaction.
~~GB~~[3]

product-development control
Case of *kinetic control* in which the *selectivity* of a reaction parallels the relative (thermodynamic) stabilities of the products.
Note: Product-development control arises because whatever effect stabilizes or destabilizes a product is already operative at the *transition state*. Therefore it is usually associated with a transition state occurring late on the *minimum-energy reaction path*.
See also *steric-approach control*, *thermodynamic control*.
~~GB~~[3]

promotion
See *pseudo-catalysis*.
~~GB~~[3]

propagation
See *chain reaction*.
~~GB~~[3]

propargylic substitution
See *allylic substitution reaction*.

protic
See *protogenic*.
~~GB~~[3]

protic solvent
Solvent that is capable of acting as a *hydrogen-bond* donor.
See *HBD solvent*.

protofugality

168

1   See also *hydronation*.

proton–transfer reaction
Chemical reaction, the main feature of which is the intermolecular or intramolecular transfer of a proton (*hydron*) from one binding site to another.
   Example:
       $CH_3COOH + (CH_3)_2C=O \rightarrow CH_3CO_2^- + (CH_3)_2C=OH^+$
   Note: 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) or just to the proton-transfer event (including solvent rearrangement) by itself.
   See also *autoprotolysis*, *microscopic diffusion control*, *tautomerism*.
   GB[3]

protophilic (solvent)
   See *HBA (hydrogen bond acceptor) solvent*.
   rev[3]
   revGB

protophilicity
Special case of *nucleophilicity*, describing the relative rates of reactions of a series of *Lewis base*s with a common *Brønsted acid*. This term has the advantage over the commonly used "kinetic basicity" that philicity and fugality are associated with kinetics, while acidity and basicity are associated with thermodynamics.
   See [194].
   See also *Brønsted basicity*, *nucleophilicity*, *protofugality*.

prototropic rearrangement (prototropy)
   See *tautomerization*.
   GB[3]

pseudo-catalysis
Increase of the rate of a reaction by an acid or base present in nearly constant concentration throughout a reaction in solution (owing to buffering or to the use of a large excess), even though that acid or base is consumed during the process, so that the acid or base is not a *catalyst* and the phenomenon strictly cannot be called *catalysis* according to the established meaning of these terms in chemical kinetics.

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Note 1: Although the *mechanism* of such a process is often closely related to that of a catalysed reaction, it is recommended that the term pseudo-catalysis be used in these and analogous cases. 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 the hydrolysis of an amide should be described as pseudo-catalysis because the acid pseudo-catalyst is stoichiometrically consumed during the reaction through formation of an ammonium ion.

Note 2: 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*.

Note 3: The terms acid- and base-promoted, acid- and base-accelerated, and acid- and base-induced are sometimes used for reactions that are pseudo-catalysed by or bases. However, the term promotion also has a different meaning in other chemical contexts.

rev[3]

~~GB~~

pseudo-first-order rate coefficient

See *order of reaction, rate coefficient*.

~~GB~~[3]

pseudopericyclic

Feature of a *concerted* *transformation* in which the primary changes in bonding occur within a cyclic array of atoms but in which one (or more) nonbonding and bonding *atomic orbital*s interchange roles.

Examples: enol-to-enol *tautomerism* of 4-hydroxypent-3-en-2-one (where the electron pairs in the O–H bond and in the lone pair on the other O are in σ orbitals whereas the other three electron pairs are in π orbitals) and hydroboration (where the B uses an sp^2 bonding orbital and a vacant p orbital)

Note: Because the 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. It is therefore not governed by the rules that express *orbital symmetry* restrictions applicable to pericyclic reactions.

170

1　　See [354,355].

2　　See also *coarctate*.

3　　rev[3]

4　~~revGB-revPOC~~

5

6　**push-pull conjugation**

7　Feature of an extended conjugated π system bearing an electron donor group at one

8　end and an electron acceptor group at the other end.

9　　See [356].

10　　See also *cross-conjugation*.

11

12　**pyrolysis**

13　*Thermolysis*, usually associated with exposure to a high temperature.

14　　See also *flash vacuum pyrolysis*.

15　~~GB~~[3]

16

17　**π-adduct (pi-adduct)**

18　*Adduct* formed by electron-pair donation from a π *orbital* into a σ* orbital, or from a σ

19　orbital into a π* orbital, or from a π orbital into a π* orbital.

20　　*Example:*

21

22　　*Note*: Such an adduct has commonly been known as a π *complex*, but, as the

23　bonding is not necessarily weak, it is better to avoid the term complex, in accordance

24　with the recommendations in this Glossary.

25　　See also *coordination*.

26　~~GB~~[3]

27

28　**π-bond (pi bond)**

29　Interaction between two atoms whose p *orbital*s overlap sideways.

30　　*Note:* The designation as π is because the p orbitals are antisymmetric with respect

31　to a defining plane containing the two atoms.

32　　See *sigma, pi*.

33　rev[3]

34　~~revGB-rev POC~~

171

π-complex

See *π-adduct*.

~~GB~~[3]

π-electron acceptor

Substituent capable of electron withdrawal by resonance (e.g., NO_2).

See *electronic effect*, *polar effect*, *π-electron donor*, *σ-constant*.

rev[3]

~~revGB-revPOC~~

π-electron donor

Substituent capable of electron donation by resonance (e.g., OCH_3).

See *electronic effect*, *polar effect*, *π-electron acceptor*, *σ-constant*.

rev[3]

~~revGB~~

quantitative structure-activity relationship (QSAR)

Regression model to correlate biological activity or chemical reactivity with predictor parameters based on measured or calculated features of molecular structure.

See [357,358].

See also *correlation analysis*.

rev[3]

~~revGB-revPOC~~

quantitative structure-property relationship (QSPR)

Regression model to correlate chemical properties such as boiling point or chromatographic retention time with predictor parameters based on measured or calculated features of molecular structure.

See [359].

See also *correlation analysis*.

quantum yield

Number of defined events that occur per photon absorbed by the system.

Note 1: The integral quantum yield Φ is the number of events divided by the number of photons absorbed in a specified wavelength range.

Note 2: For a photochemical reaction $\Phi(\lambda)$ is the amount of reactant consumed or product formed divided by the number of photons absorbed at wavelength λ.

Note 3: The differential quantum yield for a homogeneous system is

172

$$\Phi(\lambda) = \frac{\left|\dfrac{\mathrm{d}x}{\mathrm{d}t}\right|}{q_{p,\lambda}[1 - 10^{A(\lambda)}]}$$

where $|\mathrm{d}x/\mathrm{d}t|$ is the rate of change of a quantity x that measures the progress of a reaction, $q_{p,\lambda}$ is the spectral photon flux (mol or its non-SI equivalent einstein) incident per unit time at wavelength λ, and $A(\lambda)$ is the decadic absorbance at the excitation wavelength λ.

Note 4: When the quantity x is an amount concentration, it is convenient to use in the denominator the rate (in moles) of photons absorbed per volume.

See [9,10].

rev[3]

revGB-revPOC

radical

free radical (obsolete)

Molecular entity possessing an unpaired electron.

Examples: •CH_3, •SnR_3, Cl•

Note 1: In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if possible.

Note 2: Paramagnetic metal ions are not normally regarded as radicals. However, in the *isolobal* analogy the similarity between certain paramagnetic metal ions and radicals becomes apparent.

Note 3: Depending upon the core atom that possesses the highest spin density, the radicals can be described as carbon-, oxygen-, nitrogen-, or metal-centred radicals.

Note 4: If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed σ or π radicals.

Note 5: The term radical has also been used to designate a *substituent* group within a molecular entity, as opposed to "free radical", which is now simply called radical. The bound entities may be called *groups* or substituents, but should no longer be called radicals.

See [40,97].

See also *diradical*.

rev[3]

GB

radical combination

Formation of a *covalent bond* by reaction of one *radical* with another.

See *colligation*.

173

rev[3]
~~rev~~GB

radical ion
Radical that carries a net electric charge.

    Note 1: A positively charged radical is called a radical cation (e.g., the benzene radical cation $C_6H_6^{•+}$); a negatively charged radical is called a radical anion (e.g., the benzene radical anion $C_6H_6^{•-}$ or the benzophenone radical anion $Ph_2C–O^{•-}$).

    Note 2: 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 $^{•}+$ or $^{•}-$, as suggested by the name radical ion. However, the usage in mass spectrometry is to place the charge symbol before the dot [7].

    Note 3: In the first edition of this Glossary it was recommended to place the charge designation directly above the dot. This format is now discouraged because of the difficulty of extending it to ions bearing more than one charge and/or more than one unpaired electron.

~~GB~~[3]

radical pair
geminate pair
Two *radical*s in close proximity in solution, within a solvent *cage*.

    Note 1: The two radicals may be formed simultaneously by some *unimolecular* process, e.g., peroxide decomposition or *photolysis*, or they may have come together by diffusion.

    Note 2: 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*.

    See [9,40].

~~GB~~[3]

radiolysis
Cleavage of one or several *bond*s resulting from exposure to high-energy radiation.

    Note: The term is also often used loosely to specify the method of irradiation (e.g., pulse radiolysis) used in any radiochemical reaction, not necessarily one involving bond cleavage.

~~GB~~[3]

rate coefficient

174

1 Empirical constant k in the equation for the rate of a reaction that is expressible by an
2 equation of the form

4     $v = k[A]^a[B]^b....$

6   *Note 1*: It is recommended that the term *rate constant* be confined to reactions that
7 are believed to be *elementary reactions*.
8   *Note 2*: When a rate coefficient relates to a reaction occurring by a composite
9 mechanism, it may vary not only with temperature and pressure but also with the
10 concentration of reactants. For example, in the case of a *unimolecular* gas reaction the
11 rate at sufficiently high pressures is given by

13     $v = k[A]$

15 whereas at low pressures the rate expression is

17     $v = k'[A]^2$

19 Similarly, for a second-order reaction, the rate is given by

21     $v = k_2[A][B]$

23 But under conditions where [B] remains constant at $[B]_0$, as when B is a *catalyst* or is
24 present in large excess,

26     $v = k_2[A][B]_0 = k[A]$

28 where the rate coefficient $k = k_2[B]_0$, which varies with $[B]_0$.
29   Such a rate coefficient k, which varies with the concentration [B], is called a first-
30 order rate coefficient for the reaction, or a *pseudo first-order rate constant* even though
31 it is not a rate constant.
32   *Note*: *Rate constant* and *rate coefficient* are often used as synonyms, see [12],
33 section 2.12, p.63.
34   See [13].
35   See *order of reaction*.
36   rev[3]
37   revGB-revPOC

39 **rate constant**
40 *k*

175

Term generally used for the *rate coefficient* of a reaction that is believed to be an *elementary reaction*. See [13].

Note 1: In contrast to a rate coefficient, a rate constant should be independent of concentrations, but in general both rate constant and rate coefficient vary with temperature.

Note 2: Rate constant and rate coefficient are often used as synonymous, see [12], section 2.12, p.63.

See *order of reaction*.

rev[3]

revGB-revPOC

rate-controlling step

See *rate-determining states, rate-limiting step*.

rev[3]

GB

rate law

empirical differential rate equation

Expression for the *rate of 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 the equations under *kinetic equivalence*, and under *steady state*.

GB[3]

rate-limiting step

rate-controlling step

rate-determining step

Step in a multistep reaction that is the last step in the sequence whose *rate constant* appears in the rate equation.

See [13].

Example: Two-step reaction of A with B to give *intermediate* C, which then reacts further with D to give products:

$$A + B \xrightleftharpoons[k_{-1}]{k_1} C \quad (\text{Step 1})$$

$$C + D \xrightarrow{k_2} \text{products} \quad (\text{Step 2})$$

If [C] reaches a *steady state*, then the observed rate is given by

$$v = -d[A]/dt = k_1 k_2 [A][B][D]/(k_{-1} + k_2[D])$$

1
2
3
4
5   176
6
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11

1   *Case 1:* If $k_2[D] \gg k_{-1}$, then the observed rate simplifies to

2

3            $v = -d[A]/dt = k_1[A][B]$

4

5   Because k_2 disappears from the rate equation and k_1 is the last rate constant to remain,
6   step (1) is said to be rate-limiting.

7   *Case 2:* If $k_2[D] \ll k_{-1}$, then the observed rate is given by

8

9            $v = k_1k_2[A][D]/k_{-1} = Kk_2[A][B][D]$

10

11   where K, equal to k_1/k_{-1}, is the *equilibrium* constant for the *pre-equilibrium* (Step 1).
12   Because k_2 remains in the rate equation, Step 2 is said to be rate-limiting. Notice that
13   in this case, where Step 2 involves another reactant D, which step is rate-limiting can
14   depend on [D]: Step 1 at high [D] and Step 2 at low [D].

15

16   *Specific example*: Acid-catalyzed bromination of a methyl ketone

17

18
19

20   where $k_1 = k_1'[H^+]$, $k_{-2} = k_{-2}'[H^+]$, $k_3 = k_3'[Br_2]$, $k_{-3} = k_{-3}'[Br^-]$.

21

22   According to the *steady-state* approximation,

23

24            $v = k_{obs}[RCOCH_3] = k_1k_2k_3k_4[RCOCH_3]/\{k_2k_3k_4 + k_{-1}k_3k_4 + k_{-1}k_{-2}(k_{-3} + k_4)\}$.

25

26   or $k_{obs} = k_1k_2k_3k_4/\{k_2k_3k_4 + k_{-1}k_3k_4 + k_{-1}k_{-2}(k_{-3} + k_4)\}$.

27

28   If $k_4 \gg k_{-3}$, k_{-3} can be ignored in the parentheses, so that k_{obs} simplifies to
29      $k_1k_2k_3k_4/\{k_2k_3k_4 + k_{-1}k_3k_4 + k_{-1}k_{-2}k_4\}$. Then if $k_3 \gg k_{-2}$, k_{obs} simplifies further to
30      $k_1k_2k_3k_4/\{k_2k_3k_4 + k_{-1}k_3k_4\}$, where k_3k_4 cancels and k_{obs} becomes $k_1k_2/\{k_{-1} + k_2\}$, so that
31   k_2 is the last rate constant remaining in k_{obs}. The second step is rate-limiting, and the
32   rate is independent of k_3 or of [Br$_2$].

33   *Note 1*: Although the expressions rate-controlling, rate-determining, and rate-limiting
34   are often regarded as synonymous, rate-limiting is to be preferred, because in Case 2
35   all three rate constants enter into the rate equation, so that all three are rate-controlling
36   and rate-determining, but the first step is not rate-limiting.

37   *Note 2:* If the concentration of any intermediate builds up to an appreciable extent,
38   then the steady-state approximation no longer holds, and the reaction should be
39   analyzed as though that intermediate is the reactant.

177

Note 3: It should be noted that a *catalytic cycle* does not have a rate-determining step. Instead, under steady-state conditions, all steps proceed at the same rate because the concentrations of all intermediates adjust so as to offset the differences in the corresponding rate constants [360].

See also *Gibbs energy diagram*, *microscopic diffusion control*, *mixing control*.

rev[3]

~~revGB-revPOC~~

rate of reaction

v

(unit: mol dm^{-3} s^{-1} or mol L^{-1} s^{-1})

For the general *chemical reaction*

$$a \text{ A} + b \text{ B} = p \text{ P} + q \text{ Q} \ldots$$

occurring under constant-volume conditions, without an appreciable build-up of reaction *intermediate*s, 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 inside square brackets denote concentrations (conventionally expressed in unit mol dm^{-3}). The symbols R and r are also used instead of *v*. It is recommended that the unit of time be the second.

Example:

$$Cr_2O_7^{2-} + 3 (CH_3)_2CHOH + 8 H^+ = 2 Cr^{3+} + 3 (CH_3)_2C{=}O + 7 H_2O$$

$$v = -\frac{d[Cr_2O_7^{2-}]}{dt} = -\frac{1}{3}\frac{d[(CH_3)_2CHOH]}{dt} = \frac{1}{2}\frac{d[Cr^{3+}]}{dt} = \frac{1}{3}\frac{d[(CH_3)_2C{=}O]}{dt}$$

Note: For a *stepwise reaction* this definition of rate of reaction 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]/d*t*) or rate of appearance of P (i.e., d[P]/d*t*) be used, depending on the particular *chemical species* that is actually observed. In some cases reference to the *chemical flux* observed may be more appropriate.

See [13].

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See also *chemical relaxation*, *lifetime*, *order of reaction*.
rev[3]
revGB-revPOC

reaction coordinate
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 as a measure of the progress along a *minimum-energy reaction path*.
   Note 1: The term "reaction coordinate" is often used to refer to a geometric variable itself (typically a bond distance or bond angle, or a combination of distances and/or angles) as well as (or instead of) the value of that variable. Although strictly incorrect, this usage is very commonly encountered.
   Note 2: In cases where the location of the transition structure is unknown, an internal coordinate of the system (e.g., a geometric variable or a bond order, or an energy gap between reactant-like and product-like valence-bond structures) is often selected as a reaction coordinate. A *potential-energy profile* obtained by energy minimization over other coordinates for a succession of fixed values of an arbitrary reaction coordinate is not guaranteed to pass through the *transition structure* unless it is a continuous function of that reaction coordinate. Similarly, a free-energy profile obtained as a *potential of mean force* with respect to an arbitrary reaction coordinate is not guaranteed to pass through the lowest-energy *transition state*.
   Note 3: "Reaction coordinate" is sometimes used as an undefined label for the horizontal axis of a *potential-energy profile* or a *Gibbs energy diagram*.
   See [349,361].
   See also *Gibbs energy diagram*, *potential-energy profile*, *potential-energy surface*.
rev[3]
revGB-revPOC

reaction path
(1) Synonym for *mechanism*.
(2) Trajectory on the *potential-energy surface*.
rev[3]
revGB-revPOC

reaction step
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.
GB[3]

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reactive intermediate
intermediate

reactivity (n.), reactive (adj.)
Kinetic property of a *chemical species* by which (for whatever reason) it has a different rate constant for a specified *elementary reaction* than some other (reference) species.
   Note 1: 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.
   Note 2: Term also used more loosely as a phenomenological description not restricted to elementary reactions. When applied in this sense, the property under consideration may reflect not only rate constants but also equilibrium constants.
   See also *stable*, *unreactive*, *unstable*.
   GB[3]

reactivity index
Numerical quantity derived from quantum-mechanical model calculations or from a *linear Gibbs-energy relationship (linear free-energy relationship)* that permits the prediction or correlation of relative reactivities of different molecular sites.
   Note: 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 π-electron energy and π-*electron density*.
   rev[3]
   revGB-revPOC

reactivity-selectivity principle (RSP)
Idea that the more *reactive* a reagent is, the less *selective* it is.
   Note: There are many examples in which the RSP is followed, but there are also many counterexamples. Although the RSP is in accord with intuitive feeling, it is now clear that selectivity can decrease, increase, or remain constant as *reactivity* increases, so that the RSP is unreliable as a guide to reactivity.
   See [126,346,362,363,364,365].
   rev[3]
   revGB-revPOC

rearrangement
   See *degenerate rearrangement*, *molecular rearrangement*, *sigmatropic rearrangement*.

180

1 ~~GB~~[3]

2

3 **reduction**
4 (1) Transfer of one or more electrons to a *molecular entity*, usually inorganic.
5 (2) Decrease in the *oxidation number* of any atom within any *substrate* [344].
6 (3) Loss of oxygen or halogen and/or gain of hydrogen of an organic *substrate*.
7   See *oxidation.*
8   rev[3]
9   ~~revGB-revPOC~~

10

11 **reductive elimination**
12 Reverse of *oxidative addition*.
13   ~~GB~~[3]

14

15 **regioselectivity** (*n.*)**, regioselective** (*adj.*)
16 Property of a reaction in which one position of *bond* making or breaking occurs
17 preferentially over all other possible positions.
18   *Note 1:* The resulting regioisomers are *constitutional isomers.*
19   *Note 2*: Reactions are termed completely (100 %) regioselective if the discrimination
20 is complete, or partially (*x* %) if the product of reaction at one site predominates over
21 the product of reaction at other sites. The discrimination may also be referred to semi-
22 quantitatively as high or low regioselectivity.
23   *Note 3*: Historically the term was restricted to *addition reaction*s of unsymmetrical
24 reagents to unsymmetrical alkenes.
25   *Note 4*: In the past, the term regiospecificity was proposed for 100 % regioselectivity.
26 This terminology is not recommended, owing to inconsistency with the terms
27 *stereoselectivity* and *stereospecificity.*
28   See [366,367].
29   See also *chemoselectivity.*
30   rev[3]
31   ~~revGB-revPOC~~

32

33 **Reichardt E_T parameter**
34   See *Dimroth-Reichardt $E_T(30)$ parameter*.

35

36 **relaxation**
37 Passage of a system that has been perturbed from *equilibrium*, by radiation excitation
38 or otherwise, toward or into thermal equilibrium with its environment.
39   See [9].
40   See also *chemical relaxation*.

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rev[3]

~~revGB-revPOC~~

reorganization energy

Gibbs energy required to distort the reactants (and their associated solvent molecules) from their relaxed nuclear configurations to the relaxed nuclear configurations of the products (and their associated solvent molecules).

Note 1: This approach was originally formulated for one-electron transfer reactions, $A + D \rightarrow A^{-\cdot} + D^{+\cdot}$, in the framework of the *Marcus equation*, assuming weak coupling between the reactants [368].

Note 2: Reorganization energy is not the same as distortion energy, which is the energy required to distort the reactants to the nuclear configuration of the *transition state*.

Note 3: This approach has been extended to enzyme-catalysed reactions [369].

Note 4: Marcus theory has been shown to be valid for some complex reactions (*cycloaddition*, S_N2), even though the weak-coupling assumption is clearly not valid. In these cases the reorganization energy (in terms of activation strain) is counteracted by stabilizing interactions (electrostatic and orbital) [166].

See also *distortion interaction model*, *intrinsic barrier*, *Marcus equation*.

rev[3]

~~revGB-revPOC~~

resonance

Representation of the electronic structure of a *molecular entity* in terms of contributing *Lewis structure*s.

Note 1: Resonance means that the *wavefunction* is represented by mixing the wavefunctions of the contributing Lewis structures.

Note 2: The contributing Lewis structures are represented as connected by a double-headed arrow ($\leftrightarrow$), rather than by the double arrow ($\rightleftarrows$) representing *equilibrium* between species.

Note 3: This 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.

Note 4: This term has a completely different meaning in physics.

See [75,370].

See also [371].

rev[3]

~~revGB-revPOC~~

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resonance effect

Experimentally observable influence (on reactivity, etc.) of a *substituent* through electron *delocalization* to or from the substituent.

   See [126,173,191].

   See also *inductive effect*.

   rev[3]

resonance energy

Difference in potential energy between the actual *molecular entity* and the contributing *Lewis structure* of lowest potential energy.

   Note: The resonance energy cannot be measured experimentally, but only estimated, since contributing Lewis structures are not observable molecular entities.

   See *resonance*.

   rev[3]

   revGB-revPOC

resonance form

resonance structure, contributing structure, canonical form

One of at least two *Lewis structure*s, with fixed single, double, and triple bonds, that is a contributing structure to the valence-bond *wavefunction* of a molecule that cannot be described by a single Lewis structure.

   Note 1: Although the valence-bond wavefunction is a linear combination of the wavefunctions of the individual resonance forms, the coefficients and the relative contributions of the various resonance forms are usually kept qualitative. For example, the major resonance forms for the conjugate base of acetone are $CH_2=C(CH_3)–O^-$ and $H_2C^-–C(CH_3)=O$, with the former contributing more.

   Note 2: Resonance forms are connected by a double-headed arrow ($\leftrightarrow$). This must not be confused with the double arrow connecting species in *equilibrium* ($\rightleftharpoons$).

   See also *delocalization*, *Kekulé structure*, *resonance*.

resonance hybrid

Molecular entity whose electronic structure is represented as the superposition of two or more *resonance form*s (or *Lewis structure*s) with different formal arrangements of electrons but identical arrangements of nuclei.

   Note 1: Whereas each contributing resonance form represents a localized arrangement of electrons which, considered by itself, would imply different bond lengths (say) for formal single and double bonds, *resonance* between two or more contributors requires each to have the same geometry, namely that of the resulting hybrid, which represents a delocalized arrangement of electrons. A particular bond in the hybrid may have a length that is, loosely, an "average" of formal single-bond and double-bond

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values implied by its contributing individual resonance forms, but the hybrid does not oscillate among these as if they were in *equilibrium*.

Note 2: The resonance forms are connected by a double-headed arrow (↔), rather than by the double arrow (⇌) representing equilibrium between species.

~~diffGB~~

retrocycloaddition

deprecated

Cycloelimination.

[3]

~~GB~~

Ritchie equation

Linear Gibbs-energy relation (linear free-energy relation)

$$\lg \{k_N\} = \lg \{k_0\} + N_+$$

applied to the reactions between nucleophiles and certain large and relatively stable organic cations, e.g., arenediazonium, triarylmethyl, and aryltropylium cations, in various solvents, where $\{k_N\}$ is the (reduced) second-order *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 (reduced) first-order rate constant for the same cation with water in water, and N_+ is a parameter characteristic of the nucleophilic system and independent of the *electrophilic* reaction partner.

The discrepancy between second-order and first-order rate constants must be reconciled by writing the equation with arguments of the logarithms of dimension 1, i.e., by using reduced rate constants (as denoted by the curly brackets in the defining equation):

$$\lg [k_N/(dm^3\ mol^{-1}s^{-1})] = \lg (k_0/s^{-1}) + N_+$$

Note 1: 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 decadic log (lg) units. The equation thus involves a gigantic breakdown of the *reactivity-selectivity principle*.

Note 2: The Ritchie equation is a special case of the more general *Mayr-Patz equation*.

See [193,372,373]. See also [125,374].

rev[3]

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ρ-value (rho-value)

Quantitative measure of the susceptibility of the *rate constant* or *equilibrium* constant of an organic reaction to the influence of *substituent* groups, usually on an *aromatic* ring.

   Note 1: Defined by Hammett to describe the effects of substituents at the *meta*- and *para*-positions on rate or equilibrium of a reaction on the side chain of a substituted benzene, the empirical equation has the general form

$$\lg(k_X/k_H) \text{ or } \lg(K_X/K_H) = \rho\sigma_X$$

in which σ_X is a constant characteristic of the substituent X and of its position in the reactant molecule.

   Note 2: More generally (not only for aromatic series), ρ-values (modified with appropriate subscripts and superscripts) are used to designate the susceptibility to substituent effects of reactions of families of organic compounds, as given by the modified set of σ-constants in an empirical correlation.

   Note 3: Reactions with a positive ρ-value are accelerated (or the equilibrium constants 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 involve a *transition state* (or reaction product) with an increased *electron density* at the *reactive* site of the substrate.

   See also *Hammett equation*, *σ-constant*, *Taft equation*.
rev[3]
revPOC

$\rho\sigma$-equation (rho-sigma equation)

   See *Hammett equation*, *ρ-value*, *σ-constant*, *Taft equation*.
GB[3]

salt effect

   See *kinetic electrolyte effect*.
GB[3]

saturation transfer

   See *magnetization transfer*.
rev[3]

185

1 ~~revGB-revPOC~~

2

Saytzeff rule
Preferential removal of a hydrogen from the β carbon that has the fewest hydrogens in dehydrohalogenation of secondary and tertiary haloalkanes.

Note 1: The rule was originally formulated by A. Saytzeff (Zaitsev) to generalize the orientation in *β-elimination* reactions of haloalkanes. It 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.

Note 2: Exceptions to the Saytzeff rule are exemplified by the *Hofmann rule*.

See [375].

See also *Markovnikov rule*.

~~revGB-revPOC~~[3]

scavenger
Substance that reacts with (or otherwise removes) a trace component (as in the scavenging of trace metal ions) or traps a *reactive intermediate*.

See also *inhibition*.

~~GB~~[3]

selectivity
Discrimination shown by a reagent in competitive attack on two or more *substrate*s or on two or more positions or diastereotopic or enantiotopic faces of the same substrate.

Note 1: Selectivity is quantitatively expressed by the ratio of *rate constant*s of the competing reactions, or by the decadic logarithm of such a ratio.

Note 2: In the context of *aromatic substitution* (usually *electrophilic*, for monosubstituted benzene derivatives), the selectivity factor S_f (expressing discrimination between *p*- and *m*-positions in PhZ) is defined as

$$S_f = \lg (p_f^Z/m_f^Z)$$

where the *partial rate factors* p_f^Z and m_f^Z express the *reactivity* of para and meta positions in the aromatic compound PhZ relative to that of a single position in benzene.

See [347].

See also *isoselective relationship*, *partial rate factor*, *regioselectivity*, *stereoselectivity*.

~~rev~~[3]

~~revGB-revPOC~~

self-assembly

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1   Process whereby a system of single-molecule components spontaneously forms an
2   organized structure, owing to *molecular recognition*.
3

4   **shielding**
5   Extent to which the effective magnetic field is reduced for a nucleus in a molecule
6   immersed in an external magnetic field, relative to that experienced by a bare nucleus
7   in that field.
8   *Note 1*: The reduction is due to the circulation of the electrons around the observed
9   and the neighbouring nuclei. The external field induces a magnetic moment that is
10   oriented in the opposite direction to the external field, so that the local field at the central
11   nucleus is weakened, although it may be strengthened at other nuclei (deshielding).
12   *Note 2*: This phenomenon is the origin of the structural dependence of the resonance
13   frequencies of the nuclei.
14   See also *chemical shift*.
15   GB[3]
16

17   **shift reagent**
18   Paramagnetic substance that induces an additional change of the NMR resonance
19   frequency of a nucleus near any site in a molecule to which the substance binds.
20   See *chemical shift*.
21

22   **sigma, pi**
23   See σ, π
24   rev[3]
25   revGB-revPOC
26

27   **sigmatropic rearrangement**
28   *Molecular rearrangement* that involves both the creation of a new σ *bond* between
29   atoms previously not directly linked and the breaking of an existing σ bond.
30   *Note 1*: There is normally a concurrent relocation of π bonds in the molecule
31   concerned, but neither the number of π bonds nor the number of σ bonds changes.
32   *Note 2*: The *transition state* of such a reaction may be visualized as an *association*
33   of two fragments connected at their termini by two partial σ bonds, one being broken
34   and the other being formed as, for example, the two allyl fragments in (a'). Considering
35   only atoms within the (real or hypothetical) cyclic array undergoing reorganization, if the
36   numbers of these in the two fragments are designated i and j, then the rearrangement
37   is said to be a sigmatropic change of order [i,j] (conventionally $i \le j$). Thus rearrangement
38   (a) is of order [3,3], whereas rearrangement (b) is a [1,5]sigmatropic shift of hydrogen.
39   (By convention the square brackets [...] here refer to numbers of atoms, in contrast with
40   current usage in the context of *cycloaddition*.)

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(a) ⇌   (a')

(b) ⇌

The descriptors a and s (*antarafacial* and *suprafacial*) may also be annexed to the numbers *i* and *j*; (b) is then described as a $[1_s,5_s]$ sigmatropic rearrangement, since it is suprafacial with respect to both the hydrogen atom and the pentadienyl system:
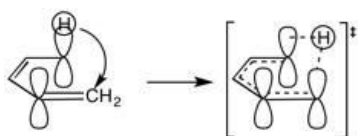
See also *cycloaddition*, *tautomerization*.
rev[3]
revGB-revPOC

silylene
(1) Generic name for H_2Si: 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*.)
(2) The silanediyl group ($H_2Si<$), analogous to the methylene group ($H_2C<$).
GB[3]

single-electron transfer mechanism (SET)
Reaction *mechanism* characterized by the transfer of a single electron between two species, occurring in one of the steps of a multistep reaction.
GB[3]

single-step reaction
one-step reaction
Reaction that proceeds through a single *transition state* (or no transition state).
GB[3]

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skeletal formula

bond-line formula

Two-dimensional representation of a *molecular entity* in which bonds are indicated as lines between vertices representing octet carbon atoms with attached hydrogens omitted and in which other atoms are represented by their chemical symbols.

Examples: ethanol, cyclohexene, 4-pyridone
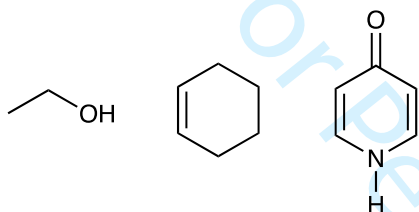
See *line formula*.

Slater-type orbital (STO)

Function centred on an atom for which the radial dependence has the form $\phi(r) \propto r^{n-1}$ $\exp(-\zeta r)$, used to approximate *atomic orbital*s in the LCAO-MO method.

Note 1: n is the effective principal quantum number and ζ is the orbital exponent (screening constant) derived from empirical considerations.

Note 2: The angular dependence is usually introduced by multiplying the radial function by a spherical harmonic $Y_{1m}(\theta,\phi)$.

Note 3: Owing to difficulties in computing the integrals of STOs analytically for molecules with more than two atoms they are often replaced by linear combinations of *Gaussian orbitals*.

See [8].

rev[3]

revGB-revPOC

solvation

Stabilizing interaction between a solute (or solute moiety) and the solvent.

Note: Such interactions generally involve electrostatic forces and *van der Waals forces*, as well as chemically more specific effects such as *hydrogen bond* formation.

See also *cybotactic region*.

GB[3]

solvatochromic relationship

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Linear Gibbs-energy relationship (linear free-energy relationship) based on *solvatochromism*.

See also *Dimroth-Reichardt E*$_T$ *parameter*, *Kamlet-Taft solvent parameters*.

~~revGB-revPOC~~[3]

solvatochromism

Pronounced change in position and sometimes intensity of an electronic absorption or emission band, accompanying a change in the *polarity* of the *medium*.

Note: Negative (positive) solvatochromism corresponds to a *hypsochromic shift* (*bathochromic shift*) with increasing solvent polarity.

See [9,17,376].

See also *Dimroth-Reichardt E*$_T$ *parameter*, *Z-value*.

~~GB~~[3]

solvatomers

Isomers that differ in their solvation environment.

Note 1: Because the solvation environment fluctuates rapidly, solvatomers interconvert rapidly.

Note 2: Species that differ in the type of solvent molecules should not be called solvatomers, because they are not isomers.

solvent parameter

Quantity that expresses the capability of a solvent for interaction with solutes, based on experimentally determined physicochemical quantities, in particular: relative *permittivity*, refractive index, *rate constant*s, Gibbs energies and enthalpies of reaction, and ultraviolet-visible, infrared, and NMR spectra.

Note 1: Solvent parameters are used in *correlation analysis* of solvent effects, either in single-parameter or in multiple-parameter equations.

Note 2: Solvent parameters include those representing a bulk property, such as relative *permittivity* (dielectric constant) as well as those that describe a more localized solute/solvent interaction, such as hydrogen-bonding acceptance or donation and Lewis acid/base adduct formation.

See [17,377].

See also: *acceptor number*, *Catalán solvent parameters*, *Dimroth-Reichardt E*$_T$ *parameter*, *Grunwald-Winstein equation*, *Kamlet-Taft solvent parameters*, *Laurence solvent parameters*, *Koppel-Palm solvent parameters*, *linear solvation energy relationship*, *Z-value*.

rev[3]

~~revGB-revPOC~~

190

solvolysis

Reaction with solvent.

Note 1: Such a reaction generally involves the rupture of one or more *bond*s in the solute. More specifically the term is used for *substitution*, *elimination,* and *fragmentation* reactions in which a solvent species serves as *nucleophile* or *base*.

Note 2: A solvolysis can also be classified as a *hydrolysis*, alcoholysis, or ammonolysis, etc., if the solvent is water, alcohol, or ammonia, etc.

Note 3: Often a solvolysis is a *nucleophilic substitution* (usually S_N1, accompanied by E1 *elimination*), where the nucleophile is a solvent molecule.

rev[3]

revGB-revPOC

SOMO

Singly **O**ccupied **M**olecular **O**rbital (such as the half-filled *HOMO* of a radical).

See also *frontier orbitals*.

GB[3]

special salt effect

Steep increase of the rate of certain solvolysis reactions observed at low concentrations of some non-common-ion salts.

Note: The effect is attributed to trapping of an intimate *ion pair* that would revert to reactant in the absence of the salt.

See also *kinetic electrolyte effect*.

rev[3]

revGB-revPOC

specific catalysis

Acceleration of a reaction by a unique *catalyst*, rather than by a family of related substances.

Note: The term is most commonly used in connection with specific hydrogen-ion or hydroxide-ion (*lyonium ion* or *lyate ion*) catalysis.

See also *general acid catalysis*, *general base catalysis*, *pseudo-catalysis*.

GB[3]

spectator mechanism

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.,

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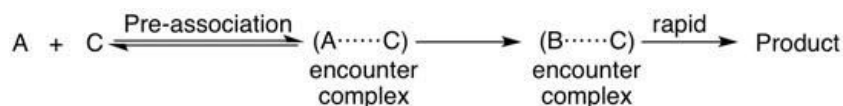
Note: The formation of B from A may itself be a bimolecular reaction with some other reagent. Since C does not assist the formation of B, it is described as being present as a spectator.

See also *microscopic diffusion control*.

GB[3]

spin adduct

See *spin trapping*.

GB[3]

spin counting

See *spin trapping*.

GB[3]

spin density

Unpaired *electron density* at a position of interest, usually at carbon, in a *radical* or a *triplet state*.

Note: Spin density is often measured experimentally by electron paramagnetic resonance/electron spin resonance (EPR/ ESR) spectroscopy through hyperfine splitting of the signal by neighbouring magnetic nuclei.

See also *radical centre*.

GB[3]

spin label

Stable paramagnetic *group* (typically an *aminoxy* radical, $R_2NO^•$) that is attached to a part of a *molecular entity* whose chemical environment may be revealed by its electron spin resonance (ESR) spectrum.

Note: When a paramagnetic molecular entity is used without covalent attachment to the molecular entity of interest, it is frequently referred to as a spin probe.

GB[3]

spin trapping

Formation of a more *persistent* radical from interaction of a *transient radical* with a diamagnetic reagent.

Note 1: The product radical accumulates to a concentration where detection and, frequently, identification are possible by EPR/ESR spectroscopy.

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1　　*Note 2*: The key reaction is usually one of *attachment*; the diamagnetic reagent is
2　said to be a spin trap, and the persistent product radical is then the spin *adduct*. The
3　procedure is referred to as spin trapping, and is used for monitoring reactions involving
4　the intermediacy of *reactive* radicals at concentrations too low for direct observation.
5　Typical spin traps are *C*-nitroso compounds and nitrones, to which reactive radicals will
6　rapidly add to form *aminoxy* radicals.
7　　*Example:*

8
9　　*Note 3*: A quantitative development in which essentially all reactive radicals
10　generated in a particular system are intercepted has been referred to as spin counting.
11　　*Note 4*: Spin trapping has also been adapted to the interception of radicals generated
12　in both gaseous and solid phases. In these cases the spin adduct is in practice
13　transferred to a liquid solution for EPR/ESR observation.
14　　~~GB~~[3]
15

16　**stable**
17　Having a lower standard Gibbs energy, compared to a reference *chemical species*.
18　　*Note 1*: Quantitatively, in terms of Gibbs energy, a chemical species A is more stable
19　than its isomer B if $\Delta_r G°$ is positive for the (real or hypothetical) reaction A → B.
20　　*Note 2*: For the two reactions
21
22　　　　　P　→　X　+　Y　　　　$\Delta_r G_1°$
23　and　　　Q　→　X　+　Z　　　　$\Delta_r G_2°$
24
25　if $\Delta_r G_1° > \Delta_r G_2°$, then P is more stable relative to its product Y than is Q relative to Z.
26　　*Note 3*: Both in qualitative and quantitative usage the term stable is therefore always
27　used in reference to some explicitly stated or implicitly assumed standard.
28　　*Note 4*: The term should not be used as a synonym for *unreactive* or less *reactive*
29　since this confuses thermodynamics and kinetics. A relatively more stable chemical
30　species may be more reactive than some reference species towards a given reaction
31　partner.
32　　See also *inert*, *unstable*.
33　　~~GB~~[3]
34

35　**stationary state**

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1 (1) (in quantum mechanics): *Wavefunction* whose probability density $|\Psi|^2$ remains
2 constant and whose observable properties do not evolve with time.
3 (2) (in kinetics): See *steady state*.
4 ~~GB~~[3]

5

6 **steady state (or stationary state)**
7 (1) Approximation that the kinetic analysis of a complex reaction involving *unstable*
8 intermediates in low concentration can be simplified by setting the rate of change of
9 each such *intermediate* equal to zero, so that the rate equation can be expressed as a
10 function of the concentrations of *chemical species* present in macroscopic amounts.
11   For example, if X is an *unstable* intermediate in the reaction sequence:

12
13
14 Since [X] is negligibly small, d[X]/dt, the rate of change of [X], can be set equal to zero.
15 The steady state approximation then permits solving the following equation
16
17   d[X]/dt = k_1[A] − k_{-1}[X] − k_2[X][C] = 0
18
19 to obtain the steady-state [X]:
20
21   [X] = k_1[A]/(k_{-1} + k_2[C])
22
23 whereupon the rate of reaction is expressed:
24
25   d[D]/dt = k_2[X][C] = $k_1 k_2$[A][C]/(k_{-1} + k_2[C])
26
27   *Note*: The steady-state approximation does not imply that [X] is even approximately
28 constant, only that its absolute rate of change is very much smaller than that of [A] and
29 [D].
30 (2) Regime in a stirred flow reactor such that all concentrations are independent of time.
31   See [13].
32 ~~GB~~[3]
33

34 **stepwise reaction**
35 *Chemical reaction* with at least one reaction *intermediate* and involving at least two
36 consecutive *elementary reaction*s.
37   See also *composite reaction, reaction step*.
38 ~~GB~~[3]

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stereoelectronic
Pertaining to the dependence of the properties (especially energy or *reactivity*) of a *molecular entity* or of a *transition state* on the relative disposition of electron pairs owing to the nuclear geometry.
　　Note: Stereoelectronic effects are ascribed to the differing overlaps of *atomic orbital*s in different *conformation*s.
　　See [11].
　　~~GB~~[3]

stereogenic centre
Atom within a molecule bearing groups such that interchanging any two of them leads to a *stereoisomer* of the original molecule.
　　See [11,378].

stereoisomers
Isomers that have the same bonds (*connectivity*) but differ in the arrangement of their atoms and cannot be interconverted by rapid rotation around single bonds.
　　See [11].
　　~~GB~~

stereoselectivity (stereoselective)
Preferential formation in a *chemical reaction* of one *stereoisomer* over another.
　　Note 1: When the stereoisomers are *enantiomer*s, the phenomenon is called enantioselectivity and is quantitatively expressed by the enantiomeric excess or enantiomeric ratio; when they are *diastereoisomers*, it is called *diastereoselectivity* and is quantitatively expressed by the diastereomeric excess or diastereomeric ratio.
　　Note 2: Reactions are termed 100 % stereoselective if the preference is complete, or partially (*x* %) stereoselective if one product predominates. The preference may also be referred to semiquantitatively as high or low stereoselectivity
　　See [11,140].
　　~~revGB~~[3]

stereospecificity (stereospecific)
Property of those *chemical reaction*s in which different stereoisomeric reactants are converted into different stereoisomeric products.
　　Example: electrocyclization of *trans,cis,trans*-octa-2,4,6-triene produces *cis*-5,6-dimethylcyclohexa-1,3-diene, whereas c*is,cis,trans*-octa-2,4,6-triene produces racemic *trans*-5,6-dimethylcyclohexa-1,3-diene.

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Note 1: A stereospecific process is necessarily *stereoselective* but not all stereoselective processes are stereospecific. Stereospecificity may be total (100 %) or partial.

Note 2: The term is also applied to situations where reaction can be performed with only one stereoisomer. For example the exclusive formation of racemic *trans*-1,2-dibromocyclohexane upon bromination of cyclohexene is a stereospecific process, even though the analogous reaction with (*E*)-cyclohexene has not been performed.

Note 3: Stereospecificity does NOT mean very high stereoselectivity. This usage is unnecessary and is strongly discouraged.

See [11,140].

For the term stereospecific polymerization see [379].

rev[3]

revGB

steric-approach control
Situation in which the *stereoselectivity* of a reaction under *kinetic control* is governed by steric hindrance to attack of the reagent, which is directed to the less hindered face of the molecule.

Note: Partial bond making at the *transition state* must be strong enough for steric control to take place, but the transition state should not be so close to products that the steric demand of the reagent at the transition state is the same as the steric demand of the group as present in the product.

An example is LiAlH$_4$ reduction of 3,3,5-trimethylcyclohexan-1-one, where steric hindrance by an axial methyl directs hydride addition to the equatorial position, even though the more stable product has the H axial and the OH equatorial.

See also *product-development control*.

rev[3]

revGB

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steric effect
Consequences for molecular geometry, thermochemical properties, spectral features, solvation, or reaction rates resulting from the fact that atoms repel each other at close distance. The repulsion is due to the quantum-mechanical Pauli exclusion principle. Substitution of hydrogen atoms by groups with a larger van der Waals radius may lead to situations where atoms or groups of atoms repel each other, thereby affecting distances and angles.

　Note 1: It is in principle difficult to separate the steric effect from other electronic effects.

　Note 2: For the purpose of *correlation analysis* or *linear Gibbs-energy relations* (*linear free-energy relation*s) various scales of steric parameters have been proposed, notably *A values*, Taft's E_S and Charton's *v* scales.

　Note 3: A steric effect on a rate process may result in a rate increase (steric acceleration) or a decrease (steric retardation) depending on whether the transition state or the reactant state is more affected by the steric effect.

　Note 4: Bulky groups may also attract each other if at a suitable distance.

　See [290,380].

　See *Taft equation*, *van der Waals forces*.

　rev[3]

　revGB-revPOC

steric hindrance
Steric effect whereby the crowding of substituents around a reaction centre retards the attack of a reagent.

　rev[3]

　revGB-revPOC

stopped flow
Technique for following the kinetics of reactions in solution (usually in the millisecond time range) in which two, or more, 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 a method with a rapid response (e.g., optical absorption spectroscopy).

　See *mixing control*.

　rev[3]

　revGB-revPOC

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strain

Feature of a *molecular entity* or *transition structure* for which the energy is increased because of unfavourable non-bonded (steric) interactions, bond lengths, bond angles, or dihedral angles (torsional strain), relative to a standard.

Note 1: The strain energy is quantitatively defined as the standard enthalpy of a structure relative to that of a strainless structure (real or hypothetical) made up from the same atoms with the same types of bonding.

For example, the enthalpy of formation of cyclopropane is +53.6 kJ mol^{-1}, whereas the hypothetical 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.

See *molecular mechanics*.

GB[3]

structural isomers

discouraged term for *constitutional isomers*.

subjacent orbital

Next-to-**H**ighest **O**ccupied **M**olecular **O**rbital (NHOMO, also called HOMO−1).

Note: Subjacent and *superjacent* orbitals sometimes play an important role in the interpretation of molecular interactions according to the *frontier orbital* approach.

See [381].

GB[3]

substituent

Any 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).

GB[3]

substitution

Chemical reaction, elementary or stepwise, of the form A–B + C → A–C + B, in which one atom or group in a molecular entity is replaced by another atom or group.

Examples

$CH_3Cl + HO^- \rightarrow CH_3OH + Cl^-$

$C_6H_6 + NO_2^+ \rightarrow C_6H_5NO_2 + H^+$

Note: A substitution reaction can be distinguished as an *electrophilic substitution* or a *nucleophilic substitution*, depending on the nature of the reactant that is considered to react with the *substrate*.

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1 rev[3]
2 ~~revGB-revPOC~~
3

4 **substrate**
5 *Chemical species*, the reaction of which with some other chemical reagent is under
6 observation (e.g., a compound that is transformed under the influence of a catalyst).
7   *Note*: The term should be used with care. Either the context or a specific statement
8 should always make it clear which chemical species in a reaction is regarded as the
9 substrate.
10   See also *transformation*.
11 ~~GB~~[3]
12

13 **successor complex**
14 *Chemical species* formed by the transfer of an electron or of a hydrogen (atom or ion)
15 from a donor D to an acceptor A after these species have diffused together to form the
16 precursor or *encounter complex*:

$$A + D \longrightarrow (A\ D) \longrightarrow (A^{\cdot-}\ D^{\cdot+})$$

$$A + DH \longrightarrow (A\ DH) \longrightarrow (AH^{\cdot-}\ D^{\cdot+})\ or\ (AH^+\ D^-)$$

17
18 rev[3]
19 ~~revGB-revPOC~~
20

21 **suicide inhibition**
22   See *mechanism-based inhibition*.
23 ~~GB~~[3]
24

25 **superacid**
26 Medium having a high *acidity*, generally greater than that of 100 % sulfuric acid. The
27 common superacids are made by dissolving a powerful *Lewis acid* (e.g., SbF_5) in a
28 suitable *Brønsted acid*, such as HF or HSO_3F.
29   *Note 1*: An equimolar mixture of HSO_3F and SbF_5 is known by the trade name Magic
30 Acid.
31   *Note 2*: An uncharged gas-phase substance having an endothermicity (enthalpy) of
32 deprotonation (dehydronation) lower than that of H_2SO_4 is also called a superacid.
33 Nevertheless such a superacid is much less acidic in the gas phase than similar cationic
34 acids.
35   See [18,382,383,384].
36   See *acidity, superbase*.
37 rev[3]
38 ~~revGB-revPOC~~
39

199

superbase

Compound having a very high *basicity*.

Examples include amide bases such as LDA, potassium *tert*-butoxide + organolithium, some phosphazenes.

See *superacid*.

See [385].

rev[3]

revGB-revPOC

superjacent orbital

Second **L**owest **U**noccupied **M**olecular **O**rbital (SLUMO).

Note: *Subjacent* and superjacent orbitals sometimes play an important role in the interpretation of molecular interactions according to the *frontier orbital* approach.
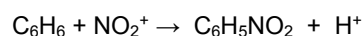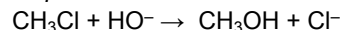
See [381].

suprafacial

See *antarafacial*.

GB[3]

supramolecular

Description of a system of two or more *molecular entities* that are held together and organized by means of intermolecular (noncovalent) binding interactions.

See [386].

revGB[3]

Swain-Lupton equation

Dual-parameter approach to the correlation analysis of substituent effects, which involves a field constant (F) and a resonance constant (R).

$$\lg(k_X/k_H) = fF_X + rR_X$$

See [191,387].

Note 1: The original treatment was modified later.

Note 2: The procedure has often been applied, but also often criticized.

See [388,389,390,391,392].

revGB-revPOC[3]

Swain-Scott equation

Linear Gibbs-energy relation (*linear free-energy relation*) of the form

200

1 $\lg(k/k_0) = sn$

applied to the variation of *reactivity* of a given *electrophilic* substrate towards a series
of *nucleophilic* reagents, where k_0 is a *rate constant* for reaction with water, k is the
corresponding rate constant for reaction with any other nucleophilic reagent, n is a
measure of the *nucleophilicity* of the reagent (n = 0.0 for water) and s is a measure of
the sensitivity of the substrate to the nucleophilicity of the reagent (s = 1.0 for CH_3Br).
    See [192].
    See also *Mayr-Patz equation, Ritchie equation*.
    ~~GB~~[3]

symproportionation
comproportionation
    ~~GB~~[3]

syn
    See *anti*.
    See [11].
    ~~GB~~[3]

synartetic acceleration
    See *neighbouring group participation*.
    ~~GB~~[3]

synchronization
    See *principle of nonperfect synchronization.*
    rev[3]
    ~~GB~~

synchronous
Feature of a *concerted* process in which all the changes (generally bond rupture and
bond formation) have progressed to the same extent at the *transition state*.
    Note 1: A synchronous reaction is distinguished from (1) a concerted reaction, which
takes place in a single kinetic step without being synchronous, (2) a reaction where
some of the changes in bonding take place earlier, followed by the rest, and (3) a two-
step reaction, which takes place in two kinetically distinct steps, via a stable
intermediate
    Note 2: The progress of the bonding changes (or other primitive changes) is not
defined quantitatively in terms of a single parameter applicable to different bonds. The
concept therefore does not admit an exact definition except in the case of concerted

201

processes involving changes in two identical bonds. If the bonds are not identical, the process should simply be described as concerted.

See [393,394,395]. For an index of synchronicity see [396].

See also *imbalance*.

rev[3]

~~GB~~

σ, π

Symmetry designations that distinguish *molecular orbital*s as being symmetric (σ) or antisymmetric (π) with respect to a defining plane containing at least one atom.

Note 1: In practice the terms are used both in this rigorous sense (for orbitals encompassing the entire molecule) and for localized two-centre orbitals or bonds. In the case of localized two-centre bonds, a π bond has a nodal plane that includes the internuclear bond axis, whereas a σ bond has no such nodal plane. (A δ bond in organometallic or inorganic chemical species has two nodes.) *Radical*s are classified by analogy into σ and π radicals.

Note 2: Such two-centre orbitals may take part in molecular orbitals of σ or π symmetry. For example, the methyl group in propene contains three C–H bonds, each of which is of local σ symmetry (i.e., without a nodal plane including the internuclear axis), but these three σ bonds can in turn be combined to form a set of group orbitals one of which has π symmetry with respect to the principal molecular plane and can accordingly interact with the two-centre orbital of π symmetry (π bond) of the double-bonded carbon atoms, to form a molecular orbital of π symmetry. Such an interaction between the CH_3 group and the double bond is an example of *hyperconjugation*. This cannot rigorously be described as σ-π conjugation since σ and π here refer to different defining planes, and interaction between orbitals of different symmetries (with respect to the same defining plane) is forbidden.

Note 3: Conjugation between a π system and a lone pair of (for example) an ether oxygen involves a lone pair of π symmetry with respect to the defining plane. It is incorrect to consider this as an interaction between the π system and one of two identical sp^3-hybrid lone pairs, which are neither σ nor π.

Note 4: The two lone pairs on a carbonyl oxygen are properly classified as σ or π with respect to the plane perpendicular to the molecular plane (dotted line perpendicular to the plane of the page), rather than as two sp^2-hybridized lone pairs. This distinction readily accounts for the facts that there are two different lone-pair *ionization energies* and two different *n*-π* *excited state*s.

202

See also [397].

~~revGB-revPOC~~

σ-adduct

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 σ bond is formed and the original *conjugation* is disrupted.

Note 1: This has generally been called a σ complex, or a Wheland complex from electrophilic addition, but adduct is more appropriate.

Note 2: The term may also be used for analogous adducts to π systems.

See also *Meisenheimer adduct*.

rev[3]

~~GB~~

σ-constant

Substituent constant for *meta-* and *para*-substituents in benzene derivatives as defined by Hammett on the basis of the *ionization* constant of a substituted benzoic acid, i.e., $lg(K_a^X/K_a^H)$, where K_a^X is the ionization constant (acid-dissociation constant) of a *m-* or *p*-substituted benzoic acid and K_a^H that of benzoic acid itself.

Note 1: A large positive σ-value implies high electron-withdrawing power by an inductive and/or resonance effect, relative to H; a large negative σ-value implies high electron-releasing power relative to H.

Note 2: 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_o are typical; also for constants which represent dissected electronic effects, such as σ_I and σ_R. For example, σ^- (sigma-minus) constants are defined on the basis of the ionization constants of *para*-substituted phenols, where such substituents as nitro show enhanced electron-withdrawing power.

See [124,125,126,191,226,398].

See also *Hammett equation*, *ρ-value*, *Taft equation*.

~~GB~~[3]

Taft equation

Linear free-energy relation (*linear Gibbs-energy relation*) involving the polar substituent constant σ^* and the steric substituent constant E_s, as derived from reactivities of aliphatic esters

203

lg $\{k\}$ = lg $\{k_0\}$ + $\rho^*\sigma^*$ + δE_s

The argument of the lg function should be of dimension 1. Thus, the reduced rate constants should be used, i.e., the *rate coefficient* divided by its units: $\{k\}$ = $k/[k]$ and $\{k_0\}$ = $k_0/[k_0]$.

Note: The standard reaction (k_0) is the *hydrolysis* of methyl acetate, whereby E_s is evaluated from the rate of acid-catalyzed hydrolysis, relative to that of methyl acetate, and σ^* is evaluated from the ratio of the rates of base- and acid-catalyzed hydrolysis. See [172,380,399,400].

See also *Hammett equation*, ρ-*value*, σ-*constant*.

rev[3]

revGB-revPOC

tautomers

Constitutional isomers that can interconvert more or less rapidly, often by *migration* of a *hydron*.

See *tautomerization*.

tautomerization

Rapid *isomerization* of the general form

G–X–Y=Z $\rightleftharpoons$ X=Y–Z–G
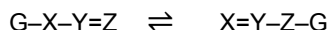
where the isomers (called *tautomers*) are readily interconvertible.

Note 1: The atoms of the groups X,Y, Z are typically any of C, H, N, O, or S, and G is a group that becomes an *electrofuge* or *nucleofuge* during isomerization.

Note 2: The commonest case, when the electrofuge is H$^+$, is also known as a *prototropic rearrangement*.

Examples:

> **Commented [s2]:** Alphabetical order, tautomers is later.

204
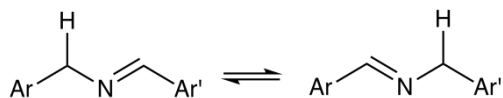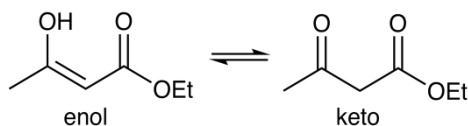
Note 3: The group Y may itself be a three-atom (or five-atom) chain extending the conjugation, as in

Note 4: Ring-chain tautomerization is the case where addition across a double bond leads to ring formation, as in
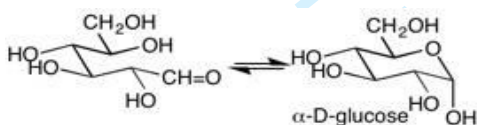
Note 5: *Valence tautomerization* is the case of rapid isomerization involving the formation and rupture of single and/or double bonds, without *migration* of atoms: for example

See [346,401].

See also *ambident*, *fluxional*, *sigmatropic rearrangement*, *valence tautomerization*.

  rev[3]

  revGB-revPOC

tautomers

Constitutional isomers that can interconvert more or less rapidly, often by *migration* of a *hydron*.

  See *tautomerization*.

***tele*-substitution**

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.

  Example

205
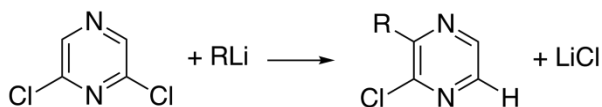
See also *cine-substitution*.

See [402,403].

rev[3]

revGB-revPOC

termination

Step(s) in a *chain reaction* in which *reactive intermediate*s are destroyed or rendered inactive, thus ending the chain.

GB[3]

tetrahedral intermediate

Reaction *intermediate* in which the bond arrangement around an initially double-bonded carbon atom (typically a carbonyl carbon) has been transformed from tricoordinate to tetracoordinate (with a *coordination number* of 4).

Example:
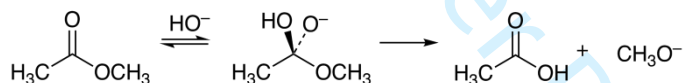
rev[3]

revGB-revPOC

thermodynamic control (of product composition)

equilibrium control

Conditions (including reaction times) that lead to reaction products in a proportion specified by the *equilibrium* constant for their interconversion.

See also *kinetic control*.

rev[3]

revGB-revPOC

thermolysis

Uncatalysed cleavage of one or more *covalent bond*s resulting from exposure of a *molecular entity* to a raised temperature, or a process of which such cleavage is an essential part.

See also *pyrolysis*.

GB[3]

through-conjugation

Phenomenon whereby electrons can be delocalized from any of three (or more) groups to any other.

206

1   *Example:* p-XC$_6$H$_4$Y, where an electron pair can be delocalized from electron-
2   donating X not only to ring carbons but also to electron-withdrawing Y.
3   *Note 1*: This may be contrasted with *cross-conjugation*.
4   *Note 2*: In Hammett-type correlations (*linear Gibbs-energy relationship*s) this
5   situation can lead to exalted substituent constants σ^+ or σ^-, as in solvolysis of p-
6   CH$_3$OC$_6$H$_4$C(CH$_3$)$_2$Cl or acidity of p-nitrophenol, respectively.
7

8   **TICT**
9   See *twisted intramolecular charge transfer*.
10

11   **torquoselectivity**
12   Preference for inward or outward rotation of substituents in *conrotatory* or *disrotatory*
13   *electrocyclic* ring-opening and ring-closing reactions, often owing to a preference for
14   electron donors (especially including large groups) to rotate outward and acceptors to
15   rotate inward.
16   See [404,405].

17
18   rev[3]
19   revGB
20

21   **transferability**
22   Assumption that a chemical property associated with an atom or group of atoms in a
23   molecule will have a similar (but not identical) value in other circumstances.
24   *Examples*: equilibrium bond length, bond force constant, NMR chemical shift.
25   GB[3]
26

207

transformation

Conversion of a *substrate* into a particular product, irrespective of the specific reagents or *mechanisms* involved.

Example: transformation of aniline ($C_6H_5NH_2$) into *N*-phenylacetamide ($C_6H_5NHCOCH_3$), which may be effected with acetyl chloride or acetic anhydride or ketene.

Note: A transformation is distinct from a reaction, the full description of which would state or imply all the reactants and all the products.

See [406].

~~GB~~[3]

transient (chemical) species

Short-lived reaction *intermediate*.

Note 1: Transiency can be defined only in relation to a time scale fixed by the experimental conditions and by the limitations of the technique employed in the detection of the intermediate. The term is a relative one.

Note 2: 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*.

~~GB~~[3]

transition dipole moment

Vector quantity describing the oscillating electronic moment induced by an electromagnetic wave, given by an integral involving the dipole moment operator **m** and the ground- and excited-state *wavefunction*s:

$$\boldsymbol{M} = \int \Psi_{exc} \, \mathbf{m} \, \Psi_{gnd} \, d\tau$$

Note: The magnitude of this quantity describes the allowedness of an electronic transition. It can often be separated into an electronic factor and a nuclear-overlap factor known as the Franck-Condon factor.

See [9].

transition state

State of a molecular system from which there are equal probabilities of evolving toward states of lower energy, generally considered as reactants and products of an *elementary reaction*.

208

Note 1: The transition state corresponds to the maximum along the minimum-Gibbs-energy path connecting reactants and products.

Note 2: The transition state can be considered to be a *chemical species* of transient existence.

Note 3: The term transition-state structure refers to a structure inferred from kinetic and stereochemical investigations; it does not necessarily coincide with a transition state or with a *transition structure*, which corresponds to a saddle point on a *potential-energy surface*, although it may represent an average structure.

Note 4: The assembly of atoms at the transition state has also been called an *activated complex*, although it is not a *complex* according to the definition in this Glossary.

Note 5: There are also reactions, such as the gas-phase *colligation* of simple *radicals* or the reactions of some *reactive intermediates* in solution, that do not require activation and do not involve a transition state.

Note 6: Ultrafast spectroscopy permits observation of transition states in some special cases.

See [349,407].

See also *Gibbs energy of activation*, *potential-energy profile*, *reaction coordinate*, *transition structure*.

rev[3]
revGB-revPOC

transition-state analogue

Species designed to mimic the geometry and electron density of the *transition state* of a reaction, usually enzymatic.

Note: A transition-state analogue is usually not a substrate for the enzyme, but rather an inhibitor.

rev[3]
revGB-revPOC

transition structure

Molecular entity corresponding to a saddle point on a *potential-energy surface*, with one negative force constant and its associated imaginary frequency.

Note 1: Whereas the *transition state* is not a specific molecular structure, but a set of structures between reactants and products, a transition structure is one member of that set with a specific geometry and energy.

Note 2: Although the saddle point coincides with the potential-energy maximum along a *minimum-energy reaction path*, it does not necessarily coincide with the maximum of Gibbs energy for an ensemble of *chemical species*.

Note 3: The term transition-state structure is not a synonym for transition structure.

209

1   See [349,408].

2   See also *activated complex*, *transition state*.

3   rev[3]

4   revGB-revPOC

5

transition vector

Normal mode of vibration of a *transition structure* corresponding to the single imaginary frequency and tangent to the *intrinsic reaction coordinate* at the saddle point. Sometimes called the reaction-coordinate vibrational mode.

Note: Infinitesimal motion along the transition vector in the two opposite senses determines the initial direction leading either toward reactants or toward products.

Note 2: The term "transition coordinate" was used in the 1994 Glossary of Terms in Physical Organic Chemistry in the sense defined here for transition vector, but apparently this usage was unique in the literature at that time and has not been generally adopted since.

See [349,409].

See *reaction coordinate*, *transition state*.

transport control

See *encounter-controlled rate*, *microscopic diffusion control*.

GB[3]

trapping

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.

See also *scavenger*.

GB[3]

triplet state

State having a total electron spin quantum number of 1.

See [9].

tunnelling

Quantum-mechanical phenomenon by which a particle or a set of particles penetrates a barrier on its *potential-energy surface* without having the energy required to surmount that barrier.

210

Note 1: In consequence of Heisenberg's Uncertainty Principle, a molecular entity has a nonzero probability of adopting a geometry that is classically forbidden because it corresponds to a potential energy greater than the total energy.

Note 2: Tunnelling is often considered to be a correction to an (over)simplified version of transition-state theory.

Note 3: Because the rate of tunnelling increases with decreasing mass, it is significant in the context of *isotope effect*s, especially of hydrogen isotopes.

See [410,411].

rev[3]

revGB-revPOC

twisted intramolecular charge transfer (TICT)

Feature of an excited electronic state formed by intramolecular electron transfer from an electron donor (D) to an electron acceptor (A), where interaction between electron and hole is restricted because D^+ and A^- are perpendicular to each other.

See [412].

umpolung

Process by which the nucleophilic or electrophilic property of a functional group is reversed.

Note: Umpolung is often achieved by temporary exchange of heteroatoms N or O by others, such as P, S, or Se, as in the conversion of electrophilic $RCH=O$ to $RCH(SR')_2$ and then with base to nucleophilic $RC(SR')_2^-$. Also the transformation of a haloalkane RX into a Grignard reagent RMgCl is an umpolung.

See [413].

rev[3]

revGB-revPOC

unimolecular

Feature of a reaction in which only one *molecular entity* is involved.

See *molecularity*.

rev[3]

revGB-revPOC

unreactive

Failing to react with a specified *chemical species* under specified conditions.

Note: The term should not be used in place of *stable*, which refers to a thermodynamic property, since a relatively more stable species may nevertheless be more *reactive* than some reference species towards a given reaction partner.

GB[3]

211

unstable

Opposite of *stable*, i.e., the *chemical species* concerned has a higher molar Gibbs energy than some assumed standard.

Note: The term should not be used in place of *reactive* or transient, although more reactive or *transient species* are frequently also more unstable.

rev[3]
revGB-revPOC

upfield

superseded but still widely used to mean shielded.

See *chemical shift*.

GB[3]

valence

Maximum number of single bonds that can be commonly formed by an atom or ion of the element under consideration.

Note: Often there is a most common maximum for a given element, and atoms in compounds where this number is exceeded, such as pentacoordinate carbocations ("carbonium ions") and iodine(III) compounds, are called *hypervalent*.

rev[3]
revGB-revPOC

valence isomer

Constitutional isomer related to another by *pericyclic reaction*.

Examples: Dewar benzene, prismane, and benzvalene are valence isomers of benzene.

Note: Valence isomers are separable, as distinguished from valence tautomers, which interconvert rapidly. See *valence tautomerization*.

rev[3]
revGB-revPOC

valence tautomerization

Rapid isomerization involving the formation and rupture of single and/or double bonds, without *migration* of atoms.

Example:

See *tautomerization*.

212

1   rev[3]
2   revGB-revPOC
3
4   **van der Waals forces**
5   Attractive or repulsive forces between *molecular entities* (or between groups within the
6   same molecular entity) other than those due to *bond* formation or to the electrostatic
7   interaction of ions or of ionic *group*s with one another or with neutral molecules.
8   *Note 1*: The term includes dipole-dipole, dipole-induced dipole, and London
9   (instantaneous induced dipole-induced dipole) forces, as well as quadrupolar *forces.*
10   *Note 2*: The term is sometimes used loosely for the totality of nonspecific attractive
11   or repulsive intermolecular forces.
12   *Note 3*: In the context of molecular mechanics, van der Waals forces correspond only
13   to the London dispersion forces plus the Pauli repulsion forces. Interactions due to the
14   average charge distribution (and not to fluctuations around the average or to induced
15   dipoles), including dipole-dipole, ion-ion and ion-dipole forces, are called Coulombic
16   forces.
17   See [290,414].
18   See also *dipole-dipole interaction*, *dipole-induced dipole forces, London forces.*
19   rev[3]
20   revGB-revPOC
21
22   **volume of activation**, $\Delta^{\ddagger}V$
23   Quantity derived from the pressure dependence of the *rate constant* of a reaction,
24   defined by the equation
25
26       $\Delta^{\ddagger}V = -RT\,[\partial \ln(k/[k])/\partial p]_T$
27
28   provided that rate constants of all reactions (except first-order reactions) are expressed
29   in pressure-independent concentration units, such as mol dm^{-3} at a fixed temperature
30   and pressure. The argument in the lg function should be of dimension 1. Thus, the rate
31   constant should be divided by its units, $[k]$.
32   *Note*: The volume of activation is interpreted as the difference between the partial
33   molar volume $^{\ddagger}V$ of the *transition state* and the sums of the partial molar volumes of the
34   reactants at the same temperature and pressure, i.e.,
35
36       $\Delta^{\ddagger}V = {}^{\ddagger}V - \Sigma(\rho V_R)$
37
38   where ρ is the order in the reactant R and V_R its partial molar volume.
39   See [13].
40   See *order of reaction*.

213

1 rev[3]
2 ~~revGB revPOC~~
3

4 **water/octanol partition coefficient (partition ratio)**
5 See *octanol-water partition ratio*
6

7 **wavefunction**
8 A mathematical expression whose form resembles the wave equations of physics,
9 supposed to contain all the information associated with a particular atomic or molecular
10 system. In particular, a solution of the Schrödinger wave equation, $H\psi = E\psi$, as an
11 eigenfunction ψ of the hamiltonian operator H, which involves the electronic and/or
12 nuclear coordinates.
13 *Note 1:* The wavefunction contains all the information describing an atomic or
14 molecular system that is consistent with the Heisenberg Uncertainty Principle.
15 *Note 2:* When a wavefunction is operated on by certain quantum-mechanical
16 operators, a theoretical evaluation of physical and chemical observables for that system
17 (the most important one being energy) can be carried out.
18 See [8,12].
19 ~~Expanded GB~~
20

21 **Wheland intermediate**
22 See *Meisenheimer adduct, σ-adduct.*
23 ~~GB~~[3]
24

25 **Woodward-Hoffmann rules**
26 See *orbital symmetry.*
27 ~~GB~~
28
29
30

31 **ylide**
32 Chemical species that can be produced by loss of a *hydron* from an atom directly
33 attached to the central atom of an *onium ion*.
34 *Example:*
35 $Ph_3P^+–CHRR' \rightarrow [Ph_3P^+–C^-RR' \leftrightarrow Ph_3P=CRR'] + H^+$
36 See [40].
37 ~~diffGB~~[3]
38

39 **Yukawa-Tsuno equation**

214

1 Multiparameter extension of the *Hammett equation* to quantify the role of enhanced
2 *resonance* effects on the reactivity of *para*–substituted benzene derivatives,
3
4     $\lg \{k\} = \lg \{k_o\} + \rho[\sigma^o + r(\sigma^+ - \sigma^o)]$
5 or $\lg \{k\} = \lg \{k_o\} + \rho[\sigma^o + r(\sigma^- - \sigma^o)]$
6
7 where the parameter *r* expresses the enhancement and where σ^o is a <u>substituent</u>
8 <u>constant</u> based on reactivities of phenylacetic acids and similar substrates, where
9 resonance interaction is weak or absent. The argument in the lg function should be of
10 dimension 1. Thus, reduced rate constants should be used $\{k\}= k/[k]$ and $\{k_o\} = k_o/[k_o]$.
11   See [398,415,416].
12   See also *dual substituent-parameter equation*, *ρ-value*, *σ-constant*, *through-*
13 *conjugation*.
14   rev[3]
15   ~~revGB-revPOC~~
16
17 **Zaitsev rule**
18   See *Saytzeff rule*.
19   ~~GB~~[3]
20
21 **zero-point energy**
22 Extent, in consequence of Heisenberg's Uncertainty Principle, by which a particle or a
23 set of particles has an energy greater than that of the minimum on the *potential-energy*
24 *surface*.
25   *Note 1*: Because of zero-point energy a molecular entity has a nonzero probability of
26 adopting a geometry whose energy is greater than that of the energy minimum.
27   *Note 2:* A molecular entity with zero-point energy may even adopt a geometry with
28 a potential energy greater than its total energy, a possibility that permits *tunnelling*.
29   *Note 3*: Because the magnitude of zero-point energy increases with decreasing
30 mass, it is significant in the context of *isotope effect*s, especially of hydrogen isotopes.
31
32 **Zucker-Hammett hypothesis**
33 Assumption that if $\lg \{k_1\}$ (= $k_1/[k_1]$, reduced pseudo-first-order rate constant of an acid-
34 catalyzed reaction) is linear in H_o (Hammett *acidity function*), then water is not involved
35 in the *transition state* of the *rate-controlling step*, whereas if $\lg \{k_1\}$ is linear in $\lg \{[H^+]\}$
36 then water is involved. The argument in the lg function should be of dimension 1. Thus,
37 reduced concentration = $\{[H^+]\}$ should be used, i.e., concentration of protons divided by
38 its units.
39   *Note*: This has been shown to be an overinterpretation.
40   See [22,417].

215

See also *Bunnett-Olsen equation*, *Cox-Yates equation*.

rev[3]

~~revGB-revPOC~~

Z-value

Quantitative measure of solvent polarity based on the UV-vis spectrum of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide.

See [143].

See *solvent parameter*.

rev[3]

~~revGB-revPOC~~

zwitterion

Highly dipolar, net uncharged (neutral) molecule having full electrical charges of opposite sign, which may be delocalized within parts of the molecule but for which no uncharged canonical resonance structure can be written.

Examples: glycine ($H_3N^+–CH_2–CO_2^-$), betaine ($Me_3N^+–CH_2–CO_2^-$).

Note 1: Sometimes also referred to as inner salts or ampholytes.

Note 2: Mesoionic compounds, such as sydnones, in which both positive and negative charge are delocalized, are sometimes considered as zwitterions, but species with a localized nonzero formal charge, such as a nitrone, $CH_3CH=N^+(–O^-)CH_3$, are not.

See [418].

rev[3]

~~revGB-revPOC~~

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GLOSSARY OF TERMS USED IN PHYSICAL ORGANIC CHEMISTRY

Abstract. This Glossary contains definitions, explanatory notes, and sources for terms used in physical organic chemistry. Its aim is to provide guidance on the terminology of physical organic chemistry, with a view to achieving a consensus on the meaning and applicability of useful terms and the abandonment of unsatisfactory ones. Owing to the substantial progress in the field, this 2021 revision of the Glossary is much expanded relative to the previous edition, and it includes terms from cognate fields.

INTRODUCTION TO THE 2021 REVISION
General Remarks

The first Glossary of Terms Used In Physical Organic Chemistry was published in provisional form in 1979 [1] and in revised form in 1983, incorporating modifications agreed to by IUPAC Commission III.2 (Physical Organic Chemistry) [2].

A further revision was undertaken under the chairmanship of Paul Müller, which was published in 1994 [3]. The work was coordinated with that of other Commissions within the Division of Organic Chemistry. In 1999 Gerard P. Moss, with the assistance of Charles L. Perrin, converted this glossary to a World Wide Web version [4]. The Compendium of Chemical Terminology [5] (Gold Book) incorporated many of the terms in the later version.

This Glossary has now been thoroughly revised and updated, to be made available as a Web document. The general criterion adopted for the inclusion of a term in this Glossary has been its wide use in the present or past literature of physical-organic chemistry and related fields, with particular attention to those terms that have been ambiguous. It is expected that the terms in this Glossary will be incorporated within the on-line version of the IUPAC Gold Book, which is the merged compendium of all glossaries [5].

The aim of this Glossary is to provide guidance on the terminology of physical-organic chemistry, with a view to achieving a far-reaching consensus on the definitions of useful terms and the abandonment of unsatisfactory ones. According to Antoine Lavoisier "Comme ce sont les mots qui conservent les idées et qui les transmettent, il en résulte qu'on ne peut perfectionner le langage sans perfectionner la science, ni la science sans le langage," (As it is the words that preserve the ideas and convey them, it follows that one cannot improve the language without improving science, nor improve

1 science without improving the language.") [6]. Our approach has been to take or update
2 entries from the previous glossary, whereas new terms were added by virtue of their
3 usage in the current literature and the diverse knowledge of the members of the Task
4 Force.

5 The Task Force is pleased to acknowledge the generous contributions of many
6 scientists who helped by proposing or defining new terms or by criticizing or modifying
7 existing ones. The following members of the Task Force have contributed to this
8 revision:

9

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26

27 **Arrangement, Abbreviations, and Symbol**s
28 The arrangement is alphabetical, terms with Greek letters following those in the
29 corresponding Latin ones. Italicized words in the body of a definition, as well as those
30 cited at the end, point to relevant cross-references. Literature references direct the
31 reader either to the original literature where the term was originally defined or to
32 pertinent references where it is used, including other IUPAC glossaries, where
33 definitions may differ from those here.
34 Definitions of techniques not directly used for measurements in physical-organic
35 chemistry are not included here but may be consulted in specialized IUPAC texts,
36 including the IUPAC Recommendations for Mass Spectrometry [7], the Glossary of
37 Terms Used In Theoretical Organic Chemistry [8], the Glossary of Terms Used in
38 Photochemistry 3rd edition [9], the Glossary of Terms Used in Photocatalysis and
39 Radiation Catalysis [10] and the Basic Terminology of Stereochemistry [11].

1   In accordance with IUPAC recommendations [12] the symbol ‡ to indicate
2 transition state ("double dagger") is used as a prefix to the appropriate quantities, e.g.,
3 $\Delta^\ddagger G$ rather than $\Delta G^\ddagger$. In equations including a logarithmic function the procedure
4 recommended by IUPAC was adopted, i.e., to divide each dimensioned quantity by its
5 units. Since this procedure often introduces a cluttering of the equations, we have in
6 some cases chosen a short-hand notation, such as ln $\{k(T)\}$, where the curly brackets
7 indicate an argument of dimension one, corresponding to $k(T)/[k(T)]$, where the square
8 brackets indicate that the quantity is divided by its units, as recommended in [12].
9
10 **Note on the identification of new and/or revised terms.**
11 Terms that are found in the previous version of this Glossary [3,4] and currently
12 incorporated in the IUPAC "Gold Book" [5] are identified with a reference to the Glossary
13 of Terms used in Physical Organic Chemistry (1994), i.e., [3], whereas revised terms
14 are designated as rev[3]. Minor changes such as better wording, additional cross-
15 referencing, or reorganization of the text without changing the concept are, in general,
16 not considered revisions. However, the improved version should replace the older one
17 in the "Gold Book". New terms and terms from other IUPAC documents are not
18 identified as such. In many cases new references have been added in the definitions.
19
20
21

1
2
3   1   *A* **factor**
4
5   2   Arrhenius factor
6   3   (SI unit same as rate constant: s^{-1} for first-order reaction).
7
8   4   Pre-exponential factor in the *Arrhenius equation* for the temperature dependence of a
9   5   reaction rate constant.
10   6   *Note 1:* According to collision theory, *A* is the frequency of collisions with the correct
11   7   orientation for reaction.
12
13   8   *Note 2:* The common unit of *A* for second-order reactions is $dm^3\ mol^{-1}\ s^{-1}$.
14   9   See also *A value*, *energy of activation*, *entropy of activation*.
15   10   See [12,13].
16
17   11   rev[3]
18   12
19   13   *A* **value**
20
21   14   Steric substituent parameter expressing the conformational preference of an equatorial
22   15   substituent relative to an axial one in a monosubstituted cyclohexane.
23   16   *Note 1*: This parameter equals $\Delta_r G^{o}$ for the equatorial to axial equilibration,
24
25   17   in $kJ\ mol^{-1}$. For example, A_{CH3} is 7.28 $kJ\ mol^{-1}$, a positive value because an axial
26   18   methyl group is destabilized by a *steric effect*.
27   19   *Note 2*: The values are also known as Winstein-Holness *A* values.
28
29   20   See [3,14,15].
30   21
31   22   **abstraction**
32
33   23   Chemical reaction or transformation, the main feature of which is the bimolecular
34   24   removal of an atom (neutral or charged) from a molecular entity.
35   25   *Examples*:
36
37   26 $CH_3COCH_3 + (i\text{-}C_3H_7)_2N^- \rightarrow [CH_3COCH_2]^- + (i\text{-}C_3H_7)_2NH$
38   27   (hydron abstraction from acetone)
39   28 $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$
40
41   29   (hydrogen atom abstraction from methane)
42   30   See *detachment*.
43   31   [3]
44
45   32
46   33   **acceptor parameter** (*A*)
47   34   acceptor number (deprecated). Unit and dimension 1.
48
49   35   Quantitative measure, devised by Gutmann [16] of the *Lewis acidity* of a solvent, based
50   36   on the ^{31}P chemical shift of dissolved triethylphosphine oxide (triethylphosphane oxide).
51   37   *Note:* The term acceptor number, designated by AN, is a misnomer and ought to be
52   38   called acceptor parameter, *A,* because it is an experimental value [17].
53
54   39   rev[3]
55   40
56
57
58
59
60

1   **acid**
2   *Molecular entity* or *chemical species* capable of donating a hydron (proton) or capable
3   of forming a bond with the electron pair of a Lewis base.
4   See *Brønsted acid,* *Lewis acid,* *Lewis base*.
5   See also *hard acid*.
6   [3]
7

8   **acidity**
9   (1) Of a compound:
10 Tendency of a *Brønsted acid* to act as a *hydron* (proton) donor, or tendency of a *Lewis*
11 *acid* to form *Lewis adduct*s and *π-adduct*s.
12   *Note*: Acidity can be quantitatively expressed by the acid dissociation constant of the
13 compound in water or in some other specified medium, by the association constants for
14 formation of Lewis adducts and π-adducts, or by the enthalpy or Gibbs energy of
15 deprotonation in the gas phase.
16 (2) Of a medium, usually one containing Brønsted acids:
17 Tendency of the medium to hydronate a specific reference base.
18   *Note 1*: The acidity of a medium is quantitatively expressed by the appropriate *acidity*
19 *function*.
20   *Note 2*: Media having an acidity greater than that of 100 % H_2SO_4 are often called
21 *superacid*s.
22   See [18].
23   rev[3]
24

25 **acidity function**
26 Measure of the thermodynamic *hydron*-donating or -accepting ability of a solvent
27 system, or a closely related thermodynamic property, such as the tendency of the *lyate*
28 *ion* of the solvent system to form *Lewis adduct*s.
29   *Note 1*: Acidity functions are not unique properties of the solvent system alone but
30 depend on the solute (or family of closely related solutes) with respect to which the
31 thermodynamic tendency is measured.
32   *Note 2*: Commonly used acidity functions are extensions of pH to concentrated acidic
33 or basic solutions. Acidity functions are usually established over a range of
34 compositions of such a system by UV/Vis spectrophotometric or NMR measurements
35 of the degree of hydronation (or Lewis adduct formation) for the members of a series of
36 structurally similar indicator bases (or acids) of different strength: the best known of
37 these is the Hammett acidity function H_o (for primary aromatic amines as indicator
38 bases).
39   For detailed information on other acidity functions, on *excess acidity*, on the
40 evaluation of acidity functions, and on the limitations of the concept, see [19,20,21,22].

1

2

1   [3]

2

3   **activated complex**

4   See *activated state.*

5   rev[3]

6

7   **activated state**

8   In theories of unimolecular reactions an energized *chemical species*, often

9   characterized by the superscript ‡, where the excitation is specific and the molecule is

10   poised for reaction.

11   *Note 1*: Often used as a synonym for *activated complex* or *transition state*, but not

12   restricted to transition-state theory.

13   *Note 2*: This is distinct from an energized *molecule*, often characterized by the

14   superscript *, in which excitation energy is dispersed among internal degrees of

15   freedom.

16   *Note 3:* This is not a *complex* according to the definition in this Glossary.

17   See also *transition state, transition structure*.

18

19   **activation energy**

20   See *energy of activation*.

21   See [12], section 2.12.

22   [3]

23

24   **activation strain model**

25   See *distortion interaction model*.

26

27   **addition reaction**

28   *Chemical reaction* of two or more reacting *molecular entities*, resulting in a product

29   containing all atoms of all components, with formation of two chemical bonds and a net

30   reduction in bond multiplicity in at least one of the reactants.

31   *Note 1*: The addition to an entity may occur at only one site (1,1-addition, *insertion*),

32   at two adjacent sites (1,2-addition) or at two non-adjacent sites (1,3- or 1,4-addition,

33   etc.).

34   *Examples*

35

36        $R_3C–H + H_2C\colon \rightarrow R_3C–CH_3$ (1,1-addition of a carbene)

37        $Br_2 + CH_2=CH–CH=CH_2 \rightarrow BrCH_2–CH(Br)–CH=CH_2$ (1,2-addition) +

38                                $BrCH_2–CH=CH–CH_2Br$ (1,4-addition)

39

Note 2: This is distinguished from *adduct* formation, which is less specific about bonding changes.

Note 3: The reverse process is called an *elimination* reaction.

See also *cheletropic reaction*, *cycloaddition*, *insertion*.

rev[3]

additivity principle

Hypothesis that each of several structural features of a *molecular entity* makes an independent, transferable, and additive contribution to a property of the substance concerned.

Note 1: 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 *chemical reaction*.

Note 2: The enthalpies of formation of series of compounds can be described by additivity schemes [23].

Note 3: Deviations from additivity may be remedied by including terms describing interactions between atoms or groups.

See *transferability* [24,25].

rev[3]

adduct

New *chemical species* AB, each *molecular entity* of which is formed by direct combination of two (or more) separate molecular entities A and B in such a way that there is no loss of atoms from A or B.

Example: adduct formed by interaction of a *Lewis acid* with a *Lewis base*:

$(CH_3)_3N^+-^-BF_3$

Note 1: Stoichiometries other than 1:1 are also possible, e.g., a bis-adduct (2:1).

Note 2: An *intramolecular* adduct can be formed when A and B are *groups* contained within the same molecular entity.

Note 3: If adduct formation is prevented by *steric hindrance*, *frustrated Lewis pair*s may result.

See also *addition reaction, frustrated Lewis pair, Lewis adduct, Meisenheimer adduct, π-adduct*.

rev[3]

agostic

Feature of a structure in which a hydrogen atom is bonded to both a main-group atom and a metal atom.

Example, [(1–3-η)-but-2-en-1-yl-$η^2$-C^4,H^4]($η^5$-cyclopentadienyl)cobalt(+1).

1
2
3
4
5
6   *Note*: The expression η-hydrido-bridged is also used to describe the bonding
7   arrangement with a bridging hydrogen, but this usage is deprecated.
8   See [26,27,28,29].
9   rev[3]
10

11   **alcoholysis**
12   Reaction with an alcohol solvent.
13   *Examples:*
14
15   $C_3H_5(OCOR)_3$ (triglyceride) + 3 $CH_3OH \rightarrow C_3H_5(OH)_3$ (glycerol) + 3 RCOOH
16   $(CH_3)_3CCl + CH_3OH \rightarrow (CH_3)_3COCH_3 + H^+ + Cl^-$
17
18   See *solvolysis*.
19   rev[3]
20
21
22   **allotropes**
23   Different structural modifications of an element, with different bonding arrangements of
24   the atoms.
25   *Examples* for carbon include diamond, *fullerenes*, graphite, and *graphene*.
26   See [29].
27

28   **allylic substitution reaction**
29   *Substitution* reaction on an allylic system with *leaving group* (*nucleofuge*) at position 1
30   and double bond between positions 2 and 3. The incoming group may become attached
31   to atom 1, or else the incoming group may become attached at position 3, with
32   movement of the double bond from 2,3 to 1,2.
33   *Example*:
34   $CH_3CH=CHCH_2Br + HOAc \rightarrow CH_3CH=CHCH_2OAc$ or $CH_3CH(OAc)CH=CH_2$
35
36   *Note*: This term can be extended to systems such as:
37
38   $CH_3CH=CH–CH=CH–CH_2Br \rightarrow CH_3CH(OAc)–CH=CH–CH=CH_2 +$
39   $CH_3CH=CH–CH(OAc)–CH=CH_2 + CH_3CH=CH–CH=CH–CH_2OAc$
40

1 and also to propargylic substitution, with a triple bond between positions 2 and 3 and
2 possible rearrangement to an allenic product.
3 rev[3]
4

5 **alternant**
6 Property of a _conjugated system_ of π electrons whose atoms can be divided into two
7 sets (marked as "starred" and "unstarred") so that no atom of either set is directly linked
8 to any other atom of the same set.
9 _Examples_
10
11
12
13
14
15
16

(two unstarred atoms
are linked)

17 _Note 1:_ According to several approximate theories (including _HMO theory_), the π
18 MOs for an alternant hydrocarbon are paired, such that for an orbital of energy $\alpha + x\beta$
19 there is another of energy $\alpha - x\beta$. The coefficients of paired molecular orbitals at each
20 atom are the same, but with opposite sign for the unstarred atoms, and the π electron
21 density at each atom in a neutral alternant hydrocarbon is unity.
22 See [30,31,32].
23 rev[3]
24

25 **ambident**
26 ambidentate, bidentate
27 Characteristic of a _chemical species_ whose _molecular entities_ each possess two
28 alternative, distinguishable, and strongly interacting reactive centres, to either of which
29 a _bond_ may be made.
30 _Note 1_: Term most commonly applied to _conjugated nucleophiles_, for example an
31 enolate ion (which may react with _electrophiles_ at either the α-carbon atom or the
32 oxygen) or a 4-pyridone, and also to the vicinally ambident cyanide ion and to cyanate
33 ion, thiocyanate ion, sulfinate ions, nitrite ion, and unsymmetrical hydrazines.
34

35
36

37 _Note 2_: Ambident electrophiles are exemplified by carboxylic esters RC(O)OR',
38 which react with nucleophiles at either the carbonyl carbon or the alkoxy carbon, and

1 by Michael acceptors, such as enones, that can react at either the carbonyl or the α-
2 carbon.

3 *Note 3*: Molecular entities containing two non-interacting (or feebly interacting)
4 reactive centres, such as dianions of dicarboxylic acids, are not generally considered
5 to be ambident or bidentate and are better described as bifunctional.

6 *Note 4*: The Latin root of the word implies two reactive centres, but the term has also
7 been applied to chemical species with more than two reactive centres, such as an acyl
8 thiourea, RCONHCSNHR', with nucleophilic O, S, and N. For such species the term
9 polydentate (or multidentate) is more appropriate.

10 See [33,34,35,36].

11 [3]

12

13 **ambiphilic**

14 Both *nucleophilic* and *electrophilic*.

15 *Example*:

16 $CH_2=O$

17 See also *amphiphilic*, but the distinction between ambi (Latin: both) and amphi
18 (Greek: both) and the application to hydrophilic and lipophilic or to nucleophilic and
19 electrophilic is arbitrary.

20

21 **aminoxyl**

22 Compound having the structure

23 $R_2N-O^\bullet \leftrightarrow R_2N^{\bullet+}-O^-$

24 *Note*: The synonymous term 'nitroxyl radical' erroneously suggests the presence of
25 a nitro group; its use is deprecated.

26

27 **amphiphilic**

28 Both hydrophilic and lipophilic, owing to the presence in the molecule of a large organic
29 cation or anion and also a long hydrocarbon chain (or other combination of polar and
30 nonpolar groups, as in nonionic surfactants)

31 *Examples*:

32

33 $CH_3(CH_2)_nCO_2^-M^+$, $CH_3(CH_2)_nSO_3^-M^+$, $CH_3(CH_2)_nN(CH_3)_3^+X^-$ ($n > 7$).

34

35 *Note*: The presence of distinct polar (hydrophilic) and nonpolar (hydrophobic) regions
36 promotes the formation of *micelles* in dilute aqueous solution.

37 See also *ambiphilic*.

38 [3]

39

40 **amphiprotic (solvent)**

1 Feature of a self-ionizing solvent possessing characteristics of both _Brønsted acid_ and
2 _base_.
3   _Examples_: H_2O, CH_3OH.
4   [3]
5

amphoteric
7 Property of a _chemical species_ that can behave as either an acid or as a base.
8   _Examples_: H_2O, HCO_3^- (hydrogen carbonate)
9   _Note_: This property depends upon the medium in which the species is investigated.
10 For example HNO_3 is an acid in water but becomes a base in H_2SO_4.
11   rev[3]
12

anchimeric assistance
14 _neighbouring group participation_
15   [3]
16

anionotropy
18 Rearrangement or _tautomerization_ in which the migrating group moves with its electron
19 pair.
20   See [37].
21   [3]
22

annelation
24 Alternative, but less desirable term for _annulation_.
25   _Note_: The term is widely used in German and French languages.
26   [3]
27

annulation
29 _Transformation_ involving fusion of a new ring to a molecule via two new bonds.
30   _Note_: Some authors use the term _annelation_ for the fusion of an additional ring to an
31 already existing one, and annulation for the formation of a ring from an acyclic
32 precursor.
33   See [38,39].
34   See also _cyclization_.
35   [3]
36

annulene
38 Conjugated monocyclic hydrocarbon of the general formula C_nH_n (_n_ even) with the
39 maximum number of noncumulative double bonds and without side chains.

1 *Note*: In systematic nomenclature an annulene may be named [*n*]annulene, where *n*
2 is the number of carbon atoms, e.g., [8]annulene for cycloocta-1,3,5,7-tetraene.
3   See [40].
4   See *aromatic*, *Hückel (4n + 2) rule*.
5   [3]
6

anomeric effect
7 Tendency of an electronegative substituent alpha to a heteroatom in a six-membered
8 ring to prefer the axial position, as in the *anomers* of glucopyranose.
9   *Note 1*: The effect can be generalized to the conformational preference of an
10 electronegative substituent X to be antiperiplanar to a lone pair of atom Y in a system
11 R–Y–C–X with geminal substituents RY and X.
12   *Note 2:* The effect can be attributed, at least in part, to *n-σ* delocalization* of the lone
13 pair on Y into the C–X σ* orbital.
14   See [11,41,42,43,44].
15

anomers
16 The two stereoisomers (epimers) of a cyclic sugar or glycoside that differ only in the
17 *configuration* at C1 of aldoses or C2 of ketoses (the anomeric or acetal/ketal carbon).
18   *Example:*

α-D-glucose   β-D-glucose

19   See [11].
20   [3]
21

antarafacial, suprafacial
22 Two spatially different ways whereby bonding changes can occur when a part of a
23 molecule undergoes two changes in bonding (*bond*-making or bond-breaking), either
24 to a common centre or to two related centres external to itself. These are designated
25 as antarafacial if opposite faces of the molecule are involved, and suprafacial if both
26 changes occur at the same face. The concept of face is clear from the diagrams in the
27 cases of planar (or approximately planar) frameworks with interacting π orbitals.

antarafacial   suprafacial

For examples of the use of these terms see *cycloaddition*, *sigmatropic rearrangement*.

See also *anti*, *σ*, *π*.

rev[3]

anti

Stereochemical relationship of two substituents that are on opposite sides of a reference plane, in contrast to *syn*, which means "on the same side".

Note 1: 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 90º, in contrast to *syn* if it is less than 90º.

Note 2: A further distinction is made between antiperiplanar, synperiplanar, anticlinal and synclinal.

See [11,45,46,47].

Note 3: 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*:

(3)   Aldol reaction (where *syn* and *anti* designate the relative orientation of CH_3 and OH in the product)

Note 4: In examples (1) and (2) *anti* processes are always *antarafacial*, and *syn* processes are *suprafacial*.

Note 5: 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*.

See [11].

rev[3]

anti-Hammond effect

If a structure lying off the *minimum-energy reaction path* (MERP) is stabilized, the position of the *transition state* moves toward that structure.

See *Hammond Postulate, More O'Ferrall - Jencks diagram, perpendicular effect*.

rev[3]

aprotic (solvent)

non-HBD solvent (non-Hydrogen-Bond Donating solvent)

Solvent that is *not* capable of acting as a hydrogen-bond donor.

Note: Although this definition applies to both polar and nonpolar solvents, the distinction between HBD and non-HBD (or between protic and aprotic) is relevant only for polar solvents.

See *HBD solvent*.

rev[3]

aquation

Incorporation of one or more integral molecules of water into a species, with or without displacement of one or more other atoms or groups.

Example: The incorporation of water into the inner *ligand* sphere of an inorganic *complex*.

See [48].

See also *hydration*.

[3]

aromatic (*adj.*), **aromaticity** (*n.*)

(1) Having a chemistry typified by benzene (traditionally).

(2) Feature of a cyclically *conjugated molecular entity* whose electronic energy is significantly lower or whose stability is significantly greater (owing to *delocalization*) than that of a hypothetical localized structure (e.g., *Kekulé structure*).

Note 1: If the molecular entity is of higher energy or less stable than a hypothetical localized structure, the entity is said to be antiaromatic.

Note 2: A geometric parameter indicating bond-length equalization has been used as a measure of aromatic character, as expressed in the harmonic oscillator model of aromaticity [49].

Note 3: The magnitude of the magnetically induced ring current, as observed experimentally by NMR spectroscopy or by the calculated nucleus-independent chemical shift (NICS) value, is another measure of aromaticity [50].

Note 4: 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, whereby a cycle with ($4n+2$) electrons and a Möbius cycle with $4n$ electrons are aromatic. Reactions of molecules in the *ground state* involving antiaromatic transition states proceed much less easily than those involving aromatic transition states.

See [51,52,53]. See 19 articles in [54].

See also *Hückel (4n + 2) rule*, *Möbius aromaticity*.

[3]

Arrhenius equation

Empirical expression for the temperature dependence of a reaction rate constant k as

$$k(T) = A \exp(-E_A/RT),$$

with A the pre-exponential factor (Arrhenius *A factor*) and E_A the Arrhenius *energy of activation*, both considered to be temperature-independent.

rev[3]

1

aryne

Hydrocarbon derived from an arene by formal removal of two vicinal hydrogen atoms.

Example: 1,2-didehydrobenzene (benzyne)

Note 1: 1,4-Didehydrobenzene ("*p*-benzyne *diradical*", structure above right). Despite common usage this is not an aryne because there is no triple bond, and the usage is deprecated.

Note 2: Arynes are usually *transient species*.

Note 3: The analogous heterocyclic compounds are called heteroarynes or hetarynes.

See [40,55].

rev[3]

association

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.

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

[3]

asymmetric induction

Preferential formation in a *chemical reaction* of one *enantiomer* or *diastereoisomer* over the other as a result of the influence of a *chiral centre* (*stereogenic centre*, *chiral feature*) in the substrate, reagent, *catalyst*, or environment.

Note: The term also refers to the formation of a new chiral centre or chiral feature preferentially in one *configuration* under such influence.

See [11].

rev[3]

atomic charge

Net charge due to the nucleus and the average electronic distribution in a given region of space. This region is considered to correspond to an atom in a *molecular entity*.

1   *Note 1*: The boundary limits of an atom in a polyatomic molecular entity cannot be
2 defined, as they are not a quantum-mechanical observable. Therefore, different
3 conceptual schemes of dividing a molecule into individual atoms will result in different
4 atomic charges.

5   *Note 2:* The atomic charge on an atom should not be confused with its *formal charge*.
6 For example, the N in NH_4^+ is calculated to carry a net negative charge even though its
7 formal charge is +1, and each H is calculated to carry a net positive charge even though
8 its formal charge is 0.

9   See [8].

10

atomic orbital

12 Wavefunction that depends explicitly on the spatial coordinates of only one electron
13 around a single nucleus.

14   See also *molecular orbital*.

15   See [8].

16   [3]

17

atropisomers

19 Stereoisomers that are enantiomeric owing to hindered rotation about a single bond.

20   *Example* (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, BINAP):

28   See [11].

29

attachment

31 *Transformation* by which one *molecular entity* (the *substrate*) is converted into another
32 by the formation of one (and only one) two-centre *bond* between the substrate and
33 another molecular entity and which involves no other changes in *connectivity* in the
34 substrate.

35   *Example*: formation of an acyl cation by attachment of carbon monoxide to a
36 *carbenium* ion (R⁺):

37                              $R^+ + CO \rightarrow (RCO)^+$

38   See also *colligation*.

39   rev[3]

40

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1 **autocatalytic reaction**
2 *Chemical reaction* in which a product (or a reaction *intermediate*) also functions as
3 *catalyst*.
4 *Note*: In such a reaction the observed *rate of reaction* is often found to increase with
5 time from its initial value.
6 *Example*: acid-catalyzed bromination of acetophenone, $PhCOCH_3$, because the
7 reaction generates HBr, which functions as a catalyst.
8 rev[3]
9
10 **automerization**
11 degenerate rearrangement
12 [3]
13
14 **autoprotolysis**
15 *Proton transfer reaction* (*hydron* transfer reaction) between two identical *amphoteric*
16 molecules (usually of a solvent), one acting as a *Brønsted acid* and the other as a
17 *Brønsted base*.
18 *Example*:
19 $2 H_2O \rightarrow H_3O^+ + HO^-$
20 [3]
21
22 **autoprotolysis constant**
23 Product of the activities of the species produced as the result of *autoprotolysis*.
24 *Example*: The autoprotolysis constant for water, K_w (or K_{AP}), is equal to the product
25 of the relative activities of the hydronium and hydroxide ions at equilibrium in pure water.
26
27 $K_w = a(H_3O^+)a(HO^-) = 1.0 \times 10^{-14}$ at 25 °C and 1 standard atmosphere.
28
29 *Note:* Since the relative activity $a(H_2O)$ of water at equilibrium is imperceptibly
30 different from unity (with mole fraction as the activity scale and pure un-ionized water
31 as the standard state), the denominator in the expression for the thermodynamic
32 equilibrium constant $K_w°$ for autoprotolysis has a value very close to 1.
33
34 $$K_w° = \frac{a(H_3O^+)a(HO^-)}{a(H_2O)^2}$$
35
36 Furthermore, owing to the low equilibrium extent of dissociation, and if infinite dilution
37 is selected as the standard state, the activity coefficients of the hydronium and
38 hydroxide ions in pure water are very close to unity. This leads to the relative activities
39 of H_3O^+ and HO^- being virtually identical with the numerical values of their molar

concentrations, if the molar scale of activity is used and an activity of 1 mol dm^{-3} is
chosen as the standard state. Thus

$K_w \approx [H_3O^+][HO^-]$

where $[H_3O^+]$ and $[HO^-]$ are the numerical values of the molar concentrations. The
autoprotolysis constant has the unit (and dimension) 1 because each relative activity
has dimension 1, being a quotient of an absolute activity (including units) divided by a
common unit standard state activity (including units).
See [56,57].
   rev[3]

α (alpha)
(1) Designation applied to the carbon to which a functional group is attached.
(2) In carbohydrate nomenclature a stereochemical designation of the *configuration* at
the anomeric carbon.
(3) Parameter in a *Brønsted relation* expressing the sensitivity of the rate of protonation
to *acidity.*
(4) Parameter in *Leffler's relation* expressing the sensitivity of changes in Gibbs
activation energy to changes in overall Gibbs energy for an elementary reaction.
   See [11].
   rev[3]

α-effect
Positive deviation of an α nucleophile (one bearing an unshared pair of electrons on an
atom adjacent to the nucleophilic site) from a Brønsted-type plot of lg $\{k_{nuc}\}$ vs. pK_a. The
argument in the lg function should be of dimension 1. Thus, reduced *rate coefficient*s
should be used. Here $\{k_{nuc}\} = k_{nuc}/[k_{nuc}]$ is the reduced k_{nuc}.
   Note 1: More generally, it is the influence on the reactivity at the site adjacent to the
atom bearing a lone pair of electrons.
   Note 2: The term has been extended to include the effect of any substituent on an
adjacent reactive centre, e.g., the α-silicon effect.
   See [58,59,60].
   See also *Brønsted relation*.
   rev[3]

α-elimination
1,1-elimination
Transformation of the general type

1   RR'ZXY → RR'Z + XY (or X + Y, or X^+ + Y^-)

3 where the central atom Z is commonly carbon.

4   See also *elimination*.

5   rev[3]

Baldwin's rules

8 Set of empirical rules for closures of 3- to 7-membered rings.

9   *Note*: The favoured pathways are those in which the length and nature of the linking
10 chain enable the terminal atoms to achieve the proper geometry and *orbital* overlaps
11 for reaction.

12   *Example*: Hex-5-en-1-yl radical undergoes 5-exo-trig cyclization to cyclopentylmethyl
13 radical rather than 6-endo-trig cyclization to cyclohexyl radical.

17   See [61,62].
18   rev[3]

base

21 *Chemical species* or *molecular entity* having an available pair of electrons capable of
22 forming a *bond* with a *hydron* (proton) (see *Brønsted base*) or with the vacant orbital of
23 some other species (see *Lewis base*).

24   See also *hard base*, *superbase*.

25   [3]

basicity

28 (1) Tendency of a *Brønsted base* to act as *hydron* (proton) acceptor.

29   *Note 1*: The basicity of a *chemical species* is normally expressed by the *acidity* or
30 acid-dissociation constant of its conjugate acid (see *conjugate acid-base pair*).

31   *Note 2:* To avoid ambiguity, the term pK_{aH} should be used when expressing basicity
32 by the acid-dissociation constant of its conjugate acid. Thus the pK_{aH} of NH_3 is 9.2,
33 while its pK_a, expressing its acidity, is 38.

34 (2) Tendency of a *Lewis base* to act as a *Lewis acid* acceptor.

35   *Note 3*: For Lewis bases, basicity is expressed by the association constants of *Lewis
36 adduct*s and *π-adduct*s, or by the enthalpy of an acid/base reaction.

37   *Note 4*: Spectroscopic shifts induced by acid/base adduct formation can also be used
38 as a measure of the strength of interaction.

39   See [63].

1   rev[3]

2

3   **bathochromic shift (effect)**

4   Shift of a spectral band to lower frequencies (longer wavelengths).

5   *Note*: This is informally referred to as a red shift and is opposite to a *hypsochromic*

6   *shift* ("blue shift"), but these historical terms are discouraged because they apply only

7   to visible transitions.

8   See [9].

9   [3]

10

11   **Bell-Evans-Polanyi principle**

12   Linear relation between energy of activation (E_A) and enthalpy of reaction ($\Delta_r H$),

13   sometimes observed within a series of closely related reactions.

14

15    $E_A = a + b\ \Delta_r H$

16

17   See [64,65,66,67].

18   rev[3]

19

20   **benzyne**

21   1,2-Didehydrobenzene (a C_6H_4 *aryne* derived from benzene) and its derivatives formed

22   by substitution.

23   *Note*: The terms *m*- and *p*-benzyne are occasionally used for 1,3- and 1,4-

24   didehydrobenzene, respectively, but these are incorrect because there is no triple bond.

25   See [40,55].

26   [3]

27

28   **bidentate**

29   Feature of a *ligand* with two potential binding sites.

30

31   **bifunctional catalysis**

32   Catalysis (usually of *hydron* transfer) by a *chemical species* involving a mechanism in

33   which two *functional groups* are implicated in the *rate-limiting step*, so that the

34   corresponding *catalytic coefficient* is larger than that expected for catalysis by a

35   chemical species containing only one of these functional groups.

36   *Example*: Hydrogen carbonate is a particularly effective *catalyst* for the hydrolysis of

37   4-hydroxybutyranilide (*N*-phenyl-4-hydroxybutanamide), because it catalyzes the

38   breakdown of the tetrahedral intermediate to expel aniline:

39

1

2

3   *Note*: The term should not be used to describe a *concerted process* involving the
4   action of two different catalysts.

5   See [68,69,70,71,72].

6   rev[3]

7

8   **bifurcation**

9   Feature on a *potential-energy surface* whereby a *minimum-energy reaction path*
10   (MERP) emanating from a saddle point (corresponding to a *transition structure*) splits
11   in two and leads to alternative products without intervening minima or secondary
12   barriers to overcome. A bifurcation arises when the curvature of the surface in a
13   direction perpendicular to the MERP becomes zero and then negative; it implies the
14   existence of a lower-energy transition structure with a *transition vector* orthogonal to
15   the original MERP.

16   See [73,74].

17

18   **bimolecular**

19   See *molecularity*.

20   [3]

21

22   **binding site**

23   Specific region (or atom) in a *molecular entity* that is capable of entering into a
24   stabilizing interaction with another atomic or molecular entity.

25   *Example*: an active site in an enzyme that interacts with its *substrate*.

26   *Note 1*: Typical modes of interaction are by *covalent bonding*, *hydrogen bonding*,
27   *coordination*, and *ion-pair* formation, as well as by dipole-dipole interactions, dispersion
28   forces, hydrophobic interactions, and desolvation.

29   *Note 2*: Two binding sites in different molecular entities are said to be complementary
30   if their interaction is stabilizing.

31   [3]

32

1 **biradical**

2 *diradical*

3   See [9].

4   rev[3]

5

6 **blue shift**

7 Informal expression for *hypsochromic shift*, but this historical term is discouraged

8 because it applies only to visible transitions.

9   rev[3]

10

11 **Bodenstein approximation**

12   See *steady state*.

13   [3]

14

15 **bond**

16 Balance of attractive and repulsive forces between two atoms or groups of atoms,

17 resulting in sufficient net stabilization to lead to the formation of an aggregate

18 conveniently considered as an independent *molecular entity*.

19   *Note*: The term usually refers to the *covalent bond*.

20   See [75].

21   See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.

22   rev[3]

23

24 **bond dissociation**

25   See *heterolysis*, *homolysis*.

26   *Note*: In ordinary usage the term refers to homolysis. If not, it should be specified as

27 heterolytic.

28   [3]

29

30 **bond-dissociation energy**

31 D_e

32 (SI unit: kJ mol^{-1})

33 Energy required to break a given *bond* of some specific *molecular entity* by *homolysis*

34 from its potential-energy minimum.

35   *Note:* This is the quantity that appears in the *Morse potential*.

36   See also *bond-dissociation enthalpy*.

37   rev[3]

38

39 **bond-dissociation enthalpy**

40 DH^0, $\Delta_{diss}H^0$

1 (SI unit: kJ mol^{-1})

2 Standard molar enthalpy required to break a given *bond* of some specific *molecular*
3 *entity* by *homolysis*.

4   *Example*: For $CH_4 \rightarrow CH_3\cdot + H\cdot$ the bond-dissociation enthalpy is symbolized as
5 $DH^0(CH_3–H)$.

6   *Note:* Although DH^0 is commonly used, $\Delta_{diss}H^0$ is more consistent with the notation
7 for other thermodynamic quantities*.

8   See also *bond-dissociation energy*, *bond energy*, *heterolytic bond-dissociation*
9 *enthalpy*.

10

11 **bond energy**

12 D_0

13 (SI unit: kJ mol^{-1})

14 Enthalpy of bond dissociation at 0 K.

15   See *bond-dissociation enthalpy*.

16   rev[3]

17

18 **bond enthalpy (mean bond enthalpy, mean bond energy)**

19 Average value of the gas-phase *bond-dissociation enthalpies* (usually at a temperature
20 of 298 K) for all *bond*s of the same type within the same *chemical species*.

21   *Example*: For methane, the mean bond enthalpy is 415.9 kJ mol^{-1}, one-fourth the
22 enthalpy of reaction for

23       $CH_4(g) \rightarrow C(g) + 4 H(g)$

24   *Note*: More commonly, tabulated mean bond energies (which are really enthalpies)
25 are values of bond enthalpies averaged over a number of selected chemical species
26 containing that type of bond, such as 414 kJ mol^{-1} for C–H bonds in a group of R_3CH
27 (R = H, alkyl).

28   See [76].

29

30 **bond order**

31 Theoretical index of the degree of bonding between two atoms, relative to that of a
32 normal single *bond,* i.e., the bond provided by one localized electron pair.

33   *Example*: In ethene the C–C bond order is 2, and the C–H bond order is 1.

34   *Note 1*: In valence-bond theory it is a weighted average of the bond orders between
35 the respective atoms in the various resonance forms. In molecular-orbital theory it is
36 calculated from the weights of the atomic orbitals in each of the occupied molecular
37 orbitals. For example, in valence-bond theory the bond order between adjacent carbon
38 atoms in benzene is 1.5; in *Hückel molecular orbital theory* it is 1.67.

39   *Note 2:* Bond order is often derived from the electron distribution.

Note 3: The Pauling bond order *n* (as often used in the *bond-energy-bond-order model*) is a simple function of change in bond length *d*, where the value of the coefficient *c* is often 0.3 Å (for *n* > 1) or 0.6 Å (for *n* < 1).

$$n = \exp[(d_1 - d_n)/c]$$
rev[3]

bond-energy-bond-order model (BEBO):
Empirical procedure for estimating *activation energy,* involving relationships among bond length, *bond-dissociation energy,* and *bond order*.
   See [13,77].

bond-stretch isomers
Two (or more) molecules with the same spin multiplicity but with different lengths for one or more bonds.
   Note: This feature arises because the potential-energy surface, which describes how the energy of the molecule depends on geometry, shows two (or more) minima that are not merely symmetry-related.
   See [78,79,80,81].

borderline mechanism
Mechanism intermediate between two extremes, for example a *nucleophilic substitution* intermediate between S_N1 and S_N2, or intermediate between electron transfer and S_N2.
   [3]

Born-Oppenheimer approximation
Representation of the complete *wavefunction* as a product of electronic and nuclear parts, $\Psi(r,R) = \psi_{el}(r,R)\ \psi_{nuc}(R)$, so that the two wavefunctions can be determined separately by solving two different Schrödinger equations.
   See [8].

Bredt's rule
Prohibition of placing a double bond with one terminus at the *bridgehead* atom of a polycyclic system unless the rings are large enough to accommodate the double bond without excessive *strain*.
   Example: Bicyclo[2.2.1]hept-1-ene (A), which is capable of existence only as a *transient species,* although its higher homologues, bicyclo[3.3.1]non-1-ene (B) and bicyclo[4.2.1]non-1(8)-ene (C), with double bond at the bridgeheads, have been isolated.

1

A   B   C

See [82,83,84,85].

For limitations see [86].

Note: For an alternative formulation, based on the instability of a *trans* double bond in a small ring (fewer than 8 atoms), see [87].

rev[3]

bridged carbocation

Carbocation (real or hypothetical) in which there are two (or more) carbon atoms that could in alternative *Lewis formula*s 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.

Note: Electron-sufficient bridged carbocations are distinguished from electron-deficient bridged carbocations. Examples of the former, where the bridging uses π electrons, are phenyl-bridged ions (for which the trivial name phenonium ion has been used), such as **A**. These ions are straightforwardly classified as *carbenium ion*s. The latter type of ion necessarily involves three-centre bonding because the bridging uses σ electrons. The hydrogen-bridged carbocation **B** contains a two-coordinate hydrogen atom, whereas structures **C**, **D**, and **E** (the 2-norbornyl cation) contain five-coordinate carbon atoms.

A   B   C   D   E

See [88].

See also *carbonium ion*, *multi-centre bond*, *neighbouring group participation*.

For the definitive X-ray structure of the norbornyl cation see [89].

rev[3]

1 **bridgehead (atom)**

2 Atom that is part of two or more rings in a polycyclic molecule and that is separated

3 from another bridgehead atom by bridges all of which contain at least one other atom.

4   *Example:* C1 and C4 in bicyclo[2.2.1]heptane, but not C4a and C8a in

5 decahydronaphthalene.

6

7 **bridging ligand**

8 *Ligand* attached to two or more, usually metallic, central atoms.

9   See [29].

10   [3]

11

12 **Brønsted acid (Brönsted acid)**

13 *Molecular entity* capable of donating a *hydron* (proton) to a base (i.e., a hydron donor),

14 or the corresponding *chemical species*.

15   *Examples*: H_2O, H_3O^+, CH_3COOH, H_2SO_4, HSO_4^-, HCl, CH_3OH, NH_3.

16   See also *conjugate acid-base pair*.

17   [3]

18

19 **Brønsted base (Brönsted base)**

20 *Molecular entity* capable of accepting a *hydron* (proton) from a Brønsted acid (i.e., a

21 hydron acceptor), or the corresponding *chemical species*.

22   *Examples*: HO^-, H_2O, $CH_3CO_2^-$, HSO_4^-, SO_4^{2-}, Cl^-, CH_3O^-, NH_2^-.

23   See also *conjugate acid-base pair*.

24   [3]

25

26 **Brønsted relation (Brönsted relation)**

27 Either of the equations

28

29 $$\lg(\{k_{HA}\}/p) = C \;+\; \alpha \lg(q\{K_{HA}\}/p)$$

30

31 $$\lg(\{k_A\}/q) \;\; = C \;-\; \beta \lg(q\{K_{HA}\}/p)$$

32

33 where α, β, and *C* are constants for a given reaction series (α and β are called Brønsted

34 exponents or Brønsted parameters). The arguments in the lg functions should be of

35 dimension 1. Thus, reduced *rate coefficients* should be used: $\{k_A\} = k_A/[k_A]$ and $\{k_{HA}\} =$

36 $k_{HA}/[k_{HA}]$, which are the reduced catalytic coefficients of reactions whose rates depend

37 on the concentrations of acid HA or of its conjugate base A^-, $\{K_{HA}\} = K_{HA}/[K_{HA}]$ is the

38 reduced acid dissociation constant of HA, *p* is the number of equivalent acidic protons

39 in HA, and *q* is the number of equivalent basic sites in A^-. The chosen values of *p* and

1 q should always be specified. (The charge designations of HA and A$^-$ are only
2 illustrative.).

3   *Note 1*: The equations are often written without reduced variables, whereupon the
4 slope α or β, obtained from a graph or least-squares analysis, is correct because it is
5 the derivative of a logarithmic quantity, of dimension 1.

6   *Note 2*: The Brønsted relation is often termed the Brønsted catalysis law. Although
7 justifiable on historical grounds, use of this name is not recommended, since Brønsted
8 relations are known to apply to many uncatalysed and pseudo-catalysed reactions
9 (such as simple proton [*hydron*] transfer reactions).

10   *Note 3*: The term pseudo-Brønsted relation is sometimes used for reactions that
11 involve *nucleophilic catalysis* instead of acid-base catalysis. Various types of Brønsted
12 parameters have been proposed such as β_{nuc} or β_{lg} for nucleophile or leaving group,
13 respectively.

14   See also *linear free-energy relation* (*linear Gibbs energy relation*).
15   rev[3]

16

17 **Bunnett-Olsen equations**
18 Relations between $\lg([SH^+]/[S]) + H_o$ and $H_o + \lg\{[H^+]\}$ for base S in aqueous acid
19 solutions, where H_o is Hammett's *acidity function* and $H_o + \lg\{[H^+]\}$ represents the
20 activity function $\lg(\{\gamma_S\} \{\gamma_{H+}\} / \{\gamma_{SH+}\})$ for the nitroaniline reference bases to build H_o. and
21 where ϕ is an empirical parameter that is determined by the slope of the linear
22 correlation of $\lg([SH^+]/[S]) - \lg\{[H^+]\}$ vs. $H_o + \lg\{[H^+]\}$.

23

24          $$\lg([SH^+]/[S]) - \lg\{[H^+]\} = (\phi - 1)(H_o + \lg\{[H^+]\}) + pK_{SH+}$$

25

26          $$\lg([SH^+]/[S]) + H_o = \phi (H_o + \lg\{[H^+]\}) + pK_{SH+}$$

27

28 Arguments in the lg functions should be of dimension 1. Thus, concentrations should
29 be divided by the respective unit (unless they are eliminated as in the ratio of two
30 concentrations), i.e., the reduced quantity should be used, indicated by curly brackets.

31   *Note 1*: These equations avoid using (or defining) an acidity function for each family
32 of bases, including those for which such a definition is not possible. In many cases, ϕ
33 (or $\phi - 1$) values for base families defining an acidity function are very similar. Broadly,
34 the value of ϕ is related to the degree of solvation of SH$^+$.

35   *Note 2*: These equations are obsolete, and the *Cox-Yates equation*, with the
36 equivalent parameter m^* (= $1 - \phi$), is now preferred.

37   See [21,90].
38   See also *Cox-Yates equation*.
39   rev[3]

40

1   β, β_{nuc}, β_{lg}

2 Parameter in a *Brønsted relation* expressing the sensitivity of the rate of deprotonation

3 to *basicity*.

4   *Note*: β_{nuc} and β_{lg} are used to correlate *nucleophilic* reactivity and leaving-group

5 ability, respectively.

6

7 **β-elimination**

8 1,2-elimination

9 *Transformation* of the general type

10

11   XABY $\rightarrow$ A=B + XY (or X + Y, or X$^+$ + Y$^-$)

12

13 where the central atoms A and B are commonly, but not necessarily, carbon.

14   See also *elimination*.

15

16 **cage**

17 Aggregate of molecules, generally solvent molecules in the condensed phase, that

18 surrounds fragments formed by thermal or photochemical dissociation.

19   *Note*: Because the cage hinders the separation of the fragments by diffusion, they

20 may preferentially react with one another ("cage effect") although not necessarily to re-

21 form the precursor species.

22   *Example:*

23   RN=NR $\xrightarrow{\Delta}$ [R· N$_2$ R·]$_{cage}$ $\longrightarrow$ R-R + N$_2$

24   See also *geminate recombination*.

25   [3]

26

27 **cage compound**

28 Polycyclic compound capable of encapsulating another compound

29   *Example* (adamantane, where the central cavity is large enough to encapsulate He,

30 Ne, or Na$^+$):

31

32

33

34

35

36   *Note:* A compound whose cage is occupied is called an *inclusion complex*.

37   See [91,92].

38   rev[3]

39

40

1   **canonical form**

2   resonance form

3   rev[3]

4

5   **captodative effect**

6   Combined action of an electron-withdrawing ("captor") substituent and an electron-

7   releasing ("dative") substituent, both attached to a _radical_ centre, on the stability of a

8   carbon-centred radical.

9   _Example_:

10

11

12   etc.

13

14

15   See [93,94,95].

16   rev[3]

17

18   **carbanion**

19   Generic name for an anion containing an even number of electrons and having an

20   unshared pair of electrons on a carbon atom which satisfies the _octet rule_ and bears a

21   negative _formal charge_ in its _Lewis structure_ or in at least one of its _resonance form_s.

22   _Examples:_

23

24

25   See also _radical ion_.

26   See [40,96].

27   rev[3]

28

29   **carbene**

30   Generic name for the species H_2C**:** ("methylidene") and substitution derivatives thereof,

31   containing an electrically neutral bivalent carbon atom with two nonbonding electrons.

32   _Note 1_: The nonbonding electrons may have antiparallel spins (singlet state) or

33   parallel spins (_triplet state_).

34   _Note 2_: Use of the alternative name "methylene" as a generic term is not

35   recommended.

36   See [40].

37   See also _diradical_.

38   [3]

carbenium ion

Generic name for a *carbocation* whose electronic structure can be adequately described by two-electron-two-centre bonds.

Note 1: The name implies a hydronated carbene or a substitution derivative thereof.

Note 2: The term is a replacement for the previously used term *carbonium ion*, which now specifies a carbocation with penta- or higher-coordinate carbons. The names provide a useful distinction between tricoordinate and pentacoordinate carbons.

Note 3: To avoid ambiguity, the name should be avoided as the root for the nomenclature of *carbocation*s. For example, the term "ethylcarbenium ion" might refer to either $CH_3CH_2^+$ (ethyl cation, ethylium) or $CH_3CH_2CH_2^+$ (propyl cation, propylium).

See [40,97].

rev[3]

carbenoid

Carbene-like *chemical species* but with properties and *reactivity* differing from the free carbene, arising from additional substituents bonded to the carbene carbon.

Example: $R_1R_2C(Cl)M$ (M = metal)

rev[3]

carbocation

Positive ion containing an even number of electrons and with a significant portion of the excess positive charge located on one or more carbon atoms.

Note 1: This is a general term embracing *carbenium ion*s, all types of *carbonium ion*s, vinyl cations, etc.

Note 2: Carbocations may be named by adding the word "cation" to the name of the corresponding *radical* [97,98].

Note 3: Such names do not imply structure (e.g., whether three-coordinated or five-coordinated carbon atoms are present) [98].

See also *bridged carbocation*, *radical ion*.

See [40].

[3]

carbonium ion

(1) Carbocation that contains at least one carbon atom with a *coordination number* of five or greater.

(2) Carbocation whose structure cannot adequately be described by only two-electron two-centre *bond*s.

Example: methanium (CH_5^+).

1 *Note 1*: In most of the earlier literature this term was used for all types of
2 carbocations, including those that are now defined as a (tricoordinate) *carbenium ion*.
3 *Note 2*: To avoid ambiguity, the term should be avoided as the root for the
4 nomenclature of *carbocation*s. For example, the name "ethylcarbonium ion" might refer
5 to either $CH_3CH_2^+$ (ethyl cation) or $CH_3CH_2CH_2^+$ (propyl cation).
6 See [98,99].
7 rev[3]

8

carbyne

9
10 methylidyne
11 Generic name for the species HC·: and substitution derivatives thereof, such as
12 EtOCO–C·: (2-ethoxy-2-oxoethylidyne), containing an electrically neutral univalent
13 carbon atom with three non-bonding electrons.
14 *Note*: Use of the alternative name "methylidyne" as a generic term is not
15 recommended.
16 [3]

17

Catalán solvent parameters

18
19 Quantitative measure of solvent polarity, based on the solvent's hydrogen-bond-donor
20 ability, hydrogen-bond-acceptor ability, polarizability, and dipolarity.
21 See [100,101].
22 See also *solvent parameter*.

23

catalyst

24
25 Substance that increases the rate of a *chemical reaction* (owing to a change of
26 mechanism to one having a lower Gibbs energy of activation) without changing the
27 overall standard Gibbs energy change (or position of equilibrium).
28 *Note 1*: The catalyst is both a reactant and product of the reaction, so that there is
29 no net change in the amount of that substance.
30 *Note 2*: At the molecular level, the catalyst is used and regenerated during each set
31 of microscopic chemical events leading from a *molecular entity* of reactant to a
32 molecular entity of product.
33 *Note 3*: The requirement that there be no net change in the amount of catalyst is
34 sometimes relaxed, as in the base catalysis of the bromination of ketones, where base
35 is consumed, but this is properly called *pseudo-catalysis*.
36 *Note 4*: *Catalysis* can be classified as homogeneous, in which only one phase is
37 involved, and heterogeneous, in which the reaction occurs at or near an interface
38 between phases.
39 *Note 5*: Catalysis brought about by one of the products of a reaction is called
40 autocatalysis.

Note 6: The terms catalyst and catalysis should not be used when the added substance reduces the rate of reaction (see *inhibition*).

Note 7: The above definition is adequate for isothermal-isobaric reactions, but under other experimental conditions the state function that is lowered by the catalyst is not the Gibbs activation energy but the quantity corresponding to those conditions (e.g., the Helmholtz energy under isothermal-isochoric conditions).

See [13].

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*.

rev[3]

catalytic antibody (abzyme)

monoclonal antibody with enzymatic activity

Note 1: A catalytic antibody acts by binding its antigen and catalyzing a chemical reaction that converts the antigen into desired products. Despite the existence of natural catalytic antibodies, most of them were specifically designed to catalyze desired chemical reactions.

Note 2: Catalytic antibodies are produced through immunization against a transition-state analogue for the reaction of interest. The resulting antibodies bind strongly and specifically the transition-state analogue, so that they become *catalyst*s for the desired reaction.

Note 3: The concept of catalytic antibodies and the strategy for obtaining them were advanced by W. P. Jencks [102]. The first catalytic antibodies were finally produced in 1986 [103,104].

catalytic coefficient

If the *rate of reaction* v is expressible in the form

$$v = (k_0 + \Sigma k_i[C_i]^{ni}) \, [A]^a \, [B]^b...$$

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.

Note: Normally the partial *order of reaction* (n_i) with respect to a catalyst will be unity, so that k_i is an $(a + b+...+1)^{th}$-order *rate coefficient*.

[3]

1 **catalytic cycle**

2 Sequence of reaction steps in the form of a loop. One step is binding of a reactant to

3 the active *catalyst* (sometimes formed from a precatalyst), and another step is the

4 release of product and regeneration of catalyst.

5   *Example*: A + B → C, catalyzed by X formed from precatalyst X'.

6

7 **cation/π interaction**

8 Noncovalent attractive force between a positive ion (metal cation, protonated *Brønsted*

9 *base*, etc.) and a π electron system.

10   See [105].

11

12 **chain reaction**

13 Reaction in which one or more reactive *reactive intermediates* (frequently *radical*s) are

14 continuously regenerated through a repetitive cycle of elementary steps ("propagation

15 steps").

16   *Example*: Chlorination of methane by a radical *mechanism*, where Cl· is continually

17 regenerated in the chain-propagation steps:

18   Cl· + CH$_4$ → HCl + H$_3$C·

19   H$_3$C· + Cl$_2$ → CH$_3$Cl + Cl·

20   *Note*: In chain polymerization reactions, *reactive intermediate*s of the same types,

21 generated in successive steps or cycles of steps, differ in molecular mass, as in

22   RCH$_2$C·HPh + H$_2$C=CHPh → RCH$_2$CHPhCH$_2$C·HPh

23   See [106].

24   See also *chain transfer*, *initiation*, *termination*.

25   [3]

26

27 **chain transfer**

28 Chemical reaction during a chain polymerization in which the active centre is transferred

29 from the growing macromolecule to another molecule or to another site on the same

30 molecule, often by abstraction of an atom by the *radical* end of the growing

31 macromolecule.

Note 1: 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

$$RCH_2C \cdot HPh + CCl_4 \rightarrow RCH_2CHClPh + Cl_3C \cdot$$

represents a chain transfer, the radical $Cl_3C \cdot$ inducing further polymerization:

Note 2: Chain transfer also occurs in other chain reactions, such as cationic or anionic polymerization, in which case the abstraction is by the reactive cationic or anionic end of the growing chain.

See [106].

See also *telomerization*.

[3]

charge density

See *electron density*.

See [12].

[3]

charge-transfer (CT) complex

Ground-state *adduct* that exhibits an electronic absorption corresponding to light-induced transfer of electronic charge from one region of the adduct to another.

See [9].

rev[3]

chelation

Formation or presence of *bond*s (or other attractive interactions) between a single central atom (or ion) and two or more separate *binding site*s within the same *ligand*.

Note 1: A *molecular entity* in which there is chelation (and the corresponding *chemical species*) is called a chelate, while the species that binds to the central atom is called a chelant.

Note 2: The terms *bidentate*, tridentate, ... *multident*ate 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 Cu^{+2} in which both nitrogen atoms of ethylenediamine are bonded to copper.

Note 3: The use of the term is often restricted to metallic central atoms or ions.

Note 4: The phrase "separate binding sites" is intended to exclude cases such as $[PtCl_3(CH_2=CH_2)]^-$, 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.

See also *ambident*, *cryptand*.

1   See also [29].

2   [3]

3

4   **cheletropic reaction**

5   *Cycloaddition* across the terminal atoms of a π system with formation of two new σ

6   bonds to a single atom of a monocentric reagent. There is formal loss of one π bond in

7   the substrate and an increase in *coordination number* of the relevant atom of the

8   reagent.

9   *Example: addition* of sulfur dioxide to butadiene:

$$CH_2{=}CH{-}CH{=}CH_2 \;+\; SO_2 \longrightarrow$$

10

11 *Note*: The reverse of this type of reaction is designated "cheletropic elimination".

12 See [107].

13 [3]

14

15 **chelotropic reaction**

16 Alternative (and etymologically more correct) name for *cheletropic reaction*.

17 See [51].

18 [3]

19

20 **chemical flux,** ϕ

21 Unidirectional *rate of reaction*, applicable to the progress of component reaction steps

22 in a complex system or to the progress of reactions in a system at dynamic equilibrium

23 (in which there are no observable concentration changes with time), excluding the

24 reverse reaction and other reaction steps.

25 *Note 1*: Chemical flux is a derivative with respect to time, and has the dimensions of

26 amount of substance per volume transformed per time.

27   For example, for the mechanism

28          $A + B \rightleftarrows C$

29          $C + D \rightarrow E$

30 ϕ_1 is the chemical flux due to forward reaction step 1, or the rate of formation of C or

31 the rate of loss of A or B due to that step, and similarly for ϕ_{-1} and ϕ_2.

32 *Note 2*: The sum of all the chemical fluxes leading to C is designated the "total

33 chemical flux into C" (symbol $\Sigma\phi_C$), and the sum of all the chemical fluxes leading to

34 destruction of C is designated the "total chemical flux out of C" (symbol $\Sigma\phi_{-C}$), and

35 similarly for A and B. It then follows for this example that $\Sigma\phi_C = \phi_1$ and $\Sigma\phi_{-C} = \phi_{-1} + \phi_2$,

36 *Note 3*: The net rate of appearance of C is then given by

1

2   d[C]/dt = $\Sigma \phi_C - \Sigma \phi_{-C}$

3

4   *Note 4*: In this system ϕ_1 (or $\Sigma \phi_C$) can be regarded as the hypothetical rate of
5   formation of C due to the single (unidirectional) reaction 1 proceeding in the assumed
6   absence of all other reactions, and $\Sigma \phi_{-C}$ can be regarded as the hypothetical rate of
7   destruction of C due to the two (unidirectional) reactions −1 and 2.
8   *Note 5*: Even when there is no net reaction, chemical flux can often be measured by
9   NMR methods.
10   See [1].
11   See also *order of reaction*, *rate-limiting step*, *steady state*.
12   rev[3]

13

14   **chemical reaction**
15   Process that results in the interconversion of *chemical species*.
16   *Note 1*: This definition includes experimentally observable interconversions of
17   *conformer*s and *degenerate rearrangement*s.
18   *Note 2*: Chemical reactions may be *elementary reaction*s or *stepwise reaction*s.
19   *Note 3*: Detectable chemical reactions normally involve sets of *molecular entities*, as
20   indicated by this definition, but it is often conceptually convenient to use the term also
21   for changes involving single molecular entities (i.e., "microscopic chemical events"),
22   whose reactions can now be observed experimentally.
23   See also *identity reaction*.
24   rev[3]

25

26   **chemical relaxation**
27   Passage of a perturbed system toward or into chemical equilibrium.
28   *Note 1*: A *chemical reaction* at equilibrium can be disturbed from equilibrium by a
29   sudden change of some external parameter such as temperature, pressure, or electric-
30   field strength.
31   *Note 2*: In many cases, and in particular when the displacement from equilibrium is
32   slight, the progress of the system towards equilibrium can be expressed as a first-order
33   process

34

35    $c(t) - (c_{eq})_2 = [(c_{eq})_1 - (c_{eq})_2]\ \exp(-t/\tau)$

36

37   where $(c_{eq})_1$ and $(c_{eq})_2$ are the equilibrium amount concentrations of one of the chemical
38   species before and after the change in the external parameter, and $c(t)$ is its amount
39   concentration at time t. The time parameter τ, called relaxation time, is related to the

1 *rate coefficients* of the chemical reaction involved. Such measurements are commonly
2 used to follow the kinetics of very fast reactions.
3   *Note 3: Relaxation,* or the passage toward equilibrium, is more general than chemical
4 relaxation, and includes relaxation of nuclear spins.
5   See [108,109].
6   See *relaxation*.
7 rev[3]

8

9 **chemical shift (NMR)**
10 δ
11 Variation of the resonance frequency of a nucleus in nuclear magnetic resonance
12 (NMR) spectrometry as a consequence of its environment.
13   *Note 1*: The chemical shift of a nucleus X, δ_X, expressed as its frequency, ν_X, relative
14 to that of a standard, ν_{ref}, and defined as

15

16      $\delta_X = (\nu_X - \nu_{ref})/\nu_{ref}$

17

18 For ^1H and ^{13}C NMR the reference signal is usually that of tetramethylsilane (SiMe4).
19   *Note 2:* Chemical shift is usually reported in "parts per million" or ppm, where the
20 numerator has unit Hz, and the denominator has unit MHz, like the spectrometer's
21 operating frequency.
22   *Note 3*: For historical reasons that predate Fourier-transform NMR, if a resonance
23 signal occurs at higher frequency than a reference signal, it is said to be downfield, and
24 if resonance occurs at lower frequency, the signal is upfield. Resonances downfield
25 from SiMe4 have positive δ-values, and resonances upfield from SiMe4 have negative
26 δ-values. These terms have been superseded, and deshielded and shielded are
27 preferred for downfield and upfield, respectively.
28   See [110].
29   See also *shielding*.
30 rev[3]

31

32 **chemical species**
33 Ensemble of chemically identical *molecular entities* that can explore the same set of
34 molecular energy levels on the time scale of an experiment. The term is applied equally
35 to a set of chemically identical atomic or molecular structural units in a solid array.
36   *Note 1*: For example, conformational *isomer*s may be interconverted sufficiently
37 slowly to be detectable by separate NMR spectra and hence to be considered to be
38 separate chemical species on a time scale governed by the radiofrequency of the
39 spectrometer used. On the other hand, in a slow chemical reaction the same mixture of
40 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.

Note 2: Except where the context requires otherwise, the term is taken to refer to a set of molecular entities containing isotopes in their natural abundance.

Note 3: The definition given is intended to embrace not only cases such as graphite and sodium chloride but also a surface oxide, where the basic structural units may not be capable of isolated existence.

Note 4: 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*.

[3]

chemically induced dynamic nuclear polarization (CIDNP)

Non-Boltzmann nuclear spin-state distribution produced in thermal or photochemical reactions, usually from *colligation* and diffusion or *disproportionation* of *radical pair*s, and detected by NMR spectroscopy as enhanced absorption or emission signals.

See [111,112].

rev[3]

chemiexcitation

Generation, by a chemical reaction, of an electronically excited molecular entity from reactants in their ground electronic states.

See [9].

[3]

chemoselectivity

Feature of a chemical reagent that reacts preferentially with one of two or more different functional groups.

Note 1: A reagent has a high chemoselectivity if reaction occurs with only a limited number of different functional groups. For example, sodium tetrahydridoborate ($NaBH_4$) is a more chemoselective reducing agent than is lithium tetrahydridoaluminate ($LiAlH_4$). The concept has not been defined in more quantitative terms.

Note 2: The term is also applied to reacting molecules or intermediates that exhibit selectivity towards chemically different reagents.

Note 3: Usage of the term chemospecificity for 100 % chemoselectivity is discouraged.

See [113].

See also *regioselectivity*, *stereoselectivity*, *stereospecificity*.

[3]

1 **chemospecificity**

2 obsolete

3   See *chemoselectivity*.

4   [3]

5

6 **chirality**

7 Property of a structure that is not superimposable on its mirror image.

8   See [11,46].

9   [3]

10

11 **chirality centre**

12 chiral centre (superseded)

13 Atom with attached groups such that the arrangement is not superimposable on its

14 mirror image.

15   *Note*: Often this is a tetrahedral atom with four different groups attached, such as

16 CHBrClF, or C2 of $CH_3CHBrCH_2CH_3$, or the sulfur of $CH_3S(=O)Ph$, where the lone pair

17 is considered as a fourth group.

18   See [11].

19   See also *stereogenic centre*.

20   [3]

21

22 **chiral feature**

23 Structural characteristic rendering a molecule *chiral*.

24   *Examples*: four different substituents on a carbon atom (*chirality centre)*,

25 conformational helix, chiral axis (as in allenes XCH=C=CHX).

26

27 **chiral recognition**

28 Attraction between molecules through noncovalent interactions that exhibit

29 complementarity only between partners with specific chirality.

30   See also *molecular recognition*.

31

32 **chromophore**

33 Part (atom or group of atoms) of a *molecular entity* in which the electronic transition

34 responsible for a given spectral band is approximately localized.

35   *Note 1*: The term arose originally to refer to the groupings that are responsible for a

36 dye's colour.

37   *Note 2:* The electronic transition can often be assigned as involving n, π, π^*, σ, and/or

38 σ^* orbitals whose energy difference falls within the range of the visible or UV spectrum.

39   *Note 3*: The term has been extended to vibrational transitions in the infrared.

40   See [9,114,115].

1 [3]

2

3 **CIDNP**

4 Acronym for *chemically induced dynamic nuclear polarization*.

5 [3]

6

7 *cine*-**substitution**

8 *Substitution* reaction (generally *aromatic*) in which the entering group takes up a

9 position adjacent to that occupied by the *leaving group*.

10 *Example*:

11

12
13

14 See also *tele-substitution*.

15 [3]

16

17 **classical carbocation**

18 *Carbocation* whose electronic structure can be adequately described by two-electron-

19 two-centre bonds, i.e., synonymous with *carbenium ion*.

20

21 **clathrate**

22 See *host*, *inclusion compound*.

23 [3]

24

25 **coarctate**

26 *Feature of a concerted transformation* in which the primary changes in bonding occur

27 within a cyclic array of atoms but in which two nonbonding *atomic orbital*s on an atom

28 interchange roles with two bonding orbitals.

29 *Example:* epoxidation with dimethydioxirane

30

Note: Because the 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. It is therefore not governed by the rules that express *orbital symmetry* restrictions applicable to pericyclic reactions.

See [116].

See also *pseudopericyclic*.

colligation

Formation of a covalent bond by combination or recombination of two *radical*s.

Note: This is the reverse of *unimolecular homolysis*.

Example:

$$HO\cdot + H_3C\cdot \rightarrow CH_3OH$$
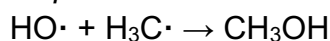
[3]

collision complex

Ensemble formed by two reaction partners, where the distance between them is equal to the sum of the van der Waals radii of neighbouring atoms.

See also *encounter complex*.

[3]

common-ion effect (on rates)

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^+).

Example: the rate of solvolysis of chlorodiphenylmethane in acetone-water is reduced by the addition of salts of the common ion Cl^-, which causes a decrease in the *steady-state* concentration of the diphenylmethyl cation:

$$Ph_2CHCl \rightleftharpoons Ph_2CH^+ + Cl^- \text{ (free ions, not ion pairs)}$$
$$Ph_2CH^+ + 2\,OH_2 \rightarrow Ph_2CHOH + H_3O^+$$

1 *Note*: This retardation due to a common ion should be distinguished from the
2 acceleration due to a salt effect of all ions.
3 rev[3]

4

5 **compensation effect**
6 Observation that a plot of $T\Delta_r S$ vs. $\Delta_r H$ (frequently $T\Delta^{\ddagger}S$ vs. $\Delta^{\ddagger}H$) for a series of reactions
7 with a range of different substituents (or other unique variable such as solvent or
8 dissolved salt), are straight lines of approximately unit slope, so that, e.g., the terms
9 $\Delta^{\ddagger}H$ and $T\Delta^{\ddagger}S$ partially compensate, and $\Delta^{\ddagger}G = \Delta^{\ddagger}H - T\Delta^{\ddagger}S$ shows less variation than
10 $\Delta^{\ddagger}H$ or $T\Delta^{\ddagger}S$ separately.
11 *Note*: Frequently such $\Delta^{\ddagger}S$ vs. $\Delta^{\ddagger}H$ correlations are statistical artifacts, arising if
12 entropy and enthalpy are extracted from the variation of an equilibrium constant or a
13 *rate constant* with temperature, so that the slope and intercept of the van't Hoff plots
14 are correlated. The problem is avoided if the equilibrium constant and the enthalpy are
15 measured independently, for example by spectrophotometry and calorimetry,
16 respectively.
17 See [117,118,119,120].
18 See also *isoequilibrium relationship, isokinetic relationship*.
19 rev[3]

20

21 **complex**
22 *Molecular entity* formed by loose *association* involving two or more component
23 molecular entities (ionic or uncharged), or the corresponding *chemical species*. The
24 attraction between the components is often due to hydrogen-bonding or van der Waals
25 attraction and is normally weaker than a covalent *bond*.
26 *Note 1*: The term has also been used with a variety of meanings in different contexts:
27 it is therefore best avoided when a more explicit alternative is applicable, such as *adduct*
28 when the association is a consequence of bond formation.
29 *Note 2*: In inorganic chemistry the term "coordination entity" is recommended instead
30 of "complex" [29,121].
31 See also *activated complex*, *adduct*, *charge transfer complex*, *electron-donor-*
32 *acceptor complex*, *encounter complex*, *inclusion complex*, *σ-adduct*, *π-adduct*,
33 *transition state*.
34 [3]

35

36 **composite reaction**
37 *Chemical reaction* for which the expression for the rate of disappearance of a reactant
38 (or rate of appearance of a product) involves *rate constant*s of more than a single
39 *elementary reaction*.

1   Examples: "opposing reactions" (where rate constants of two opposed chemical
2   reactions are involved), "parallel reactions" (for which the rate of disappearance of any
3   reactant is governed by the rate constants relating to several simultaneous reactions
4   that form different products from a single set of reactants), and *stepwise reaction*s.
5   [3]

6

comproportionation

8   Any *chemical reaction* of the type A' + A" → 2 A

9   *Example*:

10   Pb + PbO$_2$ + 2 H$_2$SO$_4$ → 2 PbSO$_4$ + 2 H$_2$O (in a lead battery)

11

12   *Note:* Other stoichiometries are possible, depending on the *oxidation number*s of the
13   species.

14   Reverse of *disproportionation*. The term "symproportionation" is also used.

15   See [122].

16   rev[3]

17

concerted

19   Feature of a process in which two or more primitive changes occur within the same
20   *elementary reaction*. Such changes will normally be "energetically coupled".

21   *Note 1*: The term "energetically coupled" means that the simultaneous progress of
22   the primitive changes involves a *transition state* of lower energy than that for their
23   successive occurrence.

24   *Note 2*: In a concerted process the primitive changes may be *synchronous* or
25   asynchronous.

26   See also *bifunctional catalysis*, *potential-energy surface*.

27   [3]

28

condensation

30   Reaction (usually stepwise) in which two or more reactants (or remote reactive sites
31   within the same *molecular entity*) yield a product with accompanying formation of water
32   or some other small molecule, e.g., ammonia, ethanol, acetic acid, hydrogen sulfide.

33   *Note 1*: The *mechanism* of many condensation reactions has been shown to
34   comprise consecutive *addition* and *elimination* reactions, as in the base-catalysed
35   formation of (*E*)-but-2-enal (crotonaldehyde) from acetaldehyde, via dehydration of 3-
36   hydroxybutanal (aldol). The overall reaction in this example is known as the aldol
37   condensation.

38   *Note 2*: The term is sometimes also applied to cases where the formation of water
39   or other simple molecule does not occur, as in "benzoin condensation".

40   [3]

condensed formula

Linear representation of the structure of a *molecular entity* in which bonds are omitted.

Example: methyl 3-methylbutyl ether (isoamyl methyl ether,

$(CH_3)_2CHCH_2CH_2OCH_3$, sometimes condensed further to $(CH_3)_2CH[CH_2]_2OCH_3$)

Note: This term is sometimes also called a *line formula*, because it can be written on a single line, but the line formula explicitly shows all bonds.

configuration (electronic)

Distribution of the electrons of an atom or a *molecular entity* over a set of one-electron wavefunctions called *orbital*s, according to the Pauli principle.

Note: 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

$$^3\Sigma_g^-, \, ^1\Delta_g, \text{ and } ^1\Sigma_g^+ \text{ multiplets}$$

See [8,9].

[3]

configuration (molecular)

Arrangement in space of the atoms of a *molecular entity* that distinguishes it from any other molecular entity having the same molecular formula and *connectivity* and that is not due to conformational differences (rotation about single bonds).

See [11].

[3]

conformations

Different spatial arrangements of a molecular entity that can be interconverted by rotation about one or more formally single bonds.

Note 1: Different conformations are often not considered to be stereoisomeric, because interconversion is rapid.

Note 2: Different or equivalent spatial arrangements of *ligands* about a central atom, such as those interconverted by pyramidal inversion (of amines) or Berry pseudorotation (as of PF_5) and other "polytopal rearrangements", are sometimes considered conformations, but they are properly described as *configuration*s.

See [11].

rev[3]

conformational isomers

conformers

1

conformer

Conformation of a *molecular entity* that corresponds to a minimum on the potential-energy surface of that molecular entity.

Note: The distinction between conformers and isomers is the height of the barrier for interconversion. Isomers are stable on macroscopic timescales because the barrier for interconversion is high, whereas a conformer cannot persist on a macroscopic timescale because the interconversion between conformations is achieved rapidly.

See [11].

conjugate acid

Brønsted acid BH^+ formed on protonation (hydronation) of the base B.

Note 1: B is called the conjugate base of the acid BH^+.

Note 2: 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, and so do NH_4^+ and its conjugate base NH_3.

rev[3]

conjugated system, conjugation

Molecular entity whose structure may be represented as a system of alternating multiple and single (or σ) bonds: e.g.,

$$CH_2=CH–CH=CH_2 \text{ or } CH_2=CH–C\equiv N$$

Note: In such systems, conjugation is the interaction of one p-orbital with another p-orbital (or d-orbital) across an intervening σ bond, including the analogous interaction involving a p-orbital containing an unshared electron pair, e.g.,

$$R_2\ddot{N}–CH=CH_2$$

or the interaction across a double bond whose π system does not interact with the p orbitals of the conjugated system, as in

$$CH_2=C=C=CH_2$$

See also *cross-conjugation, delocalization, resonance, through-conjugation*.

[3]

connectivity

Description of which atoms are bonded to which other atoms.

Note: Connectivity is often displayed in a *line formula* or other structure showing which atoms are bonded to which other atoms, but with minimal or no indication of *bond* multiplicity.

Example: The connectivity of propyne is specified by CH_3CCH.

1 rev[3]

2

3 **conrotatory**

4 Stereochemical feature of an *electrocyclic reaction* in which the substituents at the
5 interacting termini of the conjugated system rotate in the same sense (both clockwise
6 or both counterclockwise).

7 See also *disrotatory*.

8 rev[3]

9

10 **conservation of orbital symmetry**

11 An approach to understanding *pericyclic reaction*s that focuses on a symmetry
12 element (e.g., a reflection plane) that is retained along a reaction pathway. If each of
13 the singly or doubly occupied orbitals of the reactant(s) is of the same symmetry as a
14 similarly occupied orbital of the product(s), that pathway is "allowed" by orbital
15 symmetry conservation. If instead a singly or doubly occupied orbital of the reactant(s)
16 is of the same symmetry as an unoccupied orbital of the product(s), and an unoccupied
17 orbital of the reactant(s) is of the same symmetry as a singly or doubly occupied orbital
18 of the product(s), that pathway is "forbidden" by orbital symmetry conservation.

19 *Note 1*: This principle permits the qualitative construction of correlation diagrams to
20 show how molecular orbitals transform and how their energies change during chemical
21 reactions.

22 *Note 2*: Considerations of orbital symmetry are frequently grossly simplified in that,
23 for example, the π and π^* orbitals of a carbonyl group in an asymmetric molecule are
24 treated as having the same topology (pattern of local nodal planes) as those of a
25 symmetric molecule (e.g., $CH_2=O$), despite the absence of formal symmetry elements.

26 See [107,123].

27 See also *orbital symmetry*.

28

29 **constitutional isomers**

30 Species (or *molecular entities*) with the same atomic composition (*molecular formula*)
31 but with different *connectivity*.

32 *Note:* The term structural isomers is discouraged, because all isomers differ in
33 structure and because isomers may be constitutional, configurational, or
34 conformational.

35 See [11].

36

37 **contributing structure**

38 resonance form

39 rev[3]

40

1 **coordinate covalent bond**

2 dative bond

3

4 **coordination**

5 Formation of a covalent *bond*, the two shared electrons of which come from only one

6 of the two partners linked by the bond, as in the reaction of a *Lewis acid* and a *Lewis*

7 *base* to form a *Lewis adduct*; alternatively, the bonding formed in this way.

8   *Note*: In the former sense, it is the reverse of *unimolecular heterolysis*.

9   See also *dative bond*, *π-adduct*.

10   rev[3]

11

12 **coordination number**

13 Number of other atoms directly linked to a specified atom in a *chemical species*

14 regardless of the number of electrons in the bonds linking them [29, Rule IR-10.2.5].

15 For example, the coordination number of carbon in methane or of phosphorus in

16 triphenylphosphane oxide (triphenylphosphine oxide) is four whereas the coordination

17 number of phosphor is five in phosphorus pentafluoride.

18   *Note*: The term is used in a different sense in the crystallographic description of ionic

19 crystals.

20   rev[3]

21

22 **coronate**

23   See *crown ether*.

24   rev[3]

25

26 **correlation analysis**

27 Use of empirical correlations relating one body of experimental data to another, with the

28 objective of finding quantitative relationships among the factors underlying the

29 phenomena involved. Correlation analysis in organic chemistry often uses linear Gibbs-

30 energy relations (formerly *linear free-energy relation*, LFER) for rates or equilibria of

31 reactions, but the term also embraces similar analysis of physical (most commonly

32 spectroscopic) properties and of biological activity.

33   See [124,125,126,127,128].

34   See also *linear free-energy relation*, *quantitative structure-activity relationship*

35 *(QSAR)*.

36   [3]

37

38 **coupling constant (spin-spin coupling constant)**

39 *J*

40 (Unit: Hz)

1 Quantitative measure of nuclear spin-spin coupling in nuclear magnetic resonance
2 spectroscopy.
3   *Note*: Spin-spin coupling constants have been correlated with atomic hybridization
4 and with molecular conformations.
5   See [129,130,131].
6   rev[3]
7

8 **covalent bond**
9 Stabilizing interaction associated with the sharing of electron pairs between two atomic
10 centres of a molecular entity, leading to a characteristic internuclear distance.
11   See also *agostic*, *coordination*, *hydrogen bond*, *multi-centre bond*.
12   See [8].
13   rev[3]
14

15 **Cox–Yates equation**
16 Generalization of the *Bunnett-Olsen equation* of the form
17

18    $\lg([SH^+])/[S]) - \lg\{[H^+]\} = m^*X + pK_{SH+}$

19

20 where $[H^+]$ is the amount concentration of acid, X is the activity-coefficient ratio
21 $\lg(\{\gamma_s\}\{\gamma_{H+}\}/\{\gamma_{SH+}\})$ for an arbitrary reference base, pK_{SH+} is the thermodynamic
22 dissociation constant of SH^+, and m^* is an empirical parameter derived from linear
23 regression of the left-hand side vs. X. Arguments in the lg functions should be unitless.
24 Thus, the reduced quantities should be used: $\{[H^+]\}$ is $[H^+]$/units.
25   *Note*: The function X is called excess acidity because it gives a measure of the
26 difference between the acidity of a solution and that of an ideal solution of the same
27 concentration. In practice $X = - (H_o + \lg\{[H^+]\})$ and $m^* = 1 - \phi$, where H_o is the Hammett
28 *acidity function* and ϕ is the slope in the Bunnett-Olsen equation.
29   See [132,133,134].
30   See *Bunnett-Olsen equation*.
31   rev[3]
32

33 **critical micellisation concentration** *(cmc)*
34 critical micelle concentration
35 Relatively small range of concentrations separating the limit below which virtually no
36 *micelle*s are detected and the limit above which virtually all additional surfactant
37 molecules form micelles.
38   *Note* 1: Many physical properties of surfactant solutions, such as conductivity or light
39 scattering, show an abrupt change at a particular concentration of the surfactant, which
40 can be taken as the *cmc*.

1	*Note 2*: As values obtained using different properties are not quite identical, the
2	method by which the *cmc* is determined should be clearly stated.
3	See [135].
4	See also *inverted micelle*.
5	rev[3]
6

cross-conjugation
8	Phenomenon of three conjugated groups, two pairs of which exhibit conjugation but
9	without *through-conjugation* of all three, as in 2-phenylallyl, benzoate anion, divinyl
10	ether, or *m*-xylylene [1,3-$C_6H_4(CH_2)_2$].
11	See [64].
12	rev[3]
13

crown ether
15	*Molecular entity* comprising a monocyclic *ligand* assembly that contains three or more
16	*binding site*s held together by covalent bonds and capable of binding a *guest* in a central
17	(or nearly central) position. The *adduct*s formed are sometimes known as "coronates".
18	The best known members of this group are macrocyclic polyethers, such as 18-crown-
19	6, containing several repeating units –CR_2–CR_2O– (where R is most commonly H).

"18-crown-6"

20
21	See [136,137].
22	See also *host*.
23	rev[3]
24

cryptand
26	*Molecular entity* comprising a cyclic or polycyclic assembly of *binding site*s that contains
27	three or more binding sites held together by *covalent bond*s, and which defines a
28	molecular cavity in such a way as to bind (and thus "hide" in the cavity) another
29	molecular entity, the *guest* (a cation, an anion or a neutral species), more strongly than
30	do the separate parts of the assembly (at the same total concentration of binding sites).
31	*Note 1*: The *adduct* thus formed is called a "cryptate". The term is usually restricted
32	to bicyclic or oligocyclic molecular entities.

1   *Example*:

2

3   *Note 2*: Corresponding monocyclic *ligand* assemblies (*crown ether*) are sometimes
4   included in this group, if they can be considered to define a cavity in which a guest can
5   hide. The terms "podand" and "spherand" are used for certain specific ligand
6   assemblies. Coplanar cyclic polydentate ligands, such as porphyrins, are not normally
7   regarded as cryptands.
8   See [138].
9   See also *host*. See also [139].
10   [3]

11

12   **curly arrows**
13   Symbols for depicting the flow of electrons in a chemical reaction or to generate
14   additional *resonance form*s.
15   *Note 1:* The tail of the curly arrow shows where an electron pair originates, and the
16   head of the curly arrow shows where the electron pair goes.
17   *Note 2:* Single-headed curly arrows are used to depict the flow of unpaired electrons.
18   *Examples:*
19

20
21

22   See *electron pushing*.
23

24   **Curtin-Hammett principle**
25   Statement that in a *chemical reaction* that yields one product (X) from one isomer (A')
26   and a different product (Y) from another isomer (A") (and provided these two isomers
27   are rapidly interconvertible relative to the rate of product formation, whereas the
28   products do not undergo interconversion) the product composition is not directly related
29   to the relative concentrations of the isomers in the *substrate*; it is controlled only by the
30   difference in standard Gibbs energies ($G^{\ddagger}_{A'} - G^{\ddagger}_{A''}$) of the respective *transition states*.

1   *Note 1*: The product composition is given by [Y]/[X] = $(k_Y k_1)/(k_{-1} k_X)$ or $K_c k_Y / k_X$, where

2   K_c is the equilibrium constant, [A"]/[A'], and where k_Y and k_X are the respective <u>rate</u>

3   <u>constant</u>s of their reactions; these parameters are usually unknown.

4   *Note 2*: The energy diagram below represents the transformation of rapidly

5   interconverting isomers A' and A" into products X and Y.

6

$$X \xleftarrow{\quad k_X \quad} A' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A'' \xrightarrow{\quad k_Y \quad} Y$$

7    $$k_1 \gg k_X \qquad\qquad k_{-1} \gg k_Y$$

8

9   Reaction coordinate $\longrightarrow$

10

11   *Note 3*: A related concept is the Winstein-Holness equation for the overall rate of

12   product formation in a system of rapidly interconverting isomers A' and A". The overall

13   rate constant k is given by

14

15        $k = x' k_X + x'' k_Y$

16

17   where x' and x'' are the respective mole fractions of the isomers at equilibrium [15].

18   However, since x' and x'' are simple functions of K_c, the apparent dependence of the

19   overall rate on the relative concentrations of A' and A" disappears. The overall rate

20   constant is the sum $k_X + K_c k_Y$, which is a function of the same quantities that determine

21   the product ratio.

22   See [140]. See also [15,141,142].

23   rev[3]

24

25   **cybotactic region**

1 That part of a solution in the vicinity of a solute molecule in which the ordering of the
2 solvent molecules is modified by the presence of the solute molecule. The term solvent
3 "cosphere" of the solute has also been used.
4   See [143,144].
5   [3]
6

cyclization

8 Formation of a ring compound from a chain by formation of a new bond.
9   See also *annulation*.
10   [3]
11

cycloaddition

13 Reaction in which two or more unsaturated molecules (or parts of the same molecule)
14 combine with the formation of a cyclic *adduct* in which there is a net reduction of the
15 bond multiplicity.
16   *Note 1*: The following two systems of notation have been used for the more detailed
17 specification of cycloadditions, of which the second, more recent system (described
18 under (2)) is preferred:
19   (1) An (*i*+*j*+...) cycloaddition is a reaction in which two or more molecules (or parts
20   of the same molecule), respectively, provide units of *i*, *j*,... linearly connected
21   atoms: these units become joined at their respective termini by new σ bonds so
22   as to form a cycle containing (*i*+*j*+...) atoms. In this notation, (a) a Diels-Alder
23   reaction is a (4+2) cycloaddition, (b) the initial reaction of ozone with an alkene is
24   a (3+2) cycloaddition, and (c) the reaction of norbornadiene below is a (2+2+2)
25   cycloaddition. (Parentheses are used to indicate the numbers of atoms, but
26   brackets are also used.)

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14

15 would be a [14a+2s] or [π14a + π2s] cycloaddition, leading to the stereoisomer shown,
16 with hydrogens *anti*. (Brackets are used to indicate the numbers of electrons, and
17 they are also used instead of parentheses to denote the numbers of atoms.)

1
2
3 (2) The symbolism [*i+j*+...] for a cycloaddition identifies the numbers *i*, *j*,... of
4 electrons in the interacting units that participate in the transformation of reactants
5 to products. In this notation the reaction (a) and (b) of the preceding paragraph
6 would both be described as [2+4] cycloadditions, and (c) as a [2+2+2]
7 cycloaddition. The symbol a or s (a = *antarafacial*, s = suprafacial) is often added
8 (usually as a subscript after the number to designate the stereochemistry of
9 addition to each fragment. A subscript specifying the orbitals, viz., σ, π (with their
10 usual significance) or n (for an orbital associated with a single atom), may be
11 added as a subscript before the number. Thus the normal Diels-Alder reaction is
12 a [4s+2s] or [π4s + π2s] cycloaddition, whilst the reaction

Note 2: Cycloadditions may be *pericyclic reaction*s or (non-*concerted*) *stepwise reaction*s. The term "dipolar cycloaddition" is used for cycloadditions of 1,3-dipolar compounds.

    See [107,145,146].

    See also *cheletropic reaction*, *ene reaction*, *pericyclic reaction*.

    rev[3]

cycloelimination

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

    [3]

cycloreversion

obsolete

    See *cycloelimination*.

    [3]

dative bond

obsolescent

Coordination bond formed between two chemical species, one of which serves as a donor and the other as an acceptor of the electron pair that is shared in the bond.

    Examples: the N–B bond in $H_3N^+–B^-H_3$, the S–O bond in $(CH_3)_2S^+–O^-$.

    Note 1: A distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or in inert solvent follows the heterolytic bond-cleavage path.

    Note 2: The term is obsolescent because the distinction between dative bonds and ordinary covalent bonds is not useful, in that the precursors of the bond are irrelevant: $H_3N^+–B^-H_3$ is the same molecule, with the same bonds, regardless of whether the precursors are considered to have been $H_3N + BH_3$ or $H_3N^{.+} + {^-}BH_3$.

    See [8].

    See *coordination*.

    rev[3]

degenerate chemical reaction

    See *identity reaction*.

    [3]

degenerate rearrangement

Chemical reaction in which the product is indistinguishable (in the absence of isotopic labelling) from the reactant.

1   *Note 1*: The term includes both "degenerate *intramolecular* rearrangements" and
2   reactions that involve *intermolecular* transfer of atoms or groups ("degenerate
3   intermolecular reactions"): both are degenerate *isomerization*s.
4   *Note 2*: The occurrence of degenerate rearrangements may be detectable by isotopic
5   labelling or by dynamic NMR techniques. For example: the [3,3]*sigmatropic*
6   *rearrangement* of hexa-1,5-diene (Cope rearrangement),
7   *Note 3:* Synonymous but less preferable terms are "automerization", "permutational
8   isomerism", "isodynamic transformation", "topomerization".
9   See [147].
10   See also *fluxional*, *molecular rearrangement*, *narcissistic reaction*, *valence isomer*.
11   [3]
12

13   **delocalization**
14   Quantum-mechanical concept most usually applied in organic chemistry to describe the
15   redistribution of π electrons in a *conjugated system*, where each link has a fractional
16   double-bond character, or a non-integer *bond order*, rather than π electrons that are
17   localized in double or triple bonds.
18   *Note 1*: There is a corresponding "delocalization energy", identifiable with the
19   stabilization of the system relative to a hypothetical alternative in which formal

20   (localized) single and double *bond*s are present. Some degree of delocalization is
21   always present and can be estimated by quantum mechanical calculations. The effects
22   are particularly evident in *aromatic* systems and in symmetrical *molecular entities* in
23   which a lone pair of electrons or a vacant p-orbital is conjugated with a double bond
24   (e.g., carboxylate ions, nitro compounds, enamines, the allyl cation).
25   *Note 2*: Delocalization in such species may be represented by partial bonds or by
26   *resonance* (here symbolized by a two-headed arrow) between *resonance form*s.
27

28

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

4 *Note 3*: Delocalization is not limited to π electrons. *Hyperconjugation* is the
5 delocalization of electrons of σ bonds.
6 [3]

7

dendrimer
9 Large molecule constructed from a central core with repetitive branching and multiple
10 functional groups at the periphery.
11 See [148].
12 *Example:* (with 48 CH_2OH at the periphery)

13

14
15

16 *Note*: The name comes from the Greek $\delta\epsilon\nu\delta\rho o\nu$ (dendron), which translates to "tree".
17 Synonymous terms include arborols and cascade molecules.
18 See [148,149,150,151,152].

19

deshielding
21 See *shielding*.
22 [3]

23

detachment
25 Reverse of *attachment*.
26 [3]

27

28

29

1 **detailed balancing**

2 Principle that when equilibrium is reached in a reaction system (containing an arbitrary

3 number of components and reaction paths), as many atoms, in their respective

4 *molecular entities,* will pass forward in a given finite time interval as will pass backward

5 along each individual path.

6 *Note 1*: It then follows that the reaction path in the reverse direction must in every

7 detail be the reverse of the reaction path in the forward direction (provided that the

8 system is at equilibrium).

9 *Note 2*: The principle of detailed balancing is a consequence for macroscopic

10 systems of the principle of *microscopic reversibility*.

11 [3]

12

13 **diamagnetism**

14 Property of substances having a negative magnetic susceptibility (χ), whereby they are

15 repelled out of a magnetic field.

16 See also *paramagnetism*.

17 [3]

18

19 **diastereoisomerism**

20 Stereoisomerism other than *enantiomerism*.

21 See *diastereoisomers* [11].

22 [3]

23

24 **diastereomeric excess** (diastereoisomeric excess)

25 $x_1 - x_2$, where x_1 and x_2 (with $x_1 + x_2 = 1$) are the mole fractions of two *diastereoisomers*

26 in a mixture, or the fractional yields of two *diastereoisomers* formed in a reaction.

27 *Note:* Frequently this term is abbreviated to d.e.

28 See *stereoselectivity*, *diastereoisomers*.

29 See [11].

30

31 **diastereomeric ratio**

32 x_1/x_2, where x_1 and x_2 are the mole fractions of two *diastereoisomers* in a mixture formed

33 in a reaction.

34 *Note:* Frequently this term is abbreviated to d.r.

35 See *stereoselectivity*, *diastereoisomers*.

36 See [11].

37

38 **diastereoisomers (diastereomers)**

39 Stereoisomers not related as mirror images of each other.

1   *Note*: Diastereoisomers are characterized by differences in physical properties, and

2   by differences in chemical behaviour toward chiral as well as achiral reagents.

3   See [11].

4

5   diastereoselectivity

6   Preferential formation in a chemical reaction of one *diastereoisomer* over another.

7   *Note*: This can be expressed quantitatively by the *diastereoisomeric excess* or by the

8   *diastereomeric ratio*, which is preferable because it is more closely related to a Gibbs-

9   energy difference.

10   See [11].

11   See *selectivity*.

12

13   dielectric constant

14   obsolete

15   See [12].

16   See *permittivity (relative)*.

17   rev[3]

18

19   dienophile

20   Ene or yne component of a Diels-Alder reaction, including compounds with hetero-

21   double bonds and hetero-triple bonds.

22   See *cycloaddition*.

23   rev[3]

24

25   diffusion-controlled rate

26   See *encounter-controlled rate*, *microscopic diffusion control*. Contrast *mixing control*.

27   [3]

28

29   dimerization

30   *Transformation* of a *molecular entity* A to give a molecular entity A_2.

31   *Examples*:

32        $2\ CH_3\cdot \rightarrow CH_3CH_3$

33        $2\ CH_3COCH_3 \rightarrow (CH_3)_2C(OH)CH_2COCH_3$

34        $2\ RCOOH \rightarrow (RCOOH)_2$

35   See also *association*.

36   [3]

37

38   Dimroth-Reichardt E_T parameter

1   Quantitative measure of solvent polarity, based on the wavelength, λ_{max}, of the longest-
2   wavelength intramolecular charge-transfer absorption band of the _solvatochromic_
3   betaine dye 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-ium-1-yl)phenolate.
4

5
6   See [17,153,154,155].
7   See _solvent parameter_.
8   rev[3]
9

10 **dipolar aprotic solvent**
11   See _dipolar non-HBD solvent_.
12   rev[3]
13

14 **dipolar non-HBD solvent (**Non-hydrogen-bond donating solvent)
15 Solvent with a comparatively high relative _permittivity_ ("dielectric constant"), greater
16 than ca. 15, and composed of molecules that have a sizable permanent dipole moment
17 and that, although it may contain hydrogen atoms, cannot donate suitably labile
18 hydrogen atoms to form strong solvent-solute hydrogen bonds.
19   _Examples_: dimethyl sulfoxide, acetonitrile, acetone, as contrasted with methanol and
20 _N_-methylformamide.
21   _Note 1_: The term "dipolar" refers to solvents whose molecules have a permanent
22 dipole moment, in contrast to solvents whose molecules have no permanent dipole
23 moment and should be termed "apolar" or "nonpolar".
24   _Note 2_: Non-HBD solvents are often called aprotic, but this term is misleading
25 because a proton can be removed by a sufficiently strong base. The aprotic nature of
26 a solvent molecule means that its hydrogens are in only covalent C–H bonds and not
27 in polar O–H$^{\delta+}$ or N–H$^{\delta+}$ bonds that can serve as hydrogen-bond donors. Use of
28 "aprotic" is therefore discouraged, unless the context makes the term unambiguous.
29   _Note 3_: It is recommended to classify solvents according to their capability to donate
30 or not donate, as well as to accept or not accept, hydrogen bonds to or from the solute,
31 as follows:
32   Hydrogen-bond donating solvents (short: HBD solvents), formerly protic solvents
33   Non-hydrogen-bond donating solvents (short: non-HBD solvents), formerly aprotic
34   solvents
35   Hydrogen-bond accepting solvents (short: HBA solvents)

1   Non-hydrogen-bond accepting solvents (short: non-HBA solvents)
2   See [156,157].

3

dipole-dipole excitation transfer
5   *Förster resonance-energy transfer (FRET)*
6   See [9].

7

dipole-dipole interaction
9   Intermolecular or intramolecular interaction between molecules or groups having a
10   permanent electric dipole moment. The strength of the interaction depends on the
11   distance and relative orientation of the dipoles.
12   *Note*: A dipole/dipole interaction is a simplification of the electrostatic interactions
13   between molecules that originate from asymmetries in the electron densities. Such
14   interactions can be described more correctly by the use of higher-order multipole
15   moments.
16   See also *van der Waals forces*.
17   rev[3]

18

dipole-induced dipole forces
20   See *van der Waals forces*.
21   [3]

22

diradical
24   biradical
25   Even-electron *molecular entity* with two (possibly delocalized) radical centres that act
26   nearly independently of each other, e.g.,

27

28   *Note 1*: Species in which the two radical centres interact significantly are often
29   referred to as "diradicaloids". If the two radical centres are located on the same atom,
30   the species is more properly referred to by its generic name: carbene, nitrene, etc.
31   *Note 2*: The lowest-energy triplet state of a diradical lies below or at most only a little
32   above its lowest singlet state (usually judged relative to k_BT, the product of the
33   Boltzmann constant k_B and the absolute temperature T). If the two radical centres
34   interact significantly, the singlet state may be more stable. The states of those diradicals
35   whose radical centres interact particularly weakly are most easily understood in terms
36   of a pair of local doublets.

1   *Note 3*: Theoretical descriptions of low-energy states of diradicals display two
2   unsaturated valences: the dominant valence-bond structures have two dots, the low-
3   energy molecular orbital *configuration*s have only two electrons in two approximately
4   nonbonding molecular orbitals, and two of the natural orbitals have occupancies close
5   to one.
6   See [9,158,159,160,161,162,163].
7   See also *carbene*, *nitrene*.
8   [3]
9

10   **dispersion forces**
11   See *London forces, van der Waals forces*.
12   [3]
13

14   **disproportionation**
15   Any *chemical reaction* of the type A + A $\leftrightharpoons$ A' + A", where A, A' and A" are different
16   chemical species.
17   *Examples*:
18   2 $R_2COH\cdot$ (ketyl radical) → $R_2C{=}O$ + R_2CHOH
19   Cannizzaro reaction: 2 ArCH=O → $ArCH_2OH$ + ArCOOH
20

21   *Note 1*: The reverse of disproportionation is called *comproportionation*.
22   *Note 2*: A special case of disproportionation (or "dismutation") is "radical
23   disproportionation", exemplified by
24

25           $\cdot CH_2CH_3$ + $\cdot CH_2CH_3$ → $CH_2{=}CH_2$ + CH_3CH_3
26

27   *Note 3*: A somewhat more restricted usage of the term prevails in inorganic
28   chemistry, where A, A' and A" are of different oxidation states.
29   [3]
30

31   **disrotatory**
32   Stereochemical feature of an *electrocyclic reaction* in which the substituents at the
33   interacting termini of the conjugated system rotate in opposite senses (one clockwise
34   and the other counterclockwise).
35   See also *conrotatory*.
36   rev[3]
37

38   **dissociation**
39   Separation of a *molecular entity* into two or more molecular entities (or any similar
40   separation within a polyatomic molecular entity).

Example:

NH$_4^+$$_{(aq)}$ → H$_3$O$^+$ + NH$_3$ or CH$_3$COOH$_{(aq)}$ → H$_3$O$^+$ + CH$_3$CO$_2^-$

Note 1: Although the separation of the constituents of an *ion pair* into free ions is a dissociation, the *ionization* that produces the ion pair is not a dissociation, because the ion pair is a single *molecular entity*.

Note 2: The reverse of dissociation is *association*.

rev[3]

distonic ion

Radical ion in which charge and radical sites are separated.

Example: •CH$_2$CH$_2$OCH$_2^+$

See [164,165].

rev[3]

distortion interaction model (Activation Strain Model)

Method for analyzing activation energy as the sum of the energies to distort the reactants into the geometries they have in transition states plus the energy of interaction between the two distorted reactants.

See [166].

distribution ratio

partition ratio

Ratio of concentrations of a solute in a mixture of two immiscible phases at equilibrium.

See also *Hansch constant*.

See [167].

di-π-methane rearrangement

Photochemical reaction of a molecular entity with two π-systems separated by a saturated carbon, to form an ene-substituted cyclopropane.

Pattern:

See [9,168].

donicity (also called donor number, DN, which is a misnomer)

Quantitative experimental measure of the Lewis basicity of a molecule B, expressed as the negative enthalpy of the formation of the 1:1 complex B·SbCl$_5$.

Note: donicity is often used as a measure of a solvent's basicity.

1   See also *acceptor parameter*, *Lewis basicity*.
2   See [63,169,170].
3

downfield
4
5   superseded but still widely used in NMR to mean deshielded.
6   See *chemical shift*, *shielding*.
7   rev[3]
8

driving force
9
10 (1) Negative of the Gibbs energy change ($\Delta_r G^0$) on going from the reactants to the
11 products of a *chemical reaction* under standard conditions. Also called affinity.
12 (2) Qualitative term that relates the favorable thermodynamics of a reaction to a specific
13 feature of molecular structure, such as the conversion of weaker bonds into stronger
14 (CH_3–H + Br–Br → CH_3–Br + H–Br), neutralization of an acid (Claisen *condensation* of
15 2 CH_3COOEt + EtO^- to CH_3COCH^-COOEt + EtOH), or increase of entropy
16 (*cycloelimination* of cyclohexene to butadiene + ethylene).
17 *Note 1*: This term is a misnomer, because favorable thermodynamics is due to
18 energy, not force.
19 *Note 2*: This term has also been used in connection with photoinduced electron
20 transfer reactions, to indicate the negative of the estimated standard Gibbs energy
21 change for the outer sphere electron transfer ($\Delta_{ET} G^0$) [9].
22 rev[3]
23

dual substituent-parameter equation
24
25 Any equation that expresses substituent effects in terms of two parameters.
26 *Note*: In practice the term is used specifically for an equation for modeling the effects
27 of *meta*- and *para*-substituents X on chemical reactivity, spectroscopic properties, etc.
28 of a probe site in benzene or other aromatic system.
29 $P_X = \rho_I \sigma_I + \rho_R \sigma_R$
30 where P_X is the magnitude of the property for substituent X, expressed relative to the
31 property for X = H; σ_I and σ_R are inductive (or polar) and resonance substituent
32 constants, respectively, there being various scales for σ_R; ρ_I and ρ_R are the
33 corresponding regression coefficients.
34 See [171,172,173].
35 See also *extended Hammett equation*, *Yukawa-Tsuno equation*.
36 [3]
37

dynamic NMR
38
39 NMR spectroscopy of samples undergoing chemical reactions.

1   *Note*: Customarily this does not apply to samples where the composition of the
2 sample, and thus its NMR spectrum, changes with time, but rather to samples at
3 equilibrium, without any net reaction. The occurrence of chemical reactions is
4 manifested by features of the NMR line-shape or by *magnetization transfer*.
5   See *chemical flux*.
6

dyotropic rearrangement
8 Process in which two σ bonds simultaneously migrate intramolecularly.
9   *Example*

10
11   See [174,175,176].
12   rev[3]
13

educt
15 deprecated: usage strongly discouraged
16 starting material, reactant
17   *Note*: This term should be avoided and replaced by reactant, because it means
18 "something that comes out", not "something that goes in".
19   rev[3]
20

effective charge, Z_{eff}
22 Net positive charge experienced by an electron in a polyelectronic atom, which is less
23 than the full nuclear charge because of *shielding* by the other electrons.
24   rev[3]
25

effective molarity (effective concentration)
27 Ratio of the first-order rate constant or equilibrium constant of an *intramolecular*
28 reaction involving two functional groups within the same *molecular entity* to the second-
29 order *rate constant* or equilibrium constant of an analogous *intermolecular* elementary
30 reaction.
31   *Note*: This ratio has unit of concentration, $mol\ dm^{-3}$ or $mol\ L^{-1}$, sometimes denoted
32 by M.
33   See [177].
34   See also *intramolecular catalysis*.
35   [3]
36
37

1 **eighteen-electron rule**
2 Electron-counting rule that the number of nonbonding electrons at a metal plus the
3 number of electrons in the metal-*ligand* bonds should be 18.
4   *Note*: The 18-electron rule in transition-metal chemistry is an analogue of the Lewis
5 *octet rule*.
6   [3]
7

8 **electrocyclic reaction (electrocyclization)**
9 *Molecular rearrangement* that involves the formation of a σ bond between the termini
10 of a fully *conjugated* linear π-electron system (or a linear fragment of a π-electron
11 system) and a decrease by one in the number of π bonds, or the reverse of that process.
12   *Examples*:

13

14   *Note*: The stereochemistry of such a process is termed "*conrotatory*" if the
15 substituents at the interacting termini of the conjugated system both rotate in the same
16 sense, as in

17

18 or "*disrotatory*" if one terminus rotates in a clockwise and the other in a
19 counterclockwise sense, as in

20

21   See also *pericyclic reaction*.
22   [3]
23

24 **electrofuge**
25 *Leaving group* that does not carry away the bonding electron pair.

1   *Examples*: In the nitration of benzene by NO_2^+, H^+ is the electrofuge, and in an S_N1

2   reaction the carbocation is the electrofuge.

3   *Note 1*: Electrofugality characterizes the relative rates of atoms or groups to depart

4   without the bonding electron pair. Electrofugality depends on the nature of the reference

5   reaction and is not the reverse of *electrophilicity* [178].

6   *Note 2*: For electrofuges in S_N1 reactions see [179].

7   See also *electrophile*, *nucleofuge*.

8   rev[3]

9

10   **electromeric effect**

11   obsolete

12   rev[3]

13

14   **electron acceptor**

15   *Molecular entity* to which an electron may be transferred.

16   *Examples*: 1,4-dinitrobenzene,1,1'-dimethyl-4,4'-bipyridinium dication,

17   benzophenone.

18   *Note 1*: A group that accepts electron density from another group is not called an

19   electron acceptor but an electron-withdrawing group.

20   Note *2*: A *Lewis acid* is not called an electron acceptor but an *electron-pair acceptor*.

21   rev[3]

22

23   **electron affinity**

24   Energy released when an additional electron (without excess energy) attaches itself to

25   a *molecular entity* (often electrically neutral but not necessarily).

26   *Note 1*: Equivalent to the minimum energy required to detach an electron from a

27   singly charged negative ion.

28   *Note 2*: Measurement of electron affinities is possible only in the gas phase, but there

29   are indirect methods for evaluating them from solution data, such as polarographic half-

30   wave potentials or charge-transfer spectra.

31   See [8,180,181].

32   rev[3]

33

34   **electron capture**

35   Transfer of an electron to a *molecular entity*, resulting in a molecular entity of

36   (algebraically) increased negative charge.

37

38   **electron-deficient bond**

39   Bond between adjacent atoms that is formed by fewer than two electrons.

1   *Example*:

2

3   *Note*: The B–H–B bonds are also called "two-electron three-centre bonds".

4   [3]

5

6   **electron density**

7   The electron density at a point with coordinates x,y,z in an atom or <u>*molecular entity*</u> is

8   the product of the probability $P(x,y,z)$ (units: m^{-3}) of finding an electron at that point with

9   the volume element $dx\,dy\,dz$ (units: m^3).

10   *Note*: For many purposes (e.g., X-ray scattering, forces on atoms) the system

11   behaves as if the electrons were spread out into a continuous distribution, which is a

12   manifestation of the wave-particle duality.

13   See also <u>*atomic charge*</u>, <u>*charge density*</u>.

14   rev[3]

15

16   **electron donor**

17   <u>*Molecular entity*</u> that can transfer an electron to another molecular entity, or to the

18   corresponding <u>*chemical species*</u>.

19   *Note 1*: After the electron transfer the two entities may separate or remain

20   associated.

21   *Note 2*: A group that donates electron density to another group is an electron-

22   donating group, regardless of whether the donation is of σ or π electrons.

23   *Note 3*: A <u>*Lewis base*</u> is not called an electron donor, but an <u>*electron-pair donor*</u>.

24   See also <u>*electron acceptor*</u>.

25   rev[3]

26

27   **electron-donor-acceptor complex**

28   obsolete

29   <u>*charge-transfer complex*</u>.

30   See also <u>*adduct*</u>, <u>*coordination*</u>.

31

32   **electron-pair acceptor**

33   <u>*Lewis acid*</u>.

34   [3]

35

36

37

electron-pair donor

Lewis base.

[3]

electron pushing

Method using *curly arrows* for showing the formal movement of an electron pair (from a lone pair or a σ or π bond) or of an unpaired electron, in order to generate additional *resonance form*s or to denote a *chemical reaction*.

Note 1: The electron movement may be *intramolecular* or *intermolecular*.

Note 2: When a single electron is transferred, a single-headed curly arrow or "fishhook" is used, but the electron movement in the opposite direction is redundant and sometimes omitted.

Examples:

electron transfer

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)*, *Marcus equation*, *outer sphere (electron transfer)*.

[3]

electron-transfer catalysis

Process describing a sequence of reactions such as shown in equations (1)-(3), leading from A to B, via species $A^{\cdot-}$ and $B^{\cdot-}$ that have an extra electron:

$$A + e^- \rightarrow A^{\cdot-} \tag{1}$$
$$A^{\cdot-} \rightarrow B^{\cdot-} \tag{2}$$
$$B^{\cdot-} + A \rightarrow B + A^{\cdot-} \tag{3}$$

Note 1: An analogous sequence involving radical cations ($A^{\cdot+}$, $B^{\cdot+}$) also occurs.

Note 2: The most notable example of electron-transfer catalysis is the $S_{RN}1$ (or $T+D_N+A_N$) reaction of haloarenes with nucleophiles.

Note 3: The term has its origin in an 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 mechanism described by equations (1)-(3).

1   See [182,183].

2   [3]

3

4 **electronation**

5 obsolete

6   See *reduction.*

7   rev[3]

8

9 **electronegativity**

10 Measure of the power of an atom to attract electrons to itself.

11   *Note 1*: The concept has been quantified by a number of authors. The first, due to

12 Pauling, is based on *bond-dissociation energies*, E_d (units: eV), and is anchored by

13 assigning the electronegativity of hydrogen as $\chi_{r,H}$ = 2.1. For atoms A and B

14

15 $$\chi_{r,A} - \chi_{r,B} = \sqrt{\{E_d(A–B)/eV - \tfrac{1}{2}\,[E_d(A–A) + E_d(B–B)]/eV\}}$$

16

17 where χ_r denotes the Pauling relative electronegativity; it is relative in the senses that

18 the values are of dimension 1 and that only electronegativity differences are defined on

19 this empirical scale. See [12] section 2.5.

20   *Note 2*: Alternatively, the electronegativity of an element, according to the Mulliken

21 scale, is the average of its atomic *ionization* energy and electron affinity. Other scales

22 have been developed by Allred and Rochow, by Sanderson, and by Allen.

23   *Note 3*: Absolute electronegativity is property derived from density functional theory

24 [8].

25   See [75,184,185,186,187,188,189,190].

26   rev[3]

27

28 **electronic effects (of substituents)**

29 Changes exerted by a substituent on a molecular property or molecular reactivity, often

30 distinguished as *inductive* (through-bond polarization), through-space electrostatics

31 (*field effect*), or *resonance*, but excluding *steric*.

32   *Note 1*: The obsolete terms mesomeric and electromeric are discouraged.

33   *Note 2*: Quantitative scales of substituent effects are available.

34   See [126,173,191].

35   See also *polar effect*.

36   rev[3]

37

38 **electrophile (n.), electrophilic (adj.)**

39 Reagent that forms a *bond* to its reaction partner (the *nucleophile*) by accepting both

40 bonding electrons from that partner.

Note 1: Electrophilic reagents are *Lewis acid*s.

Note 2: "Electrophilic catalysis" is catalysis by Lewis acids.

Note 3: The term "electrophilic" is also used to designate the apparent polar character of certain *radical*s, as inferred from their higher relative reactivities with reaction sites of higher electron density.

See also *electrophilicity*.

[3]

electrophilic substitution

Heterolytic reaction in which the entering group adds to a nucleophile and in which the leaving group, or *electrofuge*, relinquishes both electrons to its reaction partner, whereupon it becomes another potential electrophile.

Example (azo coupling)*:*

RN_2^+ (electrophile) + $H_2NC_6H_5$ (nucleophile) → p-$H_2NC_6H_4N$=NR + H^+ (electrofuge)

Note: It is arbitrary to emphasize the electrophile and ignore the feature that this is also a nucleophilic substitution, but the distinction depends on the electrophilic nature of the reactant that is considered to react with the *substrate*.

See also *substitution*.

electrophilicity

Relative reactivity of an electrophile toward a common *nucleophile*.

Note: The concept is related to *Lewis acid*ity. However, whereas Lewis acidity is measured by relative equilibrium constants toward a common Lewis base, electrophilicity is measured by relative *rate constant*s for reactions of different electrophilic reagents towards a common nucleophilic *substrate*.

See [192,193,194].

See also *nucleophilicity*.

rev[3]

element effect

Ratio of the *rate constant*s of two reactions that differ only in the identity of the element in the *leaving group*.

Example: k_{Br}/k_{Cl} for the reaction of N_3^- (azide) with CH_3Br or CH_3Cl.

rev[3]

elementary reaction

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 only one *transition state* or none.

1   See [13].

2   See also *composite reaction*, *stepwise reaction*.

3   rev[3]

4

5 **elimination**

6 Reverse of an *addition reaction*.

7   *Note 1*: In an elimination two groups (called eliminands) are lost, most often from two

8 different centres (1,2-elimination (*β-elimination*) or 1,3-elimination, etc.) with

9 concomitant formation of an unsaturation (double bond, triple bond) in the molecule, or

10 formation of a ring.

11   *Note 2*: If the groups are lost from a single carbon or nitrogen centre (1,1-elimination,

12 *α-elimination*), the resulting product is a *carbene* or *nitrene*, respectively.

13   rev[3]

14

15 **empirical formula**

16 List of the elements in a *chemical species*, with integer subscripts indicating the simplest

17 possible ratios of all elements.

18   *Note 1:* In organic chemistry C and H are listed first, then the other elements in

19 alphabetical order.

20   *Note 2:* This differs from the *molecular formula*, in which the subscripts indicate how

21 many of each element is included and which is an integer multiple of the empirical

22 formula. For example, the empirical formula of glucose is CH_2O while its molecular

23 formula is $C_6H_{12}O_6$.

24   *Note 3:* The empirical formula is the information provided by combustion analysis,

25 which has been largely superseded by mass spectrometry, which provides the

26 *molecular formula*.

27

28 **enantiomer**

29 One of a pair of stereoisomeric *molecular entities* that are non-superimposable mirror

30 images of each other.

31   See [11].

32   [3]

33

34 **enantiomeric excess**

35 Absolute value of the difference between the mole fractions of two enantiomers:

36

37      $\Delta x(\text{e.e.}) = |x_+ - x_-|$

38

39 where $x_+ + x_- = 1$.

Note: Enantiomeric excess can be evaluated experimentally from the observed specific optical rotatory power $[\alpha]_{obs}$, relative to $[\alpha]_{max}$, the (maximum) specific optical rotatory power of a pure enantiomer:

$$\Delta x(\text{e.e.}) = |\ [\alpha]_{obs}/[\alpha]_{max}\ |$$

and also by chiral chromatography, NMR, and MS methods.
    See [11].
    rev[3]

enantiomeric ratio
mole fraction of one *enantiomer* in a mixture divided by the mole fraction of the other.

$$r(\text{e.r.}) = x_+/x_-\ \text{or}\ \ x_-/x_+$$

where $x_+ + x_- = 1$
    See [11].
    rev[3]

enantioselectivity
    See *stereoselectivity*.
    [3]

encounter complex
Complex of *molecular entities* produced at an *encounter-controlled rate*, and which occurs as an intermediate in a reaction.
    Note 1: 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 for mechanisms involving *pre-association*.
    Note 2: The separation between the entities is small compared to the diameter of a solvent molecule.
    See also [9].
    rev[3]

encounter-controlled rate
Rate of reaction corresponding to the rate at which the reacting *molecular entities* encounter each other. This is also known as the "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 reacting molecular entities).

1
2

3
4
1   *Note*: At 25 °C in most solvents, including water, a *bimolecular* reaction that proceeds
5
6
2   at an encounter-controlled rate has a second-order *rate constant* of 10^9 to 10^{10} dm^3
7
3   mol^{-1} s^{-1}.
8
9
4   See also *microscopic diffusion control*.
10
5   [3]
11
6

12
13
7   ene reaction
14
8   Addition of a compound with a double bond and an allylic hydrogen (the "ene") to a
15
9   compound with a multiple bond (the "enophile") with transfer of the allylic hydrogen and
16
17
10   a concomitant reorganization of the bonding.
18
11   *Example*, with propene as the ene and ethene as the enophile.
19
20

21
22
23
24
25
26
12
27
13   *Note*: The reverse is a "retro-ene" reaction.
28
14   [3]
29
15

30
31
16   energy of activation
32
17   E_a or E_A
33
34
18   *Arrhenius energy of activation*
35
19   activation energy
36
20   (SI unit: kJ mol^{-1})
37
38
21   Operationally defined quantity expressing the dependence of a *rate constant* on
39
22   temperature according to
40
23

41
42
43
24
$$E_a(T) = -R\,\frac{\mathrm{d}\ln\{\frac{k(T)}{[k]}\}}{\mathrm{d}\left(\frac{1}{T}\right)}$$
44
45
46
25

47
26   as derived from the *Arrhenius equation*, $k(T) = A\,\exp(-E_A/RT)$, where A is the pre-
48
27   exponential factor and R the gas constant. As the argument of the ln function, k should
49
50
28   be divided by its units, i.e., by [k].
51
29   *Note 1:* According to collision theory, the pre-exponential factor A is the frequency of
52
30   collisions with the correct orientation for reaction and E_a (or E_0) is the threshold energy
53
54
31   that collisions must have for the reaction to occur.

55
56
57
58
59
60

1   *Note 2*: The term Arrhenius activation energy is to be used only for the empirical
2 quantity as defined above. There are other empirical equations with different activation
3 energies, see [12].
4   See [13].
5   See also *enthalpy of activation*.
6   rev[3]
7

8 **energy profile**
9   See *Gibbs energy diagram*, *potential-energy profile*.
10   [3]
11

12 **enforced concerted mechanism**
13 Situation where a putative intermediate possesses a lifetime shorter than a bond
14 vibration, so that the steps become concerted.
15   See [195,196,197].
16   rev[3]
17

18 **enthalpy of activation (standard enthalpy of activation)**
19 $\Delta^{\ddagger}H^{\circ}$
20 (SI unit: kJ mol^{-1})
21 Standard enthalpy difference between the *transition state* and the ground state of the
22 reactants at the same temperature and pressure. It is related experimentally to the
23 temperature dependence of the *rate coefficient k* according to equation (1) for first-order
24 *rate constant*s:
25

26
$$\Delta^{\ddagger}H^{\circ} = -R \left\{ \frac{\partial \ln\left(\frac{k/\mathrm{s}^{-1}}{T/\mathrm{K}}\right)}{\partial\left(\frac{1}{T}\right)} \right\}_{P} \tag{1}$$

27

28 and to equation (2) for second order rate coefficients
29

30
$$\Delta^{\ddagger}H^{\circ} = -R \left\{ \frac{\partial \ln\left(\frac{k/\left(\mathrm{mol\ dm^3\ s^{-1}}\right)}{T/\mathrm{K}}\right)}{\partial\left(\frac{1}{T}\right)} \right\}_{P} \tag{2}$$

31

1   This quantity can be obtained, along with the *entropy of activation* $\Delta^{\ddagger}S^{o}$, from the slope

2   and intercept of the linear least-squares fit of rate coefficients k to the equation

3

4

$$\ln\left(\frac{k/_{s^{-1}}}{T/K}\right) = \Delta^{\ddagger}S^{o}/R - \Delta^{\ddagger}H^{o}/RT + \ln[\,(k_{B}/J\ K^{-1})/(h/J\ s)\,]$$

5   for a first-order rate coefficient

6   and

7

$$\ln\left(\frac{k/(mol\ dm^{3}\ s^{-1})}{T/K}\right) = \Delta^{\ddagger}S^{o}/R - \Delta^{\ddagger}H^{o}/R\ (1/T) + \ln[\,(k_{B}/J\ K^{-1})/(h/J\ s)\,]$$

8

9   for a second-order rate coefficient where k_{B} is Boltzmann constant, h is Planck constant,

10   and $k_{B}/h = 2.08366\ldots \times 10^{10}\ K^{-1}\ s^{-1}$.

11   *Note 1*: An advantage of the least-squares fit is that it can also give error estimates

12   for $\Delta^{\ddagger}H^{o}$ and $\Delta^{\ddagger}S^{o}$.

13   *Note 2*: It is also given by

14

15     $\Delta^{\ddagger}H^{o} = RT^{2}(\partial \ln k/[k]/\partial T)_{P} - RT = E_{a} - RT$

16

17     $\Delta^{\ddagger}H^{o} = RT^{2}(\partial \ln\{k\}/\partial T)_{P} - RT$

18

19   where E_{a} is the *energy of activation*, provided that the *rate coefficient*s for reactions

20   other than first-order are expressed in temperature-independent concentration units

21   (e.g., mol kg^{-1}, measured at a fixed temperature and pressure*)*. The argument in a

22   logarithmic function should be of dimension 1. Thus k is divided by its units, i.e., by $[k]$,

23   as in the alternative form, in terms of reduced variables.

24   See also *entropy of activation*, *Gibbs energy of activation*.

25   See [12,13].

26   rev[3]

27

28   **entropy of activation**, **(standard entropy of activation)**

29   $\Delta^{\ddagger}S^{o}$

30   (SI unit: J mol^{-1} K^{-1})

31   Standard entropy difference between the *transition state* and the *ground state* of the

32   reactants, at the same temperature and pressure. It is related to the *Gibbs energy of*

33   *activation* and *enthalpy of activation* by the equations

34

35     $\Delta^{\ddagger}S^{o} = (\Delta^{\ddagger}H^{o} - \Delta^{\ddagger}G^{o})/T$

36

provided that *rate coefficient*s for reactions other than first-order reactions are expressed in temperature-independent concentration units (e.g., mol dm^{-3}, measured at fixed temperature and pressure). The numerical value of S depends on the standard state (and therefore on the concentration units selected).

Note 1: It can also be obtained from the intercept of the linear least-squares fit of rate coefficients k to the equation

$$\ln(k/[k]/T[T]) = \Delta^{\ddagger}S^{\circ}/R - \Delta^{\ddagger}H^{\circ}/R \,(1/T) + \ln(k_B/h),$$

$$\ln(\{k\}/\{T\}) = \Delta^{\ddagger}S^{\circ}/R - \Delta^{\ddagger}H^{\circ}/R \,(1/T) + \ln(k_B/h),$$

where $k_B/h = 2.08366\ldots \times 10^{10}$ K^{-1} s^{-1}. k should be divided by its units, i.e., by $[k] = $ s^{-1} for first-order, and by $[k] = $ (s^{-1} mol^{-1} dm^3) for second-order rate coefficients and T should be divided by its units $[T] = $ K, as in the second equation, in terms of reduced variables..

Note 2: The information represented by the entropy of activation may alternatively be conveyed by the pre-exponential factor A, which reflects the fraction of collisions with the correct orientation for reaction (see *energy of activation*).

See [12,13].

rev[3]

epimer

Diastereoisomer that has the opposite *configuration* at only one of two or more tetrahedral *stereogenic centre*s in the respective *molecular entity*.

See [11].

[3]

epimerization

Interconversion of *epimer*s by reversal of the configuration at one of the *stereogenic centre*s.

See [11].

[3]

equilibrium, chemical

Situation in which reversible processes (processes that may be made to proceed in either the forward or reverse direction by the infinitesimal change of one variable) have reached a point where the rates in both directions are identical, so that the amount of each species no longer changes.

Note 1: In this situation the Gibbs energy, G, is a minimum. Also, the sum of the chemical potentials of the reactants equals that of the products, so that

$$\Delta_r G^{\circ} = -RT \ln K$$

1 where the thermodynamic equilibrium constant, K (of dimension 1), is the product of
2 product activities divided by the product of reactant activities.
3 *Note 2*: In dilute solutions the numerical values of the thermodynamic activities may
4 be approximated by the respective concentrations.
5 rev[3]
6

equilibrium control
8 See *thermodynamic control*.
9 [3]
10

E_T-value
12 See *Dimroth-Reichardt E_T parameter, Z-value*.
13 [3]
14

excess acidity
16 See *Bunnett-Olsen equations, Cox-Yates equation*.
17 [3]
18

excimer ("excited dimer")
20 *Complex* formed by the interaction of an *excited* molecular entity with another identical
21 molecular entity in its ground state.
22 *Note*: The complex is not stable in the ground state.
23 See [9].
24 See also *exciplex*.
25 [3]
26

exciplex
28 Electronically excited *complex* of definite stoichiometry that is non-bonding in the
29 ground state.
30 *Note*: An exciplex is a complex formed by the noncovalent interaction of an excited
31 *molecular entity* with the ground state of a different molecular entity, but an *excimer*,
32 formed from two identical components, is often also considered to be an exciplex.
33 See [9].
34 See also *excimer*.
35 [3]
36

excited state
38 Condition of a system with energy higher than that of the ground state. This term is
39 most commonly used to characterize a *molecular entity* in one of its electronically

excited states, but may also refer to vibrational and/or rotational excitation in the electronic ground state.

See [9].

[3]

EXSY (NMR exchange spectroscopy)

Two-dimensional NMR technique producing cross peaks corresponding to site-to site chemical exchange. The cross-peak amplitudes carry information about exchange rates.

See [198].

extended Hammett equation

Multiparameter extension of the *Hammett equation* for the description of substituent effects.

Note 1: The major extensions using two parameters (*dual substituent-parameter equation*s) were devised for the separation of inductive and steric effects (*Taft equation*) or of inductive (or field) and resonance effects.

Note 2: Other parameters may be added (polarizability, hydrophobicity…) when additional substituent effects are operative.

See [191].

See also *Yukawa-Tsuno equation*.

[3]

external return (external ion-pair recombination)

Recombination of free ions formed in an S_N1 reaction (as distinguished from ion-pair collapse).

See *ion-pair recombination*.

rev[3]

extrusion

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, i.e.,

X–Y–Z → X–Z + Y

Example

1

2   *Note 1*: When Y is a metal, this process is called a reductive elimination.

3   *Note 2*: The reverse of an extrusion is called an *insertion*.

4   See also *cheletropic reaction*.

5   [3]

6

7   **field effect**

8   Experimentally observable substituent effect (on reaction rates, etc.) of *intramolecular*

9   electrostatic interaction between the centre of interest and a monopole or dipole, by

10   direct electric-field action through space rather than through bonds.

11   *Note 1*: The magnitude of the field effect depends on the monopole charge or dipole

12   moment, on the orientation of the dipole, on the distance between the centre of interest

13   and the monopole or dipole, and on the effective dielectric constant that reflects how

14   the intervening bonds are polarized.

15   *Note 2*: Although a theoretical distinction may be made between the field effect and

16   the *inductive effect* as models for the Coulomb interaction between a given site and a

17   remote monopole or dipole within the same entity, the experimental distinction between

18   the two effects has proved difficult, because the field effect and the inductive effect are

19   ordinarily influenced in the same direction by structural changes.

20   *Note 3:* The substituent acts through the electric field that it generates, and it is an

21   oversimplification to reduce that interaction to that of a monopole or dipole.

22   See also *electronic effect, inductive effect, polar effect*.

23   See [172,191,199,200].

24   rev[3]

25

26   **flash photolysis**

27   *Spectroscopic* or kinetic technique in which an *ultraviolet*, *visible*, or *infrared* radiation

28   pulse is used to produce transient species.

29   *Note 1*: Commonly, an intense pulse of short duration is used to produce a sufficient

30   concentration of transient species, suitable for spectroscopic observation. The most

31   common observation is of the absorption of the transient species (transient absorption

32   spectroscopy).

33   *Note 2*: If only photophysical processes are involved, a more appropriate term would

34   be "pulsed photoactivation". The term "flash photolysis" would be correct only if

35   chemical bonds are broken (the Greek "lysis" means dissolution or decomposition and

36   in general lysis is used to indicate breaking). However, historically, the name has been

37   used to describe the technique of pulsed excitation, independently of the process that

38   follows the excitation.

39   See [9].

40

1 **flash vacuum pyrolysis (FVP)**

2 Thermal reaction of a molecule by exposure to a short thermal shock at high
3 temperature, usually in the gas phase.

4 *Example:*

5 See [201,202,203,204].
6 rev[3]

7

8 **fluxionality**

9 Property of a *chemical species* that undergoes rapid *degenerate rearrangement*s
10 (generally detectable by methods that allow the observation of the behaviour of
11 individual nuclei in a rearranged chemical species, e.g., NMR, X-ray).

12 *Example*: tricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (bullvalene), which has 1 209 600 (=
13 10!/3) interconvertible arrangements of the ten CH groups.

14

15

16 *Note 1*: Fluxionality differs from *resonance*, where no rearrangement of nuclear
17 positions occurs.

18 *Note 2*: The term is also used to designate positional change among *ligand*s of
19 complex compounds and organometallics. In these cases the change is not necessarily
20 degenerate.

21 See also *valence tautomerization*.
22 rev[3]

23

24 **force-field calculations**

25 See *molecular mechanics calculation*.
26 GB

27

28 **formal charge**

29 Quantity (omitted if zero) attached to each atom in a *Lewis structure* according to

30

31 $Z_{formal} = N_{valence} - N_{lonepairs} - \frac{1}{2} N_{bonds}$

32

1   *Examples*: $CH_2=N^+=N^-$, H_3O^+, $(CH_3)_2C=N\text{-}O^-$

2

3   *Note:* This formalism assumes that electrons in bonds are shared equally, regardless
4   of *electronegativity*.

5

Förster resonance-energy transfer (FRET)
7   dipole-dipole excitation transfer
8   Nonradiative mechanism for transfer of electronic excitation energy from one molecular
9   entity to another, distant one. It arises from the interaction between the *transition dipole*
10   *moment*s of the two entities.
11   See [9].

12

fractionation factor, isotopic
14   Ratio $[x_1(A)/x_2(A)]/[x_1(B)/x_2(B)]$, where x is the mole fraction of the isotope designated
15   by the subscript, when the two isotopes are equilibrated between two different *chemical*
16   *species* A and B (or between specific sites A and B in the same chemical species).
17   *Note 1*: The term is most commonly met in connection with deuterium solvent *isotope*
18   *effect*s, where the fractionation factor, symbolized by ϕ, expresses the ratio
19        $\phi = [x_D(\text{solute})/x_H(\text{solute})]/[x_D(\text{solvent})/x_H(\text{solvent})]$
20   for the exchangeable hydrogen atoms in the chemical species (or sites) concerned.
21   *Note 2*: The concept is also applicable to *transition states*.
22   See [2].
23   [3]

24

fragmentation
26   (1) *Heterolytic* or *homolytic* cleavage of a molecule into more than two fragments,
27   according to the general reaction (where a, b, c, d, and X are atoms or groups of atoms)

28

29        $a–b–c–d–X \rightarrow (a–b)^+ + c=d + X^-$
30   or $a–b–c–d–X \rightarrow (a–b)\cdot + c=d + X$
31   *Examples*:
32        $Ph_3C–COOH + H^+ \rightarrow Ph_3C^+ + C=O + H_2O$
33        $CH_3N=NCH_3 \rightarrow CH_3\cdot + N_2 + CH_3$
34   See [205].

35

36   (2) Breakdown of a radical or radical ion into a closed-shell molecule or ion and a
37   smaller radical
38   *Examples*:
39        $(CH_3)_3C–O\cdot \rightarrow (CH_3)_2C=O + H_3C\cdot$
40        $[ArBr]\cdot^- \rightarrow Ar\cdot + Br^-$ (solution)

1 $[(CH_3)_3C\text{–}OH]^{\cdot+} \rightarrow (CH_3)_2C=OH^+ + H_3C\cdot$ (gas-phase, following *ionization*)

2 [3]

3

4 **Franck-Condon Principle**

5 Approximation that an electronic transition is most likely to occur without change in

6 nuclear positions.

7 *Note 1*: The resulting state is called a Franck–Condon state, and the transition

8 involved is called a vertical transition.

9 *Note 2*: As a consequence, the intensity of a vibronic transition is proportional to the

10 square of the overlap integral between the vibrational wavefunctions of the two states

11 that are involved in the transition.

12 See [9].

13

14 **free energy**

15 The thermodynamic function Gibbs energy (symbol *G*) or Helmholtz energy (symbol *A*)

16 specifically defined as

17

18 $$G = G(P,T) = H - TS$$

19 and $$A = A(V,T) = U - TS$$

20

21 where *H* is enthalpy, *U* is internal energy, and *S* is entropy. The possibility of

22 spontaneous motion for a statistical distribution of an assembly of atoms (at absolute

23 temperature *T* above 0 K) is governed by free energy and not by potential energy.

24 *Note 1*: The IUPAC recommendation is to use the specific terms Gibbs energy or

25 Helmholtz energy whenever possible. However, it is useful to retain the generic term

26 "free energy" for use in contexts where the distinction between (on the one hand) either

27 Gibbs energy or Helmholtz energy and (on the other hand) potential energy is more

28 important than the distinction between conditions either of constant pressure or of

29 constant volume; e.g., in computational modelling to distinguish between results of

30 simulations performed for ensembles under conditions of either constant *P* or constant

31 *V* at finite *T* and calculations based purely on potential energy.

32 *Note 2*: Whereas motion of a single *molecular entity* is determined by the force acting

33 upon it, which is obtained as the negative gradient of the potential energy, motion for

34 an assembly of many molecular entities is determined by the mean force acting upon

35 the statistical distribution, which is obtained as the negative gradient of the *potential of*

36 *mean force*.

37

38 **free radical**

39 See *radical*.

40 [3]

frontier orbitals

Highest-energy Occupied Molecular Orbital (HOMO) and Lowest-energy Unoccupied Molecular Orbital (LUMO) of a *molecular entity*.

Note 1: These terms should be limited to doubly occupied orbitals, and not to a singly occupied molecular orbital (sometimes designated as a *SOMO*), because HOMO and LUMO are ambiguous for molecular orbitals that are half filled and thus only partly occupied or unoccupied.

Note 2: 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 theory of chemical behaviour.

Note 3: In some cases a *subjacent orbital* (*N*ext-to-*H*ighest *O*ccupied *M*olecular *O*rbital (NHOMO) or a *S*econd *L*owest *U*noccupied *M*olecular *O*rbital (SLUMO)) may affect reactivity.

See [8,206,207].

See also *SOMO*, *subjacent orbital*.

rev[3]

frustrated Lewis acid-base pair

Acid and base for which *adduct* formation is prevented by *steric hindrance.*

See [208,209].

fullerene

Molecular entity composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube.

Note: Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes.

See [40,210].

functional group

Atom or group of atoms within *molecular entities* that are responsible for the characteristic *chemical reaction*s of those *molecular entities*. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the

1   molecule it is a part of. However, its relative reactivity can be modified by nearby
2   *substituent*s.
3   rev[3]

4

5   **gas-phase acidity**
6   Standard reaction Gibbs energy ($\Delta_r G^o$) change for the gas-phase reaction.

7         $A–H \rightarrow A^- + H^+$

8   *Note 1*: The symbol often found in the literature is $\Delta_{acid} G$ or GA.
9   *Note 2*: The corresponding enthalpy $\Delta_r H^o$ is often symbolized by $\Delta_{acid} H$ and called
10   "enthalpy of acidity" or deprotonation enthalpy, abbreviated DPE.
11   See [211,212].
12   rev[3]

13

14   **gas-phase basicity**
15   Negative of the standard reaction Gibbs energy ($\Delta_r G^o$) change for the gas-phase
16   reaction

17        $B + H^+ \rightarrow BH^+$

18   *Note*: An acronym commonly used in the literature is GB. The corresponding
19   enthalpy $\Delta_r H^o$ is called *proton affinity*, PA, even though affinity properly refers to Gibbs
20   energy. Moreover, such acronyms are not accepted by IUPAC.
21   See [213,214].
22   rev[3]

23

24   **Gaussian orbital**
25   Function centred on an atom of the form $\phi(r) \propto x^i y^j z^k \exp(-\zeta r^2)$, used to approximate
26   atomic orbitals in the LCAO-MO method.
27   See [8].

28

29   **geminate pair**
30   Pair of *molecular entities* in close proximity within a solvent cage and resulting from
31   reaction (e.g., bond scission, electron transfer, group transfer) of a precursor.
32   *Note*: Because of the proximity the pair constitutes only a single kinetic entity.
33   See also *ion pair, radical pair*.
34   rev[3]

35

36   **geminate recombination**
37   Recombination reaction of a *geminate pair*.
38   *Example:*

39        $RN=NR \xrightarrow{\Delta} [R\cdot\ \ N_2\ \ R\cdot]_{cage} \longrightarrow R\text{-}R + N_2$

1   rev[3]

2

3

4   **general acid catalysis**

5   *Catalysis* of a chemical reaction by *Brønsted acid*s (which may include the solvated

6   hydrogen ion), where the rate of the catalysed part of the reaction is given by $\Sigma_{HA}k_{HA}[HA]$

7   multiplied by some function of *substrate* concentrations.

8   *Note 1*: General acid catalysis can be experimentally distinguished from *specific*

9   *catalysis* by hydrogen cations (*hydron*s) if the *rate of reaction* increases with buffer

10   concentration at constant pH and ionic strength.

11   *Note 2*: The acid catalysts HA are unchanged by the overall reaction. This

12   requirement is sometimes relaxed, but the phenomenon is then properly called *pseudo-*

13   *catalysis*.

14   See also *catalysis*, *catalytic coefficient*, *intramolecular catalysis*, *pseudo-catalysis*,

15   *specific catalysis*.

16   rev[3]

17

18   **general base catalysis**

19   Catalysis of a *chemical reaction* by *Brønsted base*s (which may include the *lyate ion*),

20   where the rate of the catalysed part of the reaction is given by $\Sigma_{B}k_{B}[B]$ multiplied by

21   some function of *substrate* concentrations.

22   See also *general acid catalysis*.

23   [3]

24

25   **Gibbs energy diagram**

26   Diagram showing the relative standard Gibbs energies of reactants, *transition state*s,

27   reaction *intermediate*s, and products, in the same sequence as they occur in a *chemical*

28   *reaction*.

29   *Note 1*: The abscissa expresses the sequence of reactants, products, reaction

30   intermediates, and transition states and is often an undefined "reaction coordinate" or

31   only vaguely defined as a measure of progress along a reaction path. In some

32   adaptations the abscissas are however explicitly defined as *bond order*s, Brønsted

33   exponents, etc.

34   *Note 2*: These points are often connected by a smooth curve (a "Gibbs energy

35   profile", commonly referred to as a "free-energy profile", a terminology that is

36   discouraged), but experimental observation can provide information on relative

37   standard Gibbs energies only at the maxima and minima and not at the configurations

38   between them.

39   *Note 3*: It should be noted that the use of standard Gibbs energies implies a common

40   standard state for all chemical species (usually 1 M for reactions in solution). Contrary

1   to statements in many textbooks, the highest point on a Gibbs energy diagram does not
2   automatically correspond to the transition state of the *rate-limiting step*. For example,
3   in a stepwise reaction consisting of two elementary reaction steps
4   (1) $A + B \rightleftarrows C$
5   (2) $C + D \rightarrow E$
6   one of the two transition states must (in general) have a higher standard Gibbs energy
7   than the other. Under experimental conditions where all species have the standard-
8   state concentration, then the *rate-limiting step* is that whose transition state is of highest
9   standard Gibbs energy. However, under (more usual) experimental conditions where
10   all species do not have the standard-state concentration, then the value of the
11   concentration of D determines which reaction step is rate-limiting. However, if the
12   particular concentrations of interest, which may vary, are chosen as the standard state,
13   then the rate-limiting step is indeed the one of highest Gibbs energy.
14

15
16
17   See also *potential energy profile*, *potential-energy surface*, *reaction coordinate*.
18   rev[3]
19

20   **Gibbs energy of activation (standard free energy of activation)**
21   $\Delta^{\ddagger}G^o$
22   (SI unit: kJ mol^{-1})
23   Standard Gibbs energy difference between the *transition state* of an *elementary*
24   *reaction* and the ground state of the reactants for that step. It is calculated from the *rate*
25   *constant k* via the absolute rate equation:
26

27       $\Delta^{\ddagger}G^o = RT [\ln((k_B/\text{J K}^{-1})/(h/\text{J s})) - \ln(k/[k]/T/\text{K})]$

28

29       $\Delta^{\ddagger}G^o = RT [\ln(\{k_B\}/\{h\}) - \ln(\{k\}/\{T\})]$

30

1 where k_B is Boltzmann's constant, [k] are the units of k, and h Planck's constant. The

2 values of the rate constants, and hence the Gibbs energies of activation, depend upon

3 the choice of concentration units (or of the thermodynamic standard state).

4 *Note 1:* For a complex *stepwise reaction*, composed of many elementary reactions,

5 $\Delta^{\ddagger}G^{o}$, the observed Gibbs energy of activation (activation free energy), can be

6 calculated as RT [ln(k_B/J K^{-1})/(h/J s) − ln(k'/[k']/T/K)], where k' is the observed rate

7 constant, k' should be divided by its units, and T/K is the absolute temperature, of

8 dimension 1*,* since the argument of a logarithmic function should be of dimension 1, as

9 expressed by the reduced variables in the second form of the equation.

10 *Note 2:* Both $\Delta^{\ddagger}G^{o}$ and k' are non-trivial functions of the rate constants and activation

11 energies of the elementary steps.

12 See also *enthalpy of activation*, *entropy of activation*.

13 rev[3]

14

15 **graphene**

16 *Allotrope* of carbon, whose structure is a one-atom-thick planar sheet of sp^2-bonded

17 carbon atoms in a honeycomb (hexagonal) crystal lattice.

18

19 **ground state**

20 State of lowest Gibbs energy of a system [2].

21 *Note*: In *photochemistry* and quantum chemistry the lowest-energy state of a

22 chemical entity (ground electronic state) is usually meant.

23 See [9].

24 See also *excited state*.

25 rev[3]

26

27 **group**

28 See *functional group*, *substituent*.

29 rev[3]

30

31 **Grunwald-Winstein equation**

32 *Linear Gibbs-energy relation* (*Linear free-energy relation*)

33

34      $\lg(k_S/k_0) = mY$

35

36 expressing the dependence of the rate of solvolysis of a substrate on the ionizing power

37 of the solvent, where the *rate constant* k_0 applies to the reference solvent (80:20

38 ethanol-water by volume) and k_S to the solvent S.

1   *Note 1*: The parameter *m* is characteristic of the substrate and is assigned the value

2   unity for *tert*-butyl chloride (2-chloro-2-methylpropane). The value *Y* is intended to be a

3   quantitative measure of the *ionizing power* of the solvent S.

4   *Note 2*: The equation was later extended [215] to the form

5

6    $\lg(k_S/k_0) = mY + lN$

7

8   where *N* is the *nucleophilicity* of the solvent and *l* a susceptibility parameter

9   *Note 3*: The equation has also been applied to reactions other than solvolysis.

10   *Note 4*: For the definition of other *Y*-scales, see [216,217,218,219].

11   See also *Dimroth-Reichardt E_T parameter*, *polarity*.

12   rev[3]

13

14   **guest**

15   Organic or inorganic ion or molecule that occupies a cavity, cleft, or pocket within the

16   molecular structure of a *host molecular entity* and forms a *complex* with it or that is

17   trapped in a cavity within the crystal structure of a host, but with no covalent bond being

18   formed.

19   See also *crown ether*, *cryptand*, *inclusion compound*.

20   [3]

21

22   **half-life**

23    $t_{1/2}$

24   (SI unit: s)

25   Time required for the concentration of a particular reacting *chemical species* to fall to

26   one-half of its initial value.

27   *Note 1*: Half-life is independent of initial concentration only for a first-order process.

28   *Note 2*: For first-order reactions $t_{1/2} = \tau \ln 2$, where τ is the *lifetime*.

29   See also *lifetime*.

30   rev[3]

31

32   **halochromism**

33   Colour change that occurs on addition of *acid* or *base* to a solution of a compound as a

34   result of chemical reaction, or on addition of a salt as a result of changing the solvent

35   polarity.

36   See [220,221].

37   [3]

38

39   **halogen bond**

1 *Association* between a Lewis-acidic halogen atom in a *molecular entity* and a Lewis-
2 basic region in another, or the same, molecular entity, which acts as an electron-pair
3 donor, such that the balance of forces of attraction and repulsion results in net
4 stabilization.

5   *Note 1*: Typical halogen-bond donors are I_2, Br_2, ICN, and IC≡CH.
6   *Note 2*: This is analogous to a *hydrogen bond*, in which the H is the acidic atom.
7   *Note 3:* The interaction provides a stabilization of a few kJ mol^{-1}.
8   See [222,223,224,225].

9

10

Hammett equation (Hammett relation)
12 Equation of the form

13

14     $\lg \{k_X\} = \rho\, \sigma_X + \lg \{k_0\}$
15 or $\lg \{K_X\} = \rho\, \sigma_X + \lg \{K_0\}$

16

17 expressing the influence of *meta* and *para* *substituent*s X on the reactivity of the
18 functional group Y in the benzene derivatives *m*- and *p*-XC_6H_4Y, where $\{k_X\}$ and $\{K_X\}$
19 are the numerical values of the rate or equilibrium constant, respectively, for the
20 reactions of *m*- and *p*-XC_6H_4Y, σ_X is the substituent constant characteristic of *m*- or *p*-
21 X, and ρ is the reaction constant characteristic of the given reaction of Y. The values lg
22 $\{k_0\}$ and lg $\{K_0\}$ are intercepts for graphical plots of lg $\{k_X\}$ or lg $\{K_X\}$, respectively, against
23 σ_X for all substituents X (including X = H, if present).

24   *Note* 1: It is very common in the literature to find either of these equations written
25 without the curly brackets denoting a reduced rate or equilibrium constant, i.e., *k* or *K*
26 divided by its unit, [*k*] or [*K*], respectively.

27   *Note* 2: The Hammett equation is most frequently used to obtain the value of ρ which,
28 as the slope of a graph or least-squares fit, is independent of the choice of units for k_X
29 or K_X. If the equation is used to estimate the unknown value of a rate or equilibrium
30 constant for an X-substituted compound based upon the known value of σ_X, the ordinate
31 must be multiplied by [k_X] or [K_X] in order to obtain the value with its appropriate units.

32   *Note 3:* The equation is often encountered in a form with k_H or K_H incorporated into
33 the logarithm on the left-hand side, where k_H or K_H corresponds to the reaction of parent
34 C_6H_5Y, with X = H;

35

36     $\lg(k_X/k_H) = \rho\, \sigma_X$
37 or $\lg(K_X/K_H) = \rho\, \sigma_X$

38

39 This form satisfies the requirement that arguments of the lg function must be of
40 dimension 1, but it would suggest a one-parameter linear least-squares fit, whereas lg

1 k_0, lg K_0, lg $k_0/[k_0]$ and lg $K_0/[K_0]$, in the other forms correctly represent the intercept in

2 a two-parameter linear least-squares fit of lg k, lg K, lg $k/[k]$, or lg $K/[K]$ vs. σ_X.

3   See [21,22,126,191,226].

4   See also *extended Hammett equation*, *Taft equation*, *Yukawa-Tsuno equation*, *σ-*

5 *constant*, *ρ-value*.

6   rev[3]

Hammond postulate (Hammond-Leffler principle)

12 Hypothesis that, when a *transition state* leading to a high-energy reaction *intermediate*

13 (or product) has nearly the same energy as that intermediate (or product), the two are

14 interconverted with only a small reorganization of molecular structure.

15   *Note 1:* Essentially the same idea is sometimes referred to as "Leffler's assumption",

16 namely, that the *transition state* bears a greater resemblance to the less stable species

17 (reactant or reaction intermediate/product). Many textbooks and physical organic

18 chemists, however, express the idea in Leffler's form (couched in terms of Gibbs

19 energies) but attribute it to Hammond (whose original conjecture concerns structure).

20   *Note 2:* As a corollary, it follows that a factor stabilizing a reaction *intermediate* will

21 also stabilize the *transition state* leading to that *intermediate*.

22   *Note 3*: If a factor stabilizes a reaction intermediate (or reactant or product), then the

23 position of the transition state along the *minimum-energy reaction path* (MERP) for that

24 elementary step moves away from that intermediate, as shown in the energy diagram

25 (a) below left, where the transition state moves from ‡ to ‡' when the species to the

26 right is stabilized. This behaviour is often called a Hammond effect and is simply a

27 consequence of adding a linear perturbation to the parabola.

(a)   ‡   ‡'   (b)   ‡   ‡'

30   *Note 4:* If a structure lying off the MERP is stabilized, then the position of the

31 *transition state* moves toward that structure, as shown in the energy diagram (b) above

1
2
3   1   right, where the transition state moves from ‡ to ‡'. This behaviour is often called anti-
4
5   2   Hammond and arises because the transition state is a maximum along the MERP but
6   3   a minimum perpendicular to it.
7
8   4   See [227,228,229,230].
9   5   See *Leffler's relation*, *More O'Ferrall – Jencks diagram*, *parallel effect*, *perpendicular*
10   6   *effect*.
11
12   7   rev[3]
13   8
14   9   **Hansch constant**
15
16   10   Measure of the contribution of a substituent to the *partition ratio* of a solute, defined as
17   11
18   12 $\pi_X = \lg(P_X/P_H)$
19
20   13
21   14   where P_X is the partition ratio for the compound with substituent X and P_H is the partition
22   15   constant for the parent.
23
24   16   See [231,232].
25   17   rev[3]
26   18
27
28   19   **hapticity**
29   20   Topological description for the number of contiguous atoms of a *ligand* that are bonded
30   21   to a central metal atom.
31   22   *Note:* The hapticity is indicated as a superscript following the Greek letter η.
32
33   23   *Example*: $(C_5H_5)_2Fe$ (ferrocene) = bis(η^5-cyclopentadienyl)iron, where η^5 can be read
34   24   as eta-five or pentahapto.
35   25   See [29].
36
37   26
38   27   **hard acid, base**
39   28   *Lewis acid* with an acceptor centre or *Lewis base* with a donor centre (e.g., an oxygen
40
41   29   atom) of low *polarizability*.
42   30   *Note 1:* A high polarizability characterizes a soft acid or base.
43
44   31   *Note 2*: Whereas the definition above is qualitative, a theoretically consistent
45   32   definition of hardness η, in eV, is as half the second derivative of the calculated energy
46   33 E with respect to N, the number of electrons, at constant potential v due to the nuclei.
47
48   34
49   35 $$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v$$
50
51   36
52   37   *Note 3*: Other things being equal, complexes of hard acids with hard bases or of soft
53
54   38   acids with soft bases have an added stabilization (sometimes called the HSAB rule).
55   39   For limitations of the HSAB rule, see [36,233].
56
57
58
59
60

1 See [234,235,236].

2 rev[3]

3

4 **HBA solvent**

5 Strongly or weakly basic solvent capable of acting as a *hydrogen-bond* acceptor (HBA)

6 and forming strong intermolecular solute-solvent hydrogen bonds.

7 *Note:* A solvent that is not capable of acting as a hydrogen-bond acceptor is called

8 a non-HBA solvent.

9 See [17].

10

11 **HBD solvent** (*Hydrogen-Bond* Donating solvent, also *dipolar HBD solvent* and *protic*

12 *solvent*)

13 Solvent with a sizable permanent dipole moment that bears suitably acidic hydrogen

14 atoms to form strong intermolecular solvent-solute hydrogen bonds.

15 *Note:* A solvent that is not capable of acting as hydrogen-bond donor is called a *non-*

16 *HBD solvent* (formerly aprotic solvent).

17 See [17,155].

18

19 **heat capacity of activation**

20 $C_P^{\ddagger}$

21 (SI unit: J mol^{-1} K^{-1})

22 Temperature coefficient of $\Delta^{\ddagger}H$ (*enthalpy of activation*) or $\Delta^{\ddagger}S$ (*entropy of activation*) at

23 constant pressure according to the equations:

24

25 $$C_P^{\ddagger} = (\partial\Delta^{\ddagger}H/\partial T)_P = T(\partial\Delta^{\ddagger}S/\partial T)_P$$

26

27 See [237].

28 rev[3]

29

30 **Henderson-Hasselbalch equation**

31 Equation of the form

32

33 $$pH = pK_a - lg([HA]/[A^-])$$

34

35 relating the pH of a buffer solution to the ratio [HA]/[A$^-$] and the dissociation constant of

36 the acid K_a.

37 See [238].

38 rev[3]

39

40 **heterobimetallic complex**

1   Metal complex having two different metal atoms or ions.

2   rev[3]

3

4   **heteroleptic**

5   Characteristic of a transition metal or Main Group compound having more than one type

6   of *ligand*.

7   See also *homoleptic*.

8   [3]

9

10

11   **heterolysis, heterolytic bond fission**

12   Cleavage of a *covalent bond* so that both bonding electrons remain with one of the two

13   fragments between which the bond is broken, e.g.,

14   A⌢B ⟶ A⁺ + B⁻

15   See also *heterolytic bond-dissociation energy*, *homolysis*.

16   [3]

17

18   **heterolytic bond-dissociation energy**

19   Energy required to break a given *bond* of a specific compound by *heterolysis*.

20   *Note:* For the *dissociation* of a neutral molecule AB in the gas phase into A⁺ and B⁻

21   the heterolytic *bond-dissociation energy* $D(A^+B^-)$ is the sum of the homolytic bond-

22   dissociation energy, $D(A–B)$, and the adiabatic *ionization* energy of the radical A· minus

23   the electron affinity of the radical B·.

24   [3]

25

26   **high-throughput screening**

27   Automated method to quickly assay large libraries of *chemical species* for the affinity of

28   small organic molecules toward a target of interest.

29   *Note:* Currently more than 10^5 different compounds can be tested per day.

30   See [239].

31

32   **highest occupied molecular orbital (HOMO)**

33   Doubly filled molecular orbital of highest energy.

34   *Note*: Examination of the HOMO can predict whether an *electrocyclic reaction* is

35   *conrotatory* or *disrotatory*.

36   See also *frontier orbitals*.

37

38   **Hildebrand solubility parameter** [symbol δ, derived unit: $Pa^{1/2} = (kg\ m^{-1}\ s^{-2})^{1/2}$]

39   Ability of a solvent to dissolve a non-electrolyte, defined as the square root of the

40   solvent's cohesive energy density (also called cohesive pressure, equal to the energy

1   of vaporization divided by the solvent's molar volume and corresponding to the energy
2   necessary to create a cavity in the solvent).
3   See [240].
4   rev[3]
5

6 **Hofmann rule**
7 Observation that when two or more alkenes can be produced in a *β-elimination* reaction,
8 the alkene having the smallest number of alkyl groups attached to the double bond
9 carbon atoms is the predominant product.
10   *Note:* This orientation is observed in elimination reactions of quaternary ammonium
11 salts and tertiary sulfonium (sulfanium) salts, and in certain other cases where there is
12 steric hindrance.
13   See [241].
14   See also *Saytzeff rule*.
15   rev[3]
16

17 **HOMO**
18 (1) Acronym for **H**ighest **O**ccupied **M**olecular **O**rbital.
19   See also *frontier orbitals*.
20 (2) Prefix (in lower case) used to indicate a higher homologue of a compound, as
21 homocysteine for $HSCH_2CH_2CH(NH_2)COOH$, the homologue of cysteine,
22 $HSCH_2CH(NH_2)COOH$.
23   rev[3]
24

25 **homoaromatic**
26 Showing features of *aromaticity* despite a formal discontinuity in the overlap of a cyclic
27 array of p orbitals resulting from the presence of an sp^3-hybridized atom at one or
28 several positions within the cycle, in contrast to an *aromatic* molecule, where there is a
29 continuous overlap of p orbitals over a cyclic array.
30   *Note 1:* Homoaromaticity arises because p-orbital overlap can bridge an sp^3 centre.
31   *Note 2:* Pronounced homoaromaticity is not normally associated with neutral
32 molecules, but mainly with ionic species, e.g., the "homotropylium" cation, $C_8H_9^+$,

33

34   *Note 3:* In bis-, tris-, (etc.) homoaromatic species, two, three, (etc.) single sp^3 centres
35 separately interrupt the π-electron system.
36   [3]
37

1 **homodesmotic reaction**

2 Subclass of *isodesmic* reactions in which reactants and products contain not only the

3 same number of carbon atoms in each state of hybridization but also the same number

4 of each CH$_n$ group joined to n hydrogen atoms.

5 *Examples:*

6

7   cyclo-$(CH_2)_3$ + 3 CH_3CH_3 $\rightleftarrows$ 3 $CH_3CH_2CH_3$ [3CH$_2$, 6CH$_3$]

8   C_6H_6 (benzene) + 3 $CH_2=CH_2$ $\rightleftarrows$ 3 $CH_2=CH–CH=CH_2$ [6CH, 6CH$_2$]

9

10   *Note:* The definition may be extended to molecules with heteroatoms.

11   See [8].

12   rev[3]

13

14 **homoleptic**

15 Characteristic of a transition-metal or Main Group compound having only one type of

16 *ligand*, e.g., $Ta(CH_3)_5$

17   See also *heteroleptic*.

18   [3]

19

20 **homolysis**

21 Cleavage of a *bond* so that each of the molecular fragments between which the bond

22 is broken retains one of the bonding electrons.

23   *Note 1:* A *unimolecular* reaction involving homolysis of a bond not forming part of a

24 cyclic structure in a *molecular entity* containing an even number of (paired) electrons

25 results in the formation of two radicals:

      A⌒B   ⟶   A• + B•

26

27   *Note 2:* Homolysis is the reverse of *colligation*.

28   See also *bond dissociation energy*, *heterolysis*.

29   [3]

30

31 **host**

32 *Molecular entity* that forms *complexes* (*adducts)* with organic or inorganic guests, or a

33 chemical species that can accommodate guests within cavities of its crystal structure.

34   Examples include *cryptands* and *crown ethers* (where there are ion/dipole attractions

35 between heteroatoms and cations), *hydrogen-bonded* molecules that form clathrates

36 (e.g., hydroquinone or water), and host molecules of *inclusion compounds* (e.g., urea

37 or thiourea), where *intermolecular* forces and *hydrophobic interaction*s bind the guest

38 to the host molecule.

39   rev[3]

1

Hückel molecular orbital (HMO) theory

Simplest molecular orbital theory of π-conjugated molecular systems. It uses the following approximations: π-electron approximation; LCAO representation of the π molecular orbitals; neglect of electron-electron and nuclear-nuclear repulsions. The diagonal elements of the effective Hamiltonian (Coulomb integrals) and the off-diagonal elements for directly bonded atoms (resonance integrals) are taken as empirical parameters, all overlap integrals being neglected.

See [8].

rev[3]

Hückel (4n + 2) rule

Principle that monocyclic planar (or almost planar) systems of trigonally (or sometimes digonally) hybridized atoms that contain (4n + 2) π electrons (where n is an integer, generally 0 to 5) exhibit *aromatic* character.

Note 1: This rule is derived from *Hückel MO theory* calculations on planar monocyclic conjugated hydrocarbons (CH)$_m$ where integer m is at least 3, according to which (4n + 2) electrons are contained in a closed-shell system.

Examples:

Cyclopropenyl cation
(m = 3, n = 0)

Cyclopentadienide anion
(m = 5, n = 1)

Benzene
(m = 6, n = 1)

Note 2: Planar systems containing 4n π electrons (such as cyclobutadiene and cyclopentadienyl cation) are antiaromatic.

Note 3: Cyclooctatetraene, with 8 π electrons, is nonplanar and therefore neither aromatic nor antiaromatic but nonaromatic.

See [8].

See also *conjugation*, *Möbius aromaticity*.

rev[3]

hybrid orbital

Atomic orbital constructed as a linear combination of *atomic orbital*s on an atom.

Note 1: Hybrid orbitals are often used to describe the bonding in molecules containing tetrahedral (sp^3), trigonal (sp^2), and digonal (sp) atoms, whose σ bonds are constructed using 1:3, 1:2, or 1:1 combinations, respectively, of s and p atomic orbitals.

Note 2: Construction of hybrid orbitals can also include d orbitals, as on an octahedral atom, with d^{2}sp^3 hybridization.

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1 *Note 3:* Integer ratios are not necessary, and the general hybrid orbital made from s

2 and p orbitals can be designated as sp$^\lambda$.

3

4 **hydration**

5 *Addition* of water or of the elements of water (i.e., H and OH) to a *molecular entity* or to

6 a *chemical species*.

7 *Example*: hydration of ethene:

8 $CH_2=CH_2 + H_2O \rightarrow CH_3CH_2OH$

9 *Note:* In contrast to *aquation*, hydration, as in the incorporation of waters of

10 crystallization into a protein or in the formation of a layer of water on a nonpolar surface,

11 does not necessarily require bond formation.

12 See [48].

13 See also *aquation*.

14 rev[3]

15

16 **hydrogen bond**

17 An attractive interaction between a hydrogen atom from a molecule or a molecular

18 fragment X–H in which X is more electronegative than H, and an atom or a group of

19 atoms in the same or a different molecule, in which there is evidence of bond formation.

20 *Note 1:* Both electronegative atoms are usually (but not necessarily) from the first

21 row of the Periodic Table, i.e., N, O, or F.

22 *Note 2:* A hydrogen bond is largely an electrostatic interaction, heightened by the

23 small size of hydrogen, which permits proximity of the interacting dipoles or charges.

24 *Note 3:* Hydrogen bonds may be *intermolecular* or *intramolecular*.

25 *Note 4:* With few exceptions, usually involving hydrogen fluoride and fluoride and

26 other ions, the associated energies are less than 20-25 kJ mol^{-1}.

27 *Note 5:* Hydrogen bonds are important for many chemical structures, giving rise to

28 the attraction between H_2O molecules in water and ice, between the strands of DNA,

29 and between aminoacid residues in proteins.

30 See [242,243].

31 rev[3]

32

33 **hydrolysis**

34 *Solvolysis* by water, generally involving the rupture of one or more bonds in the reactant

35 and involvement of water as *nucleophile* or base.

36 *Example:* $CH_3C(=O)OCH_2CH_3 + H_2O \rightarrow CH_3C(=O)OH + CH_3CH_2OH$

37 rev[3]

38

39 **hydron**

1 General name for the ion H+ either in natural abundance or where it is not desired to
2 distinguish between the isotopes, as opposed to proton for ^{1}H+, deuteron for ^{2}H+ and
3 triton for ^{3}H+.
4   See [244].
5   [3]

6

hydronation

8 Attachment of the ion H+ either in natural abundance or where it is not desired to
9 distinguish between the isotopes.

10

hydrophilicity

12 Capacity of a _molecular entity_ or of a _substituent_ to undergo stabilizing interactions with
13 polar solvents, in particular with water and aqueous mixtures, to an extent greater than
14 with a nonpolar solvent.
15   rev[3]

16

hydrophobic interaction

18 Tendency of _lipophilic_ hydrocarbon-like groups in solutes to form _intermolecular_
19 aggregates in an aqueous _medium_.
20   _Note:_ The name arises from the attribution of the phenomenon to the apparent
21 repulsion between water and hydrocarbons. However, the phenomenon is more
22 properly attributed to the effect of the hydrocarbon-like groups to avoid disrupting the
23 favorable water-water interactions.
24   [3]

25

hyperconjugation

27 _Delocalization_ of electrons between σ bonds and a π network.
28   _Note 1:_ The concept of hyperconjugation is often applied to _carbenium ion_s and
29 _radical_s, where the interaction is between σ bonds and an unfilled or partially filled p or
30 π orbital. _Resonance_ illustrating this for the _tert_-butyl cation is:

31

32   _Note 2:_ A distinction is made between positive hyperconjugation, as above, and
33 negative hyperconjugation, where the interaction is between a filled σ or π orbital and

1 adjacent antibonding σ^* orbitals, as for example in the fluoroethyl anion (2-fluoroethan-

2 1-ide).

3

4 *Note 3:* Historically, conjugation involves only π bonds, and hyperconjugation is

5 considered unusual in involving σ bonds.

6 See [245,246,247,248].

7 See also *σ, π, delocalization*.

8 rev[3]

9

hypercoordinated

10

11 Feature of a main-group atom with a *coordination number* greater than four.

12 *Example*: the pentacoordinate carbon in the *carbonium ion* CH_5^+, where three C–H

13 bonds may be regarded as two-electron bonds and the two electrons in the remaining

14 CH_2 fragment are delocalized over three atoms. Likewise, both hydrogens in the CH_2

15 fragment are hypercoordinated.

16 See [2,8].

17 See also *agostic.*

18 rev[3]

19

hypervalency

20

21 Ability of an atom in a *molecular entity* to expand its valence shell beyond the limits of

22 the Lewis octet rule.

23 *Examples:* PF_5, SO_3, iodine(III) compounds, and pentacoordinate carbocations

24 (*carbonium ion*s).

25 *Note:* Hypervalent compounds are more common for the second- and subsequent-

26 row elements in groups 15-18 of the periodic table. A proper description of the

27 hypervalent bonding implies a transfer of electrons from the central (hypervalent) atom

28 to the nonbonding molecular orbitals of the attached *ligand*s, which are usually more

29 electronegative.

30 See [8].

31 See also *valence*.

32 rev[3]

33

hypsochromic shift

34

35 Shift of a spectral band to higher frequency (shorter wavelength) upon substitution or

36 change in medium.

37 *Note:* This is informally referred to as a blue shift and is opposite to a *bathochromic*

38 *shift* ("red shift"), but these historical terms are discouraged because they apply only to

39 visible transitions.

40 See [9].

1 rev[3]

2

3 **identity reaction**

4 *Chemical reaction* whose products are chemically identical with the reactants

5   *Examples*:

6   (i) bimolecular exchange reaction of CH_3I with I^-

7   (ii) proton transfer between NH_4^+ and NH_3

8   (iii) electron transfer between manganate(VI) MnO_4^{2-} and permanganate MnO_4^-.

9   See also *degenerate rearrangement*.

10   rev[3]

11

12 **imbalance**

13 Feature that reaction parameters characterizing different bond-forming or bond-

14 breaking processes in the same reaction change to different extents as the *transition*

15 *state* is approached (along some arbitrarily defined reaction path).

16   *Note*: Imbalance is common in reactions such as elimination, addition, and other

17 complex reactions that involve proton (*hydron*) transfer.

18   *Example*: the nitroalkane anomaly, where the Brønsted β exponent for hydron

19 removal is smaller than the Brønsted α for the nitroalkane as acid, because of

20 imbalance between the extent of bond breaking and the extent of resonance

21 delocalization in the transition state.

22   See [249].

23   See also *Brønsted relation*, *synchronization (principle of nonperfect*

24 *synchronization), synchronous*.

25   rev[3]

26

27 **inclusion compound (inclusion complex)**

28 *Complex* in which one component (the *host*) forms a cavity or, in the case of a crystal,

29 a crystal lattice containing spaces in the shape of long tunnels or channels in which

30 molecular entities of a second *chemical species* (the *guest*) are located.

31   *Note*: There is no covalent bonding between guest and host, the attraction being

32 generally due to *van der Waals forces*. If the spaces in the host lattice are enclosed on

33 all sides so that the guest species is "trapped" as in a *cage*, such compounds are known

34 as clathrates or cage compounds".

35   See [40].

36   [3]

37

38 **induction period**

39 Initial slow phase of a *chemical reaction* whose rate later accelerates.

1	*Note*: Induction periods are often observed with radical reactions, but they may also
2	occur in other reactions, such as those where a steady-state concentration of the
3	reactants is not established immediately.
4	See [13].
5	[3]

6

7	**inductive effect**
8	Experimentally observable effect (on rates of reaction, etc.) of a *substituent* through
9	transmission of charge through a chain of atoms by electrostatics.
10	*Note*: Although a theoretical distinction may be made between the *field effect* and
11	the inductive effect as models for the Coulomb interaction between a given site within
12	a *molecular entity* and a remote monopole or dipole within the same entity, the
13	experimental distinction between the two effects has proved difficult (except for
14	molecules of peculiar geometry, which may exhibit "reversed field effects"), because
15	the inductive effect and the field effect are ordinarily influenced in the same direction by
16	structural changes.
17	See [171,172,250].
18	See also *field effect*, *polar effect*.
19	rev[3]

20

21	**inert**
22	*Stable* and *unreactive* under specified conditions.
23	[3]

24

25	**inhibition**
26	Decrease in *rate of reaction* brought about by the addition of a substance (inhibitor), by
27	virtue of its effect on the concentration of a reactant, *catalyst*, or reaction *intermediate*.
28	For example, molecular oxygen or 1,4-benzoquinone can act as an inhibitor in many
29	chain reactions involving *radical*s as intermediates by virtue of its ability to act as a
30	*scavenger* toward those radicals.
31	*Note*: If the rate of a reaction in the absence of inhibitor is v_o and that in the presence
32	of a certain amount of inhibitor is v, the degree of inhibition (i) is given by

33

34	$$i = (v_o - v)/v_o$$

35

36	See also *mechanism-based inhibition*.
37	[3]

38

39	**initiation**

1 Reaction or process generating *radical*s (or some other reactive reaction *intermediate*s)
2 which then induce a *chain reaction* or catalytic cycle.
3   *Example*: In the chlorination of alkanes by a radical mechanism the initiation step
4 may be the *dissociation* of molecular chlorine.
5   rev[3]
6

inner-sphere (electron transfer)

8 Feature of an electron transfer between two metal centres that in the transition state
9 share a *ligand* or atom in their coordination shells.
10   *Note*: The definition has been extended to any situation in which the interaction
11 between the electron-donor and electron-acceptor centres in the *transition state* is
12 significant (>20 kJ mol^{-1}).
13   See [9].
14   See also *outer-sphere electron transfer*.
15   [3]
16

17 **insertion**

18 *Chemical reaction* or *transformation* of the general type
19

20   X–Z + Y $\rightarrow$ X–Y–Z
21

22 in which the connecting atom or *group* Y replaces the bond joining the parts X and Z of
23 the reactant XZ.
24   *Example*: *carbene* insertion reaction
25

26     $R_3C–H + H_2C\text{:} \rightarrow R_3C–CH_3$
27

28   *Note*: The reverse of an insertion is called an *extrusion*.
29   [3]
30

31 **intermediate (reactive intermediate)**

32 *Molecular entity* in a stepwise chemical reaction with a *lifetime* appreciably longer than
33 a molecular vibration (corresponding to a local potential energy minimum of depth
34 greater than *RT*, and thus distinguished from a *transition state*) that is formed (directly
35 or indirectly) from the reactants and reacts further to give (directly or indirectly) the
36 products of a chemical reaction.
37   See also *elementary reaction*, *reaction step*, *stepwise reaction*.
38   [3]
39

40 **intermolecular**

1 (1) Descriptive of any process that involves a transfer (of atoms, *group*s, electrons, etc.)

2 or interactions between two or more *molecular entities*.

3 (2) Relating to a comparison between different molecular entities.

4   See also *intramolecular*.

5   [3]

6

7 **internal return**

8   See *ion-pair recombination*.

9   rev[3]

10

11 **intramolecular**

12 (1) Descriptive of any process that involves a transfer (of atoms, *group*s, electrons, etc.)

13 or interactions between different parts of the same *molecular entity*.

14 (2) Relating to a comparison between different groups within the same molecular entity.

15   See also *intermolecular*.

16   [3]

17

18 **intramolecular catalysis**

19 Acceleration of a chemical transformation at one site of a *molecular entity* through the

20 involvement of another *functional* ("catalytic") *group* in the same molecular entity,

21 without that group appearing to have undergone change in the reaction product.

22   *Note 1:* The use of the term should be restricted to cases for which analogous

23 intermolecular catalysis by a *chemical species* bearing that catalytic group is

24 observable.

25   *Note 2:* Intramolecular catalysis can be detected and expressed in quantitative form

26 by a comparison of the reaction rate with that of a comparable model compound in

27 which the catalytic group is absent, or by measurement of the *effective molarity* of the

28 catalytic group.

29   See also *effective molarity*, *neighbouring group participation*.

30   [3]

31

32 **intrinsic barrier, $\Delta^{\ddagger}G_0$**

33 *Gibbs energy of activation* in the limiting case where $\Delta_r G^o = 0$, i.e., when the effect of

34 thermodynamic driving force is eliminated, as in an identity reaction, $X^* + AX \rightarrow X^*A + $

35 X, where A may be an atom, ion, or group of atoms or ions, and where the *equilibrium*

36 constant K is equal to 1.

37   *Note:* According to the *Marcus equation*, originally developed for outer-sphere

38 electron transfer reactions, the intrinsic barrier is related to λ, the *reorganization energy*

39 of the reaction, by the equation

40

1 $\Delta^{\ddagger}G^{\circ} = \lambda/4$

2

3 For a non-identity reaction, $Y + AX \rightarrow YA + X$, the intrinsic barrier $\Delta^{\ddagger}G^{\circ}(Y,X)$ is estimated
4 as $\frac{1}{2}[\Delta^{\ddagger}G(X,X) + \Delta^{\ddagger}G(Y,Y)]$, where the latter two terms are the Gibbs energies of
5 activation of the identity reactions $X^* + AX \rightarrow X^*A + X$ and $Y^* + AY \rightarrow Y^*A + Y$,
6 respectively.
7   See [251,252,253,254].
8   rev[3]

9

10 **intrinsic reaction coordinate (IRC)**
11 Minimum-energy path leading from the saddle point (corresponding to the *transition*
12 *structure*) on the *potential-energy surface* for an *elementary reaction*, obtained by
13 tracing the steepest descent in mass-weighted coordinates in both directions.
14   *Note*: The IRC is mathematically well defined, in contrast to the (generally) vague
15 *reaction coordinate*. Strictly, the IRC is a specific case of a *minimum-energy reaction*
16 *path,* and its numerical value at any point along this path is usually taken to be zero at
17 the saddle point, positive in the direction of the products, and negative in the direction
18 of the reactants.
19   See [8,255].
20   rev[3]

21

22 **inverted micelle (reverse micelle)**
23 Association colloid formed reversibly from surfactants in non-polar solvents, leading to
24 aggregates in which the polar *group*s of the surfactants are concentrated in the interior
25 and the *lipophilic* groups extend toward and into the non-polar solvent.
26   *Note:* Such association is often of the type
27   Monomer $\rightleftarrows$ Dimer $\rightleftarrows$ Trimer $\rightleftarrows \cdots \rightleftarrows$ *n*-mer
28 and a *critical micelle concentration* is consequently not observed.
29   [3]

30

31 **ion pair**
32 Pair of oppositely charged ions held together by coulomb attraction without formation
33 of a *covalent bond*.
34   *Note 1:* Experimentally, an ion pair behaves as one unit in determining conductivity,
35 kinetic behaviour, osmotic properties, etc.
36   *Note 2:* Following Bjerrum, oppositely charged ions with their centres closer together
37 than a distance

38

39 $$d = \frac{Z_+Z_-e^2}{4\pi\varepsilon_0\varepsilon_r k_B T}$$

are considered to constitute an ion pair. Here Z_+ and Z_- are the charge numbers of the ions, e is the elementary charge, ε_0 is the vacuum permittivity, ε_r is the relative *permittivity* ("dielectric constant") of the medium, k_B is Boltzmann's constant, and T is the absolute temperature. This is the distance at which the Coulomb energy equals the thermal energy, and $e^2/(4\pi\varepsilon_0 k_B)$ is approximately equal to 1.671×10^{-5} m K^{-1}.

Note 3: An ion pair, the constituent ions of which are in direct contact (and not separated by intervening solvent or by other neutral molecule) is designated as a "tight ion pair" (or "intimate" or "contact ion pair"). A tight ion pair of R$^+$ and X$^-$ is symbolically represented as R$^+$X$^-$.

Note 4: 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 R$^+$||X$^-$. The components 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.

Note 5: A further conceptual distinction has sometimes been made between two types of loose ion pairs. In "solvent-shared ion pairs" for which 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.

See [256].

See also *common-ion effect*, *dissociation*, *ion-pair return*, *special salt effect*.

[3]

ion-pair recombination (formerly **ion-pair return**)

Recombination of a pair of ions R$^+$ and X$^-$ formed from *ionization* of RX.

Note: Ion-pair recombination can be distinguished as external or internal, depending on whether the ion pair did or did not undergo dissociation to free ions.

See *ion pair*.

rev[3]

ionic liquid (ionic solvent, molten salt)

Liquid that consists exclusively or almost exclusively of equivalent amounts of oppositely charged ions.

Note 1: In practice the ions are monocations and monoanions.

Note 2: Ionic liquids that are liquid at or around room temperature are called room-temperature ionic liquids (RTILs).

Note 3: The term *ionic liquid* has been often restricted to those water-free liquids that have melting points (or glass-transition temperatures) below 100 °C, following a definition given by Walden [257], who prepared the first ionic liquid, ethylammonium nitrate, $CH_3CH_2NH_3^+ NO_3^-$, mp. 13-14 °C, for conductivity measurements.

Note 4: The terminology for ionic liquids is not yet settled, as stated by Welton [258]. Room-temperature ionic liquid, non-aqueous ionic liquid, molten salt, liquid organic salt, and fused salt are often synonymous.
    See [259,260,261].

ionic strength

I

(In concentration basis, I_c, SI unit: mol m^{-3}, more commonly mol dm^{-3} or mol L^{-1}, in molality basis, I_m , SI unit: mol kg^{-1})

In concentration basis: $I_c = 0.5 \ \Sigma_i c_i Z_i^2$, in which c_i is the concentration of a fully dissociated electrolyte in solution and Z_i the charge number of ionic species i.

In molality basis: $I_m = 0.5 \ \Sigma_i m_i Z_i^2$, in which m_i is the molality of a fully dissociated electrolyte in solution and Z_i the charge number of ionic species i.
    rev[3]

ionization

Generation of one or more ions.

Note 1: This may occur, e.g., by loss or gain of an electron from a neutral *molecular entity*, by the *unimolecular heterolysis* of that entity into two or more ions, or by a heterolytic *substitution* reaction involving neutral molecules, such as

    $M \ \rightarrow \ \ M^{+\bullet} + e^-$ (photoionization, electron ionization in mass spectrometry)

    $SF_6 + e^- \rightarrow SF_6^{-\bullet}$ (electron capture)

    $Ph_3CCl \rightarrow Ph_3C^+ Cl^-$ (*ion pair*, which may dissociate to free ions)

    $CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3CO_2^-$ (*dissociation*)

Note 2: In mass spectrometry ions may be generated by several methods, including electron ionization, photoionization, laser desorption, chemical ionization, and electrospray ionization.

Note 3: Loss of an electron from a singly, doubly, etc. charged cation is called second, third, etc. ionization.
    See also *dissociation*, *ionization energy*.
    rev[3]

ionization energy

E_i

(SI unit J)

1 Minimum energy required to remove an electron from an isolated *molecular entity* (in
2 its vibrational ground state) in the gaseous phase.
3   *Note 1:* If the resulting molecular entity is in its vibrational ground state, the energy
4 is the "adiabatic ionization energy".
5   *Note 2:* If the molecular entity produced possesses the vibrational energy determined
6 by the *Franck-Condon principle* (according to which the electron ejection takes place
7 without an accompanying change in molecular geometry), the energy is the "vertical
8 ionization energy".
9   *Note 3:* The name ionization energy is preferred to the somewhat misleading earlier
10 name "ionization potential".
11   See also *ionization*.
12   [3]
13

14 **ionizing power**
15 Tendency of a particular solvent to promote *ionization* of a solute.
16   *Note*: The term has been used in both kinetic and thermodynamic contexts.
17   See also *Dimroth-Reichardt E_T parameter*, *Grunwald-Winstein equation*, *Z-value*.
18   [3]
19

20 ***ipso* attack**
21 Attachment of an entering group to a position in an aromatic compound already carrying
22 a *substituent* group other than hydrogen.
23   *Note:* The entering group may displace that substituent group or may itself be
24 expelled or migrate to a different position in a subsequent step. The term "*ipso*-
25 substitution" is not used, since it is synonymous with substitution.
26   *Example:*

27

28 where E^+ is an *electrophile* and Z is a substituent other than hydrogen.
29   See [262].
30   See also *cine-substitution*, *tele-substitution*.
31   [3]
32

33 **isentropic**
34   See *isoentropic*.
35

36 **isodesmic**
37 Property of a reaction (actual or hypothetical) in which the types of bonds that are made
38 in forming the products are the same as those that are broken in the reactants.

Examples:

(i) PhCOOH + *p*-ClC$_6$H$_4$CO$_2^-$ $\rightleftarrows$ PhCO$_2^-$ + *p*-ClC$_6$H$_4$COOH $\qquad$ (1)

(ii) 2 CH$_3$F $\rightleftarrows$ CH$_2$F$_2$ + CH$_4$ $\qquad$ (2)

Note 1: Such processes have advantages for theoretical treatment.

Note 2: The *Hammett equation* as applied to equilibria, as in (1), succeeds because it deals with isodesmic processes.

Note 3: For the use of isodesmic processes in quantum chemistry, see [263].

See [8].

See also *homodesmotic.*

rev[3]

isoelectronic

Having the same number of valence electrons and the same structure, i.e., number and *connectivity* of atoms, but differing in some or all of the elements involved.

Examples:

(i) $\quad$ CO, N$_2$, and NO$^+$

(ii) $\quad$ CH$_2$=C=O and CH$_2$=N$^+$=N$^-$

[3]

isoentropic

Isentropic

Property of a reaction series in which the individual reactions have the same standard entropy or *entropy of activation*.

[3]

isoequilibrium relationship

Feature of a series of related substrates or of a single *substrate* under a series of reaction conditions whereby the enthalpies and entropies of reaction can be correlated by the equation

$$\Delta_r H - \beta \Delta_r S = \text{constant}$$

Note: The parameter β is called the isoequilibrium temperature.

See [264,265].

See also *compensation effect, isokinetic relationship.*

[3]

isokinetic relationship

1 Feature of a series of related substrates or of a single *substrate* under a series of
2 reaction conditions whereby the *enthalpies of activation* and *entropies of activation* can
3 be correlated by the equation

4 $\Delta^{\ddagger}H - \beta\,\Delta^{\ddagger}S$ = constant

5 *Note 1:* The parameter β is called the isokinetic temperature. At this temperature all
6 members of the series react at the same rate.

7 *Note 2:* Isokinetic relationships as established by direct correlation of $\Delta^{\ddagger}H$ with $\Delta^{\ddagger}S$
8 are often spurious, and the calculated value of β is meaningless, because errors in $\Delta^{\ddagger}H$
9 lead to compensating errors in $\Delta^{\ddagger}S$. Satisfactory methods of establishing such
10 relationships have been devised.
11 See [264,265].
12 See also *compensation effect*, *isoequilibrium relationship*, *isoselective relationship*.
13 [3]
14

15 **isolobal**
16 Feature of two molecular fragments for which the number, symmetry properties,
17 approximate energy, shape of the *frontier orbitals*, and number of electrons in them are
18 similar.
19 *Example:*

20

21 See also *isoelectronic*.
22 rev[3]
23

24 **isomer**
25 One of several species (or *molecular entities*) all of which have the same atomic
26 composition (molecular formula) but differ in their connectivity or stereochemistry and
27 hence have different physical and/or chemical properties.
28 *Note:* Conformational isomers that interconvert by rapid rotation about single bonds
29 and configurations that interconvert by rapid pyramidal inversion are often not
30 considered as separate isomers.
31 rev[3]
32

33 **isomerization**
34 *Chemical reaction* in which the product is an *isomer* of the reactant.
35 See also *molecular rearrangement*.
36 rev[3]
37

isosbestic point

Wavelength (or frequency) at which two or more components in a mixture have the same molar absorption coefficients.

Note 1: 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, as in an acid-base indicator equilibrium.

Note 2: The effect may also appear (c) in the spectra of a set of solutions of two or more non-interacting components having the same total concentration.

Note 3: 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.

Note 4: If absorption spectra of the types considered above intersect not at one or more isosbestic points but over a progressively changing range of wavelengths, this is prima facie evidence (a) for the formation of a reaction *intermediate* in substantial concentration (A → C → B) or (b) for the involvement of a third absorbing species in the equilibrium, e.g.,

$$A \rightleftarrows B + H^+_{aq} \rightleftarrows C + 2\,H^+_{aq}$$

or (c) for some interaction of A and B, e.g.,

$$A + B \rightleftarrows C$$

Note 5: Isobestic is a misspelling and is discouraged.

rev[3]

isoselective relationship

Relationship analogous to the *isokinetic relationship*, but applied to *selectivity* data of reactions.

Note: At the isoselective temperature, the selectivities of the series of reactions following the relationship are identical, within experimental error.

See [266].

See also *isoequilibrium relationship*, *isokinetic relationship*.

[3]

isotope effect

Relative difference between, or the ratio of, the *rate coefficients* or *equilibrium* constants of two reactions that differ only in the isotopic composition of one or more of their otherwise chemically identical components.

Note: The ratio k_l/k_h of rate constants (or K_l/K_h of equilibrium constants) for "light" and "heavy" reactions is most often used in studies of chemical reaction mechanisms. However, the opposite ratios are frequently used in environmental chemistry and

1 geochemistry; i.e., k_h/k_l or K_h/K_l. Furthermore the relative difference $k_h/k_l - 1$ or $K_h/K_l -$

2 1 (often expressed as the percentage deviation of the ratio from unity) is commonly

3 used to quantify isotopic fractionation.

4   See *kinetic isotope effect*, *equilibrium isotope effect*.

5   rev[3]

6

7 isotope effect, equilibrium

8 isotope effect, thermodynamic

9 Effect of isotopic substitution on an *equilibrium* constant

10   *Note 1:* For example, the effect of isotopic substitution in reactant A that participates

11 in the equilibrium:

12         $A + B \rightleftarrows C$

13 is the ratio K_l/K_h of the equilibrium constant for the reaction in which A contains the light

14 isotope to that in which it contains the heavy isotope. The ratio can also be expressed

15 as the equilibrium constant for the isotopic exchange reaction:

16         $A_l + C_h \rightleftarrows A_h + C_l$

17 in which reactants such as B that are not isotopically substituted do not appear.

18   *Note 2:* The *potential-energy surfaces* of isotopic molecules are identical to a high

19 degree of approximation, so thermodynamic isotope effects can arise only from the

20 effect of isotopic mass on the nuclear motions of the reactants and products, and can

21 be expressed quantitatively in terms of nuclear partition functions:

22

23         $K_l/K_h = [Q^l(C)/Q^h(C)]/ [Q^l(A)/Q^h(A)]$

24

25   *Note 3:* Although the nuclear partition function is a product of the translational,

26 rotational, and vibrational partition functions, the isotope effect is usually determined

27 almost entirely by the last named, specifically by vibrational modes involving motion of

28 isotopically different atoms. In the case of light atoms (i.e., protium vs. deuterium or

29 tritium) at moderate temperatures, the isotope effect is dominated by zero-point energy

30 differences.

31   See [267].

32   See also *fractionation factor*.

33   rev[3]

34

35 isotope effect, heavy-atom

36   *Isotope effect* due to isotopes other than those of hydrogen.

37   [3]

38

39 isotope effect, intramolecular

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.

Example: $PhCH_2D + Br\cdot \rightarrow BrH + PhCHD\cdot$ vs. $BrD + PhCH_2\cdot$

The intramolecular isotope effect k_H/k_D can be measured from the D content of product ($PhCH_2Br + PhCHDBr$), which is experimentally much easier than measuring the intermolecular isotope effect k_H/k_D from the separate rates of reaction of $PhCH_3$ and $PhCD_3$.
   rev[3]

isotope effect, inverse
Kinetic isotope effect in 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 $k_l/k_h > 1$.
   Note: The isotope effect will be "normal" when the vibrational frequency differences between the isotopic *transition state*s are smaller than in the reactants. Conversely, an inverse isotope effect can be taken as evidence for an increase in the force constants on passing from the reactant to the *transition state*.
   [3]

isotope effect, kinetic
Effect of isotopic substitution on a *rate constant*.
   For example in the reaction
      $A + B \rightarrow C$
   the effect of isotopic substitution in reactant A is expressed as the ratio of *rate constant*s k_l/k_h, where the superscripts l and h represent reactions in which the molecules A contain the light and heavy isotopes, respectively.
   Note 1: Within the framework of transition-state theory, where the reaction is rewritten as
      $A + B \rightleftarrows [TS]^{\ddagger} \rightarrow C$
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 (see *thermodynamic (equilibrium) isotope effect*).
   Note 2: Isotope effects like the above, involving a direct or indirect comparison of the rates of reaction of *isotopologue*s, are called "intermolecular", in contrast to intramolecular isotope effects (see *intramolecular isotope effect*), in which a single

1   substrate reacts to produce a non-statistical distribution of isotopologue product
2   molecules.
3   See [267,268].
4   [3]
5

6   **isotope effect, primary**
7   *Kinetic isotope effect* attributable to isotopic substitution of an atom to which a bond is
8   made or broken in the *rate-limiting step* or in a *pre-equilibrium* step of a reaction.
9   *Note:* The corresponding isotope effect on the *equilibrium* constant of a reaction in
10 which one or more bonds to isotopic atoms are broken is called a primary *equilibrium*
11 *isotope effect*.
12   See also *secondary isotope effect*.
13 [3]
14

15 **isotope effect, secondary**
16 *Kinetic isotope effect* that is attributable to isotopic substitution of an atom to which
17 bonds are neither made nor broken in the *rate-limiting step* or in a *pre-equilibrium* step
18 of a specified reaction.
19   *Note 1:* The corresponding isotope effect on the equilibrium constant of such a
20 reaction is called a secondary *equilibrium isotope effect*.
21   *Note 2:* Secondary isotope effects can be classified as α, β, etc., where the label
22 denotes the position of isotopic substitution relative to the reaction centre.
23   *Note 3:* Although secondary isotope effects have been discussed in terms of
24 conventional electronic effects, e.g., induction, *hyperconjugation*, *hybridization*, such an
25 effect is not electronic but vibrational in origin.
26   See [269].
27   See also *steric isotope effect*.
28   rev[3]
29

30 **isotope effect, solvent**
31 Kinetic or equilibrium isotope effect resulting from change in the isotopic composition
32 of the solvent.
33   See also *kinetic isotope effect*, *equilibrium isotope effect*.
34 [3]
35

36 **isotope effect, steric**
37 *Secondary isotope effect* attributed to the different vibrational amplitudes of
38 *isotopologue*s.
39   *Note 1:* For example, both the mean and mean-square amplitudes of vibrations
40 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.

Note 2: Ultimately the steric isotope effect arises from changes in vibrational frequencies and zero-point energies, as normally do other isotope effects.

rev[3]

isotope effect, thermodynamic

See isotope effect, equilibrium.

[3]

isotope exchange

Chemical reaction in which the reactant and product *chemical species* are chemically identical but have different isotopic composition.

Note: 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,

[3]

isotopic perturbation, method of

Measurement of the NMR shift difference due to the *isotope effect* on a fast (degenerate) *equilibrium* between two species that are equivalent except for isotopic substitution.

Note: This method can distinguish a rapidly equilibrating mixture with time-averaged symmetry from a single structure with higher symmetry.

See [270,271,272,273].

[3]

isotopic scrambling

Achievement of, or the process of achieving, a redistribution of isotopes within a specified set of atoms in a *chemical species* or group of chemical species.

1   *Examples*

(a)

2

3   (where * denotes the position of an isotopically different atom.)

4   See also *fractionation factor*.

5   [3]

6

7   **isotopologues**

8   *Molecular entities* that differ only in isotopic composition (number of isotopic

9   substitutions), e.g., CH_4, CH_3D, CH_2D_2,

10   *Note:* These are isotopic homologues. It is a misnomer to call them *isotopomers*,

11   because they are not isomers with the same atoms.

12   rev[3]

13

14   **isotopomers**

15   *Isomers* having the same number of each isotopic atom but differing in their positions.

16   The term is a contraction of "isotopic isomer".

17   *Note:* Isotopomers can be either constitutional isomers (e.g., $CH_2DCH=O$ and

18   $CH_3CD=O$) or isotopic stereoisomers (e.g., (*R*)- and (*S*)-CH_3CHDOH or (*Z*)- and (*E*)-

19   $CH_3CH=CHD$).

20   See [11].

21   [3]

22

23   **Kamlet-Taft solvent parameters**

24   Quantitative measure of solvent *polarity*, based on the solvent's hydrogen-bond donor,

25   hydrogen-bond acceptor, dipolarity/*polarizability*, and cohesive-pressure properties.

26   See [274,275,276,277,278,279].

27   See *solvent parameter*.

28   rev[3]

29

30   **Kaptein-Closs rules**

31   Rules used to predict the sign of *chemically induced dynamic nuclear polarization*

32   (CIDNP) effects.

33   See [280,281,282].

1

Kekulé structure

Representation of a *molecular entity* (usually *aromatic*) with fixed alternating single and double bonds, in which interactions between multiple bonds are ignored.

Example: For benzene the Kekulé structures are

Note: The distinction among *Lewis structure*, *Kekulé structure*, and *line formula* is now not generally observed, nor is the restriction to aromatic molecular entities.

See also *non-Kekulé structure*.

rev[3]

keto-enol tautomerization

Interconversion of ketone and enol *tautomers* by hydron migration, accelerated by acid or base catalysis.

Example:

See also *tautomerization*.

kinetic ambiguity

deprecated

See *kinetic equivalence*.

kinetic control (of product composition)

Conditions (including reaction times) that lead to reaction products in a proportion governed by the relative rates of the parallel (forward) reactions by which those products are formed, rather than by the *equilibrium* constants.

See also *thermodynamic control*.

[3]

kinetic electrolyte effect

kinetic ionic-strength effect

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1 General effect of an added electrolyte (i.e., other than, or in addition to, that due to its
2 possible involvement as a reactant or catalyst) on the *rate constant* of a reaction in
3 solution.

4   *Note 1:* At low concentrations (when only long-range coulombic forces need to be
5 considered) the effect on a given reaction is determined only by the *ionic strength* of
6 the solution and not by the chemical identity of the ions. This concentration range is
7 roughly the same as the region of validity of the Debye-Hückel limiting law for activity
8 coefficients. At higher concentrations the effect of an added electrolyte depends also
9 on the chemical identity of the ions. Such specific actions can sometimes be interpreted
10 as the incursion of a *reaction path* involving an ion of the electrolyte as reactant or
11 catalyst, in which case the action is not properly to be regarded just as a kinetic
12 electrolyte effect. At higher concentrations the effect of an added electrolyte does not
13 necessarily involve a new reaction path, but merely the breakdown of the Debye-Hückel
14 law, whereby ionic activity coefficients vary with the ion.

15   *Note 2:* Kinetic electrolyte effects are also called kinetic salt effects.

16   *Note 3:* A kinetic electrolyte effect ascribable solely to the influence of the *ionic*
17 *strength* on activity coefficients of ionic reactants and transition states is called a primary
18 kinetic electrolyte effect. A kinetic electrolyte effect arising from the influence of the
19 ionic strength of the solution upon the *pre-equilibrium* concentration of an ionic species
20 that is involved in a subsequent *rate-limiting step* of a reaction is called a secondary
21 kinetic electrolyte effect. A common case is the secondary electrolyte effect on the
22 concentration of hydrogen ion (acting as catalyst) produced from the *ionization* of a
23 weak acid in a buffer solution. To eliminate the complication of kinetic electrolyte effects
24 in buffer solutions, it is advisable to maintain constant ionic strength.

25   See [283].

26   See also *common-ion effect*, *order of reaction.*

27   [3]

28

29 **kinetic equivalence**

30 Property of two reaction schemes that imply the same *rate law*.

31   *Example*: Schemes (i) and (ii) for the formation of C from A under conditions that B
32 does not accumulate as a reaction *intermediate*:

$$\text{(i)} \quad A \underset{k_{-1},\ HO^-}{\overset{}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][HO^-]}{k_2 + k_{-1}[HO^-]}$$

$$\text{(ii)} \quad A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow[HO^-]{k_2} C$$

$$\frac{d[C]}{dt} = \frac{k_1 k_2 [A][HO^-]}{k_{-1} + k_2[HO^-]}$$

Both equations for d[C]/dt are of the form

$$\frac{d[C]}{dt} = \frac{r[A][HO^-]}{1 + s[HO^-]}$$

where r and s are constants (sometimes called *rate coefficients*). The equations are identical in their dependence on concentrations and do not distinguish whether HO^- catalyses the formation of B and its reversion to A, or is involved only in its further transformation to C. The two schemes are therefore kinetically equivalent.
[3]

Koppel-Palm solvent parameters
Quantitative measure of solvent *polarity*, based on the solvent's *permittivity*, refractive index, *basicity* or *nucleophilicity*, and *acidity* or *electrophilicity*.
See [284].
See *solvent parameter.*
rev[3]

Kosower *Z* value
See *Z-value*.
[3]

labile
Property of a *chemical species* that is relatively *unstable* and *transient* or reactive.
Note: This term must not be used without explanation of the intended meaning.
See also *inert*, *persistent*, *reactivity*, *unreactive*.
[3]

1 **Laurence solvent parameters**

2 Quantitative measures of solvent *polarity,* based on the solvent's dispersion/induction

3 interactions, electrostatic interactions between permanent multipoles, solute Lewis

4 base/solvent Lewis acid interactions, and solute HBD/solvent HBA interactions.

5   See [285].

6

7 **least nuclear motion, principle of** (hypothesis of least motion)

8 Hypothesis that, for given reactants, the reactions involving the smallest change in

9 nuclear positions will have the lowest *energy of activation*.

10   *Note:* The basis for this hypothesis is that the energy of a structural deformation

11 leading toward reaction is proportional to the sum of the squares of the changes in

12 nuclear positions, which holds only for small deformations and is therefore not always

13 valid.

14   See [8,286].

15   rev[3]

16

17 **leaving group**

18 Species (charged or uncharged) that carries away the bonding electron pair when it

19 becomes detached from another fragment in the residual part of the *substrate*.

20   *Example 1*: In the heterolytic *solvolysis* of (bromomethyl)benzene (benzyl bromide)

21 in acetic acid

22

23     $PhCH_2Br + AcOH \rightarrow PhCH_2OAc + HBr$

24

25 the leaving group is Br^-.

26   *Example 2*: In the reaction

27

28     $MeS^- + PhCH_2N^+Me_3 \rightarrow MeSCH_2Ph + NMe_3$

29

30 the leaving group is NMe_3.

31   *Note:* The historical term "leaving group" is ambiguous, because in the heterolysis of

32 R–X, both R^+ and X^- are fragments that leave from each other. For that reason, X^- (as

33 well as Br^- and NMe_3 in examples 1 and 2) can unambiguously be called nucleofuges,

34 whereas R^+ is an electrofuge.

35   See also *electrofuge, entering group, nucleofuge*.

36   rev[3]

37

38 **Leffler's relation**

39 Leffler's assumption

40 In a series of elementary reactions the changes in Gibbs activation energies are often

41 found to be proportional to the changes in Gibbs energies for the overall reaction.

$$\delta \, \Delta^{\ddagger}G = \alpha \, \Delta_r G^0$$

This relation was interpreted in terms of the simple assumption that a small change in any transition-state property $P_{\ddagger}$ is a linear combination of changes in reactant- and product-state properties, P_R and P_P.

$$\delta P_{\ddagger} = \alpha \, \delta P_P + (1 - \alpha) \, \delta P_R$$

Within the limits of this assumption, the parameter α is an approximate measure of the fractional displacement of the transition state along the _minimum-energy reaction path_ from reactants to products.

See [109].

Note: There are many exceptions to the validity of Leffler's assumption that α is a measure of the position of the transition state.

See [287].

See _Hammond postulate_.

rev[3]

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 _electron pushing_ proceeds from left to right.

See [288].

[3]

levelling effect

Tendency of a solvent to make all _Brønsted acid_s whose _acidity_ exceeds a certain value appear equally acidic.

Note 1: This phenomenon is due to the complete transfer of a hydron to a Brønsted-basic solvent 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_.

Note 2: 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.

Note 3: A corresponding levelling effect applies to strong bases in _protogenic_ solvents.

[3]

Lewis acid

1 *Molecular entity* (and the corresponding *chemical species*) that is an electron–pair
2 acceptor and therefore able to react with a *Lewis base* to form a *Lewis adduct* by
3 sharing the electron pair furnished by the Lewis base.
4   *Example:*
5
6   Me_3B (Lewis acid) + $:NH_3$ (Lewis base) $\rightarrow$ $Me_3B^- - N^+H_3$ (Lewis adduct)
7
8   See also *coordination*.
9   [3]
10
11 **Lewis acidity**
12 Thermodynamic tendency of a substrate to act as a *Lewis acid*.
13   *Note 1*: This property is defined quantitatively by the *equilibrium* constant or Gibbs
14 energy for *Lewis adduct* formation of a series of Lewis acids with a common reference
15 *Lewis base*.
16   *Note 2.* An alternative measure of Lewis acidity in the gas phase is the enthalpy of
17 *Lewis adduct* formation for that Lewis acid with a common reference *Lewis base*.
18   See also *electrophilicity, Lewis basicity*.
19   rev[3]
20
21 **Lewis adduct**
22 *Adduct* formed between a *Lewis acid* and a *Lewis base*.
23   [3]
24
25 **Lewis base**
26 *Molecular entity* (and the corresponding *chemical species*) able to provide a pair of
27 electrons and thus capable of *coordination* to a *Lewis acid*, thereby producing a *Lewis*
28 *adduct*.
29   [3]
30
31 **Lewis basicity**
32 Thermodynamic tendency of a substance to act as a *Lewis base*.
33   *Note 1:* This property is defined quantitatively by the equilibrium constant or Gibbs
34 energy of *Lewis adduct* formation for that Lewis base with a common reference *Lewis*
35 *acid*.
36   *Note 2:* An alternative measure of Lewis *basicity* in the gas phase is the enthalpy of
37 *Lewis adduct* formation for that Lewis base with a common reference *Lewis acid*.
38   See also *donicity, Lewis acidity, nucleophilicity, proton affinity*.
39   rev[3]
40

1 **Lewis structure**

2 electron-dot structure, Lewis formula

3 Representation of molecular structure in which (a) nonbonded valence electrons are
4 shown as dots placed adjacent to the atoms with which they are associated and in
5 which (b) a pair of bonding valence electrons in a _covalent bond_ is shown as two dots
6 between the bonded atoms, and in which (c) formal charges (e.g., +, −, 2+) are attached
7 to atoms to indicate the difference between the nuclear charge (atomic number) and
8 the total number of electrons associated with that atom, on the formal basis that bonding
9 electrons are shared equally between atoms they join.

10   _Examples_:

H:C̈l: :C̈l:⁻   H:C:::C:H

11

12   _Note 1:_ A double bond is represented by two pairs of dots, and a triple bond by three
13 pairs, as in the last example above.

14   _Note 2:_ Bonding pairs of electrons are usually denoted by lines, representing
15 covalent bonds, as in _line formulas_, rather than as a pair of dots, and the lone pairs are
16 sometimes omitted.

17   _Examples_:

H–Cl   Cl⁻   H-C≡C-H

18

19   _Note 3:_ The distinction among Lewis structure, _Kekulé structure_, and _line formula_ is
20 now not generally observed.

21   rev[3]

22

23 **lifetime (mean lifetime)**

24 τ

25 Time needed for the concentration of a _chemical species_ that decays in a first-order
26 process to decrease to 1/e of its original value. i.e., $c(t = \tau) = c(t = 0)/e$.

27   _Note 1:_ Statistically, it represents the mean life expectancy of the species.

28   _Note 2:_ Mathematically: $\tau = 1/k = 1/(\Sigma_i k_i)$ where k_i is the first-order _rate constant_ for
29 the _i_-th decay process of the species.

30   _Note 3:_ Lifetime is sometimes applied to processes that are not first-order. However,
31 in such cases the lifetime depends on the initial concentration of the entity or of a
32 _quencher_ and, therefore, only an initial lifetime can be defined. In this case, it should be
33 called _decay time_.

34   See [9].

35   See also _chemical relaxation_, _half-life_, _rate of reaction_.

36   [3]

37

ligand

Atom or *group* bound to a central atom in a polyatomic *molecular entity* (if it is possible to indicate such a central atom).

   See [29].

   *Note 1:*The term is generally used in connection with metallic central atoms.

   Note 2: 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.

   See [289], p. 335.

   [3]

line formula

Two-dimensional representation of *molecular entities* in which atoms are shown joined by lines representing single bonds (or multiple lines for multiple bonds), without any indication or implication concerning the spatial direction of bonds.

   Examples: methanol, ethene

   See also *condensed formula, Kekulé formula*, *Lewis formula, skeletal formula.*

   rev[3]

linear free-energy relation

linear Gibbs-energy relation

   [3]

linear Gibbs-energy relation

linear free-energy relation (LFER)

Linear correlation between the logarithm of a *rate constant* or *equilibrium* constant for a series of reactions and the logarithm of the rate constant or equilibrium constant for a related series of reactions.

   Typical examples of such relations are the *Brønsted relation* and the *Hammett equation* (see also *σ-value*).

   Note: The name arises because the logarithm of the value of an equilibrium constant (at constant temperature and pressure) is proportional to a standard Gibbs energy (free energy) change, and the logarithm of the value of a rate constant is a linear function of the Gibbs energy (free energy) of activation.

   [3]

linear solvation-energy relationship (LSER)

Application of *solvent parameter*s in the form of a single- or multi-parameter equation expressing the solvent effect on a given property: e.g., *rate of reaction*, *equilibrium* constant, spectroscopic shift.

Note: The solvent effect may be estimated as a linear combination of elementary effects on a given property P, relative to the property P_0 in the reference solvent:

$$P - P_0 = a\,A + b\,B + p\,DP\ldots$$

where A, B, DP, etc. are acidity, basicity, dipolarity, etc. parameters, and $a, b, p\ldots$ are the sensitivity of the property to each effect.

See *Catalán solvent parameters*, *Dimroth-Reichardt E_T parameter*, *Kamlet-Taft solvent parameters*, *Koppel-Palm solvent parameters*, *Laurence solvent parameters*, *Z-value*.

rev[3]

line-shape analysis

Method for determination of *rate constant*s for dynamic chemical exchange from the shapes of spectroscopic signals, most often used in nuclear magnetic resonance spectroscopy.

[3]

Lineweaver-Burk plot

See *Michaelis-Menten kinetics*.

[3]

lipophilic

Feature of *molecular entities* (or parts of molecular entities) that have a tendency to dissolve in fat-like solvents (e.g., hydrocarbons).

See also *hydrophilic*, *hydrophobic interaction*.

rev[3]

London forces

dispersion forces

Attractive forces between molecules due to their mutual *polarizability*.

Note: London forces are the principal components of the forces between nonpolar molecules.

See [290].

See also *van der Waals forces*.

[3]

1 **lone (electron) pair (nonbonding electron pair)**

2 Two spin-paired electrons localized in the valence shell on a single atom.

3 *Note*: In structural formulas lone pairs should be designated as two dots.

4 See also *Lewis structure.*

5 rev[3]

6

7 **LUMO**

8 Acronym for Lowest Unoccupied Molecular Orbital

9 See *frontier orbitals.*

10 rev[3]

11

12 **lyate ion**

13 Anion produced by *hydron* (proton, deuteron, triton) removal from a solvent molecule.

14 *Example*: the hydroxide ion is the lyate ion of water.

15 [3]

16

17 **lyonium ion**

18 Cation produced by *hydronation* (protonation, deuteronation, tritonation) of a solvent

19 molecule.

20 *Example:* $CH_3OH_2^+$ is the lyonium ion of methanol.

21 See also *onium ion*.

22 [3]

23

24

25

26 **macroscopic diffusion control**

27 See *mixing control.*

28 [3]

29

30 **magnetic equivalence**

31 Property of nuclei that have the same resonance frequency in nuclear magnetic

32 resonance spectroscopy and also identical spin-spin interactions with each nucleus of

33 a neighbouring group.

34 *Note 1:* The spin-spin interaction between magnetically equivalent nuclei is not

35 manifested in the spectrum, and has no effect on the multiplicity of the respective NMR

36 signals.

37 *Note 2:* Magnetically equivalent nuclei are necessarily chemically equivalent, but the

38 reverse is not necessarily true.

39 [3]

40

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.

Note: 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*.

[3]

Marcus equation

General expression that correlates the *Gibbs energy of activation* ($\Delta^{\ddagger}G$) with the Gibbs energy of the reaction ($\Delta_r G^o$)

$$\Delta^{\ddagger}G = (\lambda/4)(1 + \Delta_r G^o/\lambda)^2 = \Delta^{\ddagger}G_o + \tfrac{1}{2}\Delta_r G^o + (\Delta_r G^o)^2/(16\,\Delta^{\ddagger}G_o)$$

where λ is the *reorganization energy* and $\Delta^{\ddagger}G_o$ is the *intrinsic barrier*, with $\lambda = 4\Delta^{\ddagger}G_o$.

Note: Originally developed for outer-sphere electron transfer reactions, the Marcus equation applies to many atom- and group-transfer reactions. The Marcus equation captures earlier ideas that reaction thermodynamics can influence reaction barriers: e.g., the *Brønsted relation* (1926), the *Bell-Evans-Polanyi principle* (1936-38), *Leffler's relation* (1953), and the *Hammond postulate* (1955) [227]. It also implies that changes in intrinsic barriers may dominate over changes of reaction Gibbs energies and thus account for the fact that reaction rates may not be controlled by the relative thermodynamic stabilities of the products.

See [291,292,293,294,295,296].

rev[3]

Markovnikov (Markownikoff) rule

Statement of the common mechanistic observation that in electrophilic addition reactions the more electropositive atom (or part) of a polar molecule becomes attached to the carbon bearing more hydrogens.

Note 1: This rule was originally formulated by Markownikoff (Markovnikov) as "In the addition of hydrogen halides to [unsaturated] hydrocarbons, the halogen atom becomes attached to the carbon bearing the lesser number of hydrogen atoms".

Note 2: This rule can be rationalized as the addition of the more electropositive atom (or part) of the polar molecule to the end of the multiple bond that would result in the more stable *carbenium* ion (regardless of whether the carbenium ion is a stable *intermediate* or a transient structure along the *minimum-energy reaction path*).

1
2
3   1   *Note 3:* Addition in the opposite sense, as in radical addition reactions, is commonly
4
5   2   called anti-Markovnikov addition.
6   3   See [297].
7
8   4   [3]
9
10   5
11   6   **mass action, law of**
12
13   7   Statement that the velocity of a reaction depends on the active mass, i.e., the
14   8   concentrations of the reactants.
15   9   *Example:* for an association reaction (1) and its reverse (2)
16
17   10
18   11   A + B   →   AB   (1)
19   12   AB   →   A + B   (2)
20
21   13
22   14   the forward velocity is $v_1 = k_1$ [A][B], with k_1 the *rate constant* for the association reaction.
23   15   For the dissociation reaction 2 the velocity is $v_2 = k_2$ [AB]. This is valid only for
24   16   *elementary reactions*. Furthermore, the law of mass action states that, when a
25   17   reversible chemical reaction reaches *equilibrium* at a given temperature, the forward
26   18   rate is the same as the backward rate. Therefore, the concentrations of the chemicals
27   19   involved bear a constant relation to each other, described by the equilibrium constant,
28   20   i.e., for
29
30   21
31   22   A + B $\rightleftharpoons$ AB
32
33   23
34   24   in equilibrium, $v_1 = k_1$ [A][B] = $v_2 = k_2$ [AB] and one form of the equilibrium constant for
35   25   the above chemical reaction is the ratio
36
37   26
38   27 $$K_c = \frac{[AB]}{[A][B]} = \frac{k_1}{k_2}$$
39
40   28
41   29   *Note*: First recognized in 1864 as the kinetic law of mass action by Guldberg and
42   30   Waage, who first introduced the concept of dynamic equilibrium, but incorrectly
43   31   assumed that the rates could be deduced from the stoichiometric equation [298]. Only
44   32   after the work of Horstmann [299] and van't Hoff [300] a mathematical derivation of the
45   33   reaction rates considering the *order of the reaction* involved was correctly made.
46   34   See also [301,302,303].
47   35   rev[3]
48
49   36
50   37   **matrix isolation**
51

1 Technique for preparation of a reactive or unstable species by dilution in an inert solid
2 matrix (argon, nitrogen, etc.), usually condensed on a window or in an optical cell at low
3 temperature, to preserve its structure for identification by spectroscopic or other means.
4   See [304].
5   [3]

6

Mayr-Patz equation

8 *Rate constant*s for the reactions of sp^2-hybridized *electrophile*s with *nucleophile*s can
9 be expressed by the correlation

10

11    $$lg\ [k/\ (dm^3\ mol^{-1}\ s^{-1})] = s_N(E + N),$$

12

13 where E is the nucleophile-independent *electrophilicity* parameter, N is the electrophile-
14 independent *nucleophilicity* parameter, and s_N is the electrophile-independent
15 nucleophile-specific susceptibility parameter.

16   *Note 1:* This equation is equivalent to the conventional *linear Gibbs energy*
17 *relationship* lg $k = Nu + s_N E$, where $Nu = s_N N$. The use of N is preferred, because it
18 provides an approximate ranking of relative reactivities of nucleophiles.

19   *Note 2:* The correlation should not be applied to reactions with bulky electrophiles,
20 where steric effects cannot be neglected. Because of the way of parametrization, the
21 correlation is applicable only if one or both reaction centres are carbon.

22   *Note 3:* As the E parameters of the reference electrophiles are defined as solvent-
23 independent, all solvent effects are shifted into the parameters N and s_N.

24   *Note 4:* The equation transforms into the *Ritchie equation* for $s_N = 1$.

25   *Note 5:* Applications to S_N2-type reactions are possible if an electrophile-specific
26 susceptibility parameter is introduced.

27   See [305,306,307,308].
28   See also *Ritchie equation, Swain-Scott equation*.
29   The Mayr scale is available at http://www.cup.lmu.de/oc/mayr/DBintro.htm

30

mechanism

32 Detailed description of the process leading from the reactants to the products of a
33 reaction, including a characterization as complete as possible of the composition,
34 structure, energy and other properties of reaction *intermediate*s, products, and
35 *transition state*s.

36   *Note 1:* An acceptable mechanism of a specified reaction (and there may be a
37 number of such alternative mechanisms not excluded by the evidence) must be
38 consistent with the reaction stoichiometry, the *rate law*, and with all other available
39 experimental data, such as the stereochemical course of the reaction.

1   *Note 2*: Inferences concerning the electronic motions that dynamically interconvert
2   successive species along the *reaction path* (as represented by curved arrows, for
3   example) are often included in the description of a mechanism.
4   rev[3]

5

6   **mechanism-based inhibition** (suicide inhibition)
7   Irreversible *inhibition* of an enzyme by formation of covalent bond(s) between the
8   enzyme and the inhibitor, which is a substrate analogue that is converted by the enzyme
9   into a species that reacts with the enzyme.
10 rev[3]

11

12 **medium**
13 Phase (and composition of the phase) in which *chemical species* and their reactions
14 are studied.
15 [3]

16

17 **Meisenheimer adduct** (Jackson-Meisenheimer adduct)
18 *Lewis adduct* formed in nucleophilic aromatic substitution from a *nucleophile* (*Lewis*
19 *base*) and an *aromatic* or heteroaromatic compound,

20

21 *Note 1:* In cases where the substrate lacks electron-withdrawing groups, and
22 depending also on the nucleophile, the Meisenheimer adduct is not a minimum on the
23 *potential-energy surface* but a *transition state*.
24 See [309,310,311,312].
25 *Note 2:* Analogous cationic adducts, such as

26

27
28

29 which are *intermediate*s in *electrophilic* aromatic *substitution* reactions, are instead
30 called Wheland intermediates or *σ-adduct*s (or the discouraged term σ-complexes).
31 See [313,314].
32 rev[3]

1

melting point (corrected/uncorrected)

Temperature at which liquid and solid phases coexist in equilibrium, as measured with a thermometer whose reading was corrected (or not) for the emergent stem that is in ambient air.

Note: In current usage the qualification often means that the thermometer was/(was not) calibrated or that its accuracy was/(was not verified). This usage is inappropriate and should be abandoned.

[3]

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 assigned to the fragments.

See [315,316].

[3]

mesomerism, mesomeric structure

obsolete

Resonance, resonance form

rev[3]

mesophase

Phase of a liquid crystalline compound between the crystalline and the isotropic liquid phase.

See [317].

[3]

metastable (chemical species)

deprecated

Transient (chemical species).

[3]

metathesis

Process formally involving the redistribution of fragments between similar *chemical species* so that the bonds to those fragments in the products are identical (or closely similar) to those in the reactants.

1   *Example*:

$$RCH = CHR \quad \xrightarrow{\text{catalyst}} \quad \begin{matrix} RCH \\ \| \\ RCH \end{matrix} \quad \begin{matrix} RCH \\ \| \\ RCH \end{matrix}$$

$$RCH = CHR$$

2

3   *Note:* The term has its origin in inorganic chemistry, with a different meaning, but that
4   older usage is not applicable in physical organic chemistry.
5   [3]
6

7   **micellar catalysis**
8   Acceleration of a *chemical reaction* in solution by the addition of a surfactant at a
9   concentration higher than its *critical micelle concentration* so that the reaction can
10   proceed in the environment of surfactant aggregates (*micelles*).
11   *Note 1:* Rate enhancements may be due to a higher concentration of the reactants
12   in that environment, or to a more favourable orientation and solvation of the species, or
13   to enhanced *rate constant*s in the micellar pseudophase of the surfactant aggregate.
14   *Note 2:* Micelle formation can also lead to a decreased reaction rate.
15   See [318].
16   See also *catalyst*.
17   [3]
18

19   **micelle**
20   Aggregate of 1- to 1000-nm diameter formed by surfactants in solution, which exists in
21   equilibrium with the molecules or ions from which it is formed.
22   See [135].
23   See also *inverted micelle*.
24   rev[3]
25

26   **Michaelis-Menten kinetics**
27   Appearance of saturation behavior in the dependence of the initial *rate of reaction* v_0
28   on the initial concentration $[S]_0$ of a *substrate* when it is present in large excess over
29   the concentration of an enzyme or other *catalyst* (or reagent) E, following the equation,
30

31   $v_0 = V_{max} [S]_0 /(K_M + [S]_0)$,

32

33   where v_0 is the observed initial rate, V_{max} is its limiting value at substrate saturation (i.e.,
34   when $[S]_0 >> K_M$, so that all enzyme is bound to substrate), and K_M is the substrate
35   concentration at which $v_0 = V_{max}/2$.
36   *Note 1:* Empirical definition, applying to any reaction that follows an equation of this
37   general form.

Note 2: Often only initial rates are measured, at low conversion, so that $[S]_0$ can be considered as time-independent but varied from run to run.

Note 3: The parameters V_{max} and K_M (the Michaelis constant) can be evaluated from slope and intercept of a linear plot of $1/v_0$ against $1/[S]_0$ (Lineweaver-Burk plot) or from slope and intercept of a linear plot of $[S]_0/v_0$ against $[S]_0$ (Eadie-Hofstee plot), but a nonlinear fit, which is readily performed with modern software, is preferable.

Note 4: This equation is also applicable to the condition where E is present in large excess, in which case [E] appears in the equation instead of $[S]_0$.

Note 5: The term has been used to describe reactions that proceed according to the scheme

$$\text{E} \quad + \quad \text{S} \quad \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \quad \text{ES} \quad \xrightarrow{k_{cat}} \quad \text{Products} \quad + \quad \text{E}$$

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 $k_{-1} >> k_{cat}$ and $K_M = k_{-1}/k_1$; in this case K_M is a true dissociation constant (Michaelis-Menten conditions).

See [319,320].

[3]

microscopic diffusion control (encounter control)

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*.

Note: The maximum *rate constant* is usually in the range 10^9 to 10^{10} dm^3 mol^{-1} s^{-1} in common solvents at room temperature.

See also *mixing control*.

rev[3]

microscopic reversibility, principle of

In a reversible reaction the *mechanism* in one direction is exactly the reverse of the mechanism in the other direction.

See also *chemical reaction*, *detailed balancing*.

[3]

migration

Transfer (usually *intramolecular*) of an atom or *group* during the course of a *molecular rearrangement*.

Example (of a hydrogen migration):

$$RCH_2CH=CH_2 \rightarrow RCH=CHCH_3$$

1 rev[3]

2

3 migratory aptitude

4 Tendency of a *group* to participate in a *molecular rearrangement*, relative to that of
5 another group, often in the same molecule.

6   *Example:* In the Baeyer-Villiger rearrangement of PhCOCH$_3$, via *intermediate*
7 PhC(OH)(OOCOAr)CH$_3$, the major product is CH$_3$COOPh, by phenyl migration, rather
8 than PhCOOCH$_3$.

9   *Note:* In *nucleophilic* rearrangements (migration to an electron-deficient centre) the
10 migratory aptitude of a group is loosely related to its capacity to stabilize a partial
11 positive charge, but exceptions are known, and the position of hydrogen in the series is
12 often unpredictable.

13   rev[3]

14

15 migratory insertion

16 Reaction that involves the *migration* of a *group* to another position on a metal centre,
17 with insertion of that group into the bond between the metal and the group that is in that
18 other position.

19   *Example*s:
20 CO insertion

21

22
23

24 Ziegler-Natta reaction

25

26
27

28   *Note:* On repetition of the reaction the substituent alternates between the two
29 positions.

30   rev[3]

31

32 minimum structural change, principle of

33 Principle that a *chemical reaction* is expected to occur with a minimum of bond changes
34 or with a minimum redistribution of electrons (although more complex reaction
35 cascades are also possible).

36   *Example:*

37

1
2
3 where the transfer of Cl is accompanied by migration of only one carbon, rather than a
4 more extensive *molecular rearrangement* involving *migration* of three methyls.
5   See [286].
6   See also *least nuclear motion, principle of*.
7   rev[3]
8

9 **minimum-energy reaction path (MERP)**
10 Path of steepest-descent from a saddle point on a *potential-energy surface* in each
11 direction towards adjacent energy minima; equivalent to the energetically easiest route
12 from reactants to products.
13   See *intrinsic reaction coordinate*.
14   See [8].
15

16 **mixing control**
17 Experimental limitation of the rate of reaction in solution by the rate of mixing of
18 solutions of the two reactants.
19   *Note 1:* Mixing control can occur even when the reaction *rate constant* is several
20 orders of magnitude less than that for an encounter-controlled reaction.
21   *Note 2:* Analogous (and more important) effects of the limitation of reaction rates by
22 the rate of mixing are encountered in heterogeneous (solid/liquid, solid/gas, liquid/gas)
23 systems.
24   See [321].
25   See also *microscopic diffusion control*, *stopped flow*.
26   [3]
27
28
29

30 **Möbius aromaticity**
31 Feature of a monocyclic array of π orbitals in which there is a single out-of-phase
32 overlap (or, more generally, an odd number of out-of-phase overlaps), whereby the
33 pattern of aromatic character is opposite to Hückel systems; with $4n$ π electrons it is
34 stabilized (aromatic), whereas with $4n + 2$ it is destabilized (antiaromatic).
35   *Note 1:* The name is derived from the topological analogy of such an arrangement of
36 orbitals to a Möbius strip.

1 *Note 2:* The concept has been applied to transition states of pericyclic reactions.*Note*

2 *3:* In the electronically excited state $4n + 2$ Möbius π-electron systems are stabilized,

3 and 4n systems are destabilized.

4 *Note 4:* A few examples of ground-state Möbius π systems are known [322,323].

5 See [324,325].

6 See also *aromatic*, *Hückel (4n + 2) rule*.

7 rev[3]

8

9 **molecular entity**

10 Any constitutionally or isotopically distinct atom, *molecule*, ion, *ion pair*, *radical*, *radical*

11 *ion*, *complex*, *conformer*, etc., identifiable as a separately distinguishable entity.

12 *Note 1:* Molecular entity is used in this glossary as a general term for singular entities,

13 irrespective of their nature, while *chemical species* stands for sets or ensembles of

14 molecular entities. Note that the name of a substance may refer to the molecular entity

15 or to the chemical species, e.g., methane, may mean either a single molecule of CH_4

16 (molecular entity) or an ensemble of such species, specified or not (chemical species),

17 participating in a reaction.

18 *Note 2:* The degree of precision necessary to describe a molecular entity depends

19 on the context. For example "hydrogen molecule" is an adequate definition of a certain

20 molecular entity for some purposes, whereas for others it may be necessary to

21 distinguish the electronic state and/or vibrational state and/or nuclear spin, etc. of the

22 molecule.

23 [3]

24

25 **molecular formula**

26 List of the elements in a *chemical species* or *molecular entity*, with subscripts indicating

27 how many atoms of each element are included.

28 *Note:* In organic chemistry C and H are listed first, then the other elements in

29 alphabetical order.

30 See [29].

31 See also *empirical formula*.

32

33

34 **molecular mechanics (**MM**) (empirical force-field calculation)**

35 Computational method intended to give estimates of structures and energies for

36 molecules.

37 *Note:* Even though such calculations can be made with either classical or quantum

38 mechanics (or both), the term molecular mechanics is widely understood as a classical

39 mechanics method that does not explicitly describe the electronic structure of the

40 molecular entities. It is based on the assumption of preferred bond lengths and angles,

1 deviations from which lead to strain, and the existence of torsional interactions and
2 attractive and repulsive *van der Waals* and Coulombic forces between non-bonded
3 atoms, all of which are parametrized to fit experimental properties such as energies or
4 structures. In contrast, in the quantum mechanical implementation no such
5 assumptions/parameters are needed.
6   See [8,326].
7   rev[3]

8

molecular metal
10 Non-metallic material whose properties, such as conductivity, resemble those of metals,
11 usually following oxidative doping.
12   *Example:* polyacetylene following oxidative doping with iodine.
13   [3]

14

molecular orbital
16 One-electron *wavefunction* describing a single electron moving in the field provided by
17 the nuclei and all other electrons of a *molecular entity* of more than one atom.
18   *Note 1:* Molecular orbitals describing valence electrons are often delocalized over
19 several atoms of a molecule. They are conveniently expressed as linear combinations
20 of *atomic orbital*s. They can be described as two-centre, multi-centre, etc. in terms of
21 the number of nuclei (or "centres") encompassed.
22   *Note 2:* For molecules with a plane of symmetry, a molecular orbital can be classed
23 as sigma (σ) or pi (π), depending on whether the orbital is symmetric or antisymmetric
24 with respect to reflection in that plane.
25   See *atomic orbital*, *orbital*.
26   See [8].
27   rev[3]

28

molecular rearrangement
30 Reaction of a *molecular entity* that involves a change of *connectivity*.
31   *Note 1*: The simplest type of rearrangement is an *intramolecular* reaction in which
32 the product is isomeric with the reactant (intramolecular *isomerization*). An example is
33 the first step of the Claisen rearrangement.

34

35

1   *Note 2*: The definition of molecular rearrangements includes reactions in which there

2   is a *migration* of an atom or bond (unexpected on the basis of the principle of *minimum*

3   *structural change*), as in the reaction

5    $CH_3CH_2CH_2Br + AgOAc \rightarrow (CH_3)_2CHOAc + AgBr$

7   where the rearrangement step can formally be represented as the "1,2-shift" of hydride

8   between adjacent carbon atoms in a carbocation

10   $CH_3CH_2CH_2^+ \rightarrow (CH_3)_2CH^+$

12   *Note 3*: Such migrations also occur in *radical*s, e.g.,

14   $PhC(CH_3)_2–CH_2\cdot \rightarrow \cdot C(CH_3)_2CH_2Ph$ (neophyl rearrangement)

16   *Note 4*: The definition also includes reactions in which an entering group takes up a

17   different position from the *leaving group*, with accompanying *bond* migration, such as

18   in the "allylic rearrangement":

20   $(CH_3)_2C=CHCH_2Br + HO^- \rightarrow (CH_3)_2C(OH)CH=CH_2 + Br^-$

22   *Note 5*: A distinction can be made between intramolecular rearrangements (or "true"

23   molecular rearrangements) and *intermolecular* rearrangements (or apparent

24   rearrangements). In the former case the atoms and groups that are common to a

25   reactant and a product never separate into independent fragments during the

26   rearrangement stage, whereas in an intermolecular rearrangement a migrating *group*

27   becomes completely free from the parent molecule and is re-attached to a different

28   position in a subsequent step, as in the Orton reaction:

30   $C_6H_5N(Cl)COCH_3 + HCl \rightarrow C_6H_5NHCOCH_3 + Cl_2$

31                                 $\rightarrow$ *o*- and *p*-$ClC_6H_4NHCOCH_3$ + HCl

32   See [327].

33   rev[3]

35   **molecular recognition**

36   Attraction between specific molecules through noncovalent interactions that often

37   exhibit electrostatic and stereochemical complementarity between the partners

38   *Note:* The partners are usually designated as *host* and *guest*, where the host

39   recognizes and binds the guest with high selectivity over other molecules of similar size

40   and shape.

1

molecularity

Number of reactant *molecular entities* that are involved in the "microscopic chemical event" constituting an *elementary reaction*.

Note 1: 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.

Note 2: A reaction with a molecularity of one is called "*unimolecular*", one with a molecularity of two "bimolecular", and of three "termolecular".

See also *chemical reaction*, *order of reaction*.

[3]

molecule

An electrically neutral entity consisting of more than one atom.

Note: Rigorously, a molecule 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*.

[3]

More O'Ferrall - Jencks diagram

Conceptual visualization of the *potential-energy surface* for a reacting system, as a function of two coordinates, usually bond lengths or bond orders.

Note 1: The diagram is useful for analyzing structural effects on transition-state geometry and energy.

Note 2: According to the *Hammond postulate*, stabilization of the products relative to the reactants (an effect parallel to the *minimum-energy reaction path*, MERP) shifts the transition state away from the product geometry, whereas destabilization of the products shifts the *transition state* towards the product geometry. As first noted by Thornton, stabilization of a structure located off the assumed MERP in a direction perpendicular to it shifts the transition state toward that more stabilized geometry (a *perpendicular effect*); destabilization shifts the transition state in the opposite direction.

1

$B^- +$ [structure with H and + charge] $+ X^-$ $BH +$ [alkene structure] $+ X^-$

d_{C-X}

‡₃ ←——— ‡₁

‡₂

$B^- +$ [structure with H and X] d_{C-H} ———→ $BH +$ [carbanion structure with X]

2
3

4   *Figure*. More O'Ferrall-Jencks diagram for *β-elimination* reaction, with reactants,
5   products, and possible *intermediate*s at the four corners.

6

7   *Case 1*: In a concerted *elimination* the transition state (‡₁) is a saddle point near the
8   centre of the diagram, and the assumed MERP follows close to the diagonal.
9   *Case 2*: If the *carbanion* intermediate is stabilized, the transition state shifts toward
10   that *intermediate*, to a transition state (‡₂) in which the C–H bond is more extensively
11   broken and the C–X bond is more intact. Conversely, if the *carbocation* intermediate is
12   stabilized, the transition state shifts towards the top-left corner of the Figure, with less
13   C–H bond breaking and more C–X bond making
14   *Case 3*: If leaving group X^- is stabilised, energy decreases along the dotted vertical
15   arrow. It follows that in the resulting transition state (‡₃) the C–H bond is more intact but
16   there is little change in the C–X bond, the shift of the transition state is the resultant of
17   a parallel (Hammond) component away from the top-right corner and a perpendicular
18   (anti-Hammond) component towards the top-left corner, yielding a transition state (‡₃)
19   with less C–H bond breaking but approximately no change in the extent of C–X bond
20   making.
21   See [229,328,329,330,331].
22   See also *Hammond Postulate*, *anti-Hammond effect*.
23   rev[3]

24

Morse potential

V(*r*)

(unit J)

Empirical function relating the potential energy of a molecule to the interatomic distance *r* accounting for the anharmonicity of bond stretching:

$$V(r) = D_e\{1 - \exp[-a(r-r_e)]\}^2$$

where D_e is the *bond-dissociation energy*, r_e is the equilibrium bond length, and *a* is a parameter characteristic of a given molecule.

See [8].

mu

μ

(1) Symbol used to designate (as a prefix) a ligand that bridges two or more atoms.

Note: If there are more than two atoms being bridged, *μ* carries a subscript to denote the number of atoms bridged.

(2) Symbol used to designate dipole moment as well as many other terms in physics and physical chemistry.

multi-centre bond

Bond in which an electron pair is shared among three or more atomic centres.

Note 1: This may be needed when the representation of a *molecular entity* solely by localized two-electron two-centre *bonds* is unsatisfactory, or when there are not enough electrons to allow one electron pair shared between two adjacent atoms.

Note 2: This is restricted to σ bonds and does not apply to species with delocalized π electrons.

Examples include the three-centre bonds in diborane B_2H_6 and in *bridged carbocation*s.

rev[3]

multident

multidentate

See *ambident*.

[3]

nanomaterial

Substance whose particles are in the size range of 1 to 100 nm.

Note: This may have chemical properties different from those of the corresponding bulk material.

1

narcissistic reaction

Chemical reaction that can be described as the *automerization or* enantiomerization of a reactant into its mirror image (regardless of whether the reactant is *chiral*).

   Examples are cited under *degenerate rearrangement* and *fluxional*.

   See [332].

   rev[3]

neighbouring-group participation

Direct interaction of the reaction centre (usually, but not necessarily, an incipient *carbenium-ion* centre) with a lone pair of electrons of an atom or with the electrons of a σ or π bond contained within the parent molecule but not *conjugated* with the reaction centre.

   Example:

   Note 1: A distinction is sometimes made between n, σ, and π participation.

   Note 2: The neighbouring group serves as a *nucleophile*, as in S_N2 reactions, except that the nucleophile is *intramolecular*, so that this step is *unimolecular*.

   Note 3: A rate increase due to neighbouring-group participation is known as anchimeric assistance.

   Note 4: Synartetic acceleration is the name given to the special case of participation by electrons on a substituent attached to a β-carbon, relative to the *leaving group* attached to the α-carbon, as in the example above. This term is deprecated.

   See also *intramolecular catalysis*, *multi-centre bond*.

   rev[3]

NHOMO

Next-to-highest occupied *molecular orbital*.

   See *subjacent orbital*.

   rev[3]

NIH shift

Intramolecular hydrogen *migration* that can be observed in enzymatic and chemical hydroxylations of *aromatic* rings, as evidenced by appropriate deuterium labelling, as in

1
2

3 *Note 1:* In enzymatic reactions the NIH shift is thought to derive from the
4 rearrangement of arene oxide *intermediate*s, but other pathways have been suggested.
5 *Note 2:* NIH stands for National Institutes of Health, where the shift was discovered.
6 See [333].
7 [3]

8

nitrene
9
10 Generic name for the species HN and substitution derivatives thereof, containing an
11 electrically neutral univalent nitrogen atom with four nonbonding electrons.
12 *Note 1*: Two nonbonding electrons may have antiparallel spins (singlet state) or
13 parallel spins (triplet state).
14 *Note 2*: The name is the strict analogue to *carbene* and, as a generic name, it is
15 preferred to a number of alternative proposed (imene, imine radical, aminylene, azene,
16 azylene, azacarbene, imin, imidogen).
17 See [97,334].
18 [3]

19

no-bond resonance
20
21 double-bond-no-bond resonance
22 Inclusion of one or more contributing structures that lack the σ bond of another
23 contributing structure.
24 *Example:*

25

26 See *hyperconjugation*.
27 rev[3]

28

nonclassical carbocation
29
30 *Carbocation* that has delocalized (bridged) bonding σ electrons.
31 See [89,335].
32 rev[3]

33

non-Kekulé structure

Compound with unpaired electrons for which no _Lewis structure_s are possible with all bonding electrons paired in single or double bonds.

Examples:

Note: For the second example ("trimethylenemethane") the _isomer_ shown (valence tautomer methylidenecyclopropane) is a _Kekulé structure_.

See [336].

nucleofuge

Leaving group that carries away the bonding electron pair in a _nucleophilic substitution_ reaction.

Example: In the _hydrolysis_ of a chloroalkane, Cl⁻ is the nucleofuge.

$$R–Cl + H_2O \rightarrow ROH + HCl$$

Note 1: Nucleofugality, commonly called leaving-group ability, characterizes the relative rates of atoms or groups to depart with the bonding electron pair from a reference substrate. Nucleofugality depends on the nature of the reference reaction and is not the reverse of _nucleophilicity_.

Note 2: Protofugality is a special type of nucleofugality, characterizing the relative rates of proton transfer from a series of _Brønsted acid_s H–X to a common _Brønsted base_.

See [194].

See also _electrofuge_, _nucleophile_.

rev[3]

nucleophile (n.), nucleophilic (adj.)

Reactant that forms a bond to its reaction partner (the _electrophile_) by donating both of its bonding electrons.

Note 1: A "_nucleophilic substitution_ reaction" is a heterolytic reaction in which the reagent supplying the entering group acts as a nucleophile.

Example:

$$MeO^- \text{ (nucleophile)} + EtCl \rightarrow MeOEt + Cl^- \text{ (}nucleofuge\text{)}$$

1   *Note 2:* Nucleophilic reagents are *Lewis base*s.

2   *Note 3:* The term "nucleophilic" is also used to designate the apparent polar character

3   of certain *radical*s, as inferred from their higher relative reactivity with reaction sites of

4   lower electron density.

5   See also *nucleophilicity, order of reaction.*

6   [3]

7

nucleophilic catalysis

9   *Catalysis* by a *Lewis base*, involving conversion of a substrate with low *electrophilicity*

10   into an *intermediate* with higher electrophilicity.

11   *Example 1: hydrolysis* of acetic anhydride in aqueous solution, catalysed by 4-

12   (dimethylamino)pyridine

13   $Me_2NC_5H_4N + (CH_3CO)_2O \rightarrow (Me_2NC_5H_4NCOCH_3)^+ + CH_3CO_2^-$

14   then $(Me_2NC_5H_4COCH_3)^+ + H_2O \rightarrow Me_2NC_5H_4N + CH_3CO_2H + H^+_{aq}$

15

16   *Example 2:* S_N2 reaction of CH_3CH_2Cl with HO^-, catalyzed by I^-:

17

18   $CH_3CH_2Cl + I^- \rightarrow Cl^- + CH_3CH_2I$, then $CH_3CH_2I + HO^- \rightarrow CH_3CH_2OH + I^-$

19

20   See also *nucleophilicity.*

21   rev[3]

22

nucleophilic substitution

24   Heterolytic reaction in which an entering group adds to the electrophilic part of the

25   substrate and in which the leaving group, or *nucleofuge*, retains both electrons of the

26   bond that is broken, whereupon it becomes another potential *nucleophile*.

27   *Example*:

28

29   CH_3Br (substrate) + HO^- (nucleophile) $\rightarrow CH_3OH + Br^-$ (nucleofuge)

30

31   *Note 1:* It is arbitrary to emphasize the nucleophile and ignore the feature that this is

32   also an electrophilic substitution, but the distinction depends on the nucleophilic nature

33   of the reactant that is considered to react with the *substrate.*

34   *Note 2:* Nucleophilic substitution reactions are designated as S_N1 or S_N2, depending

35   on whether they are unimolecular or bimolecular, respectively. Mechanistically, these

36   correspond to two-step and one-step processes, respectively. S_N1 reactions follow first-

37   order kinetics but S_N2 reactions do not always follow second-order kinetics.

38   See *order of reaction, rate coefficient.*

39

40

1 **nucleophilicity**

2 Relative reactivity of a *nucleophile* toward a common *electrophile*.

3   *Note 1*: The concept is related to *Lewis basicity*. However, whereas the Lewis

4 basicity of a base B: is measured by its *equilibrium* constant for *adduct* formation with

5 a common acid A, the nucleophilicity of a *Lewis base* B: is measured by the *rate*

6 *coefficient* for reaction with a common *substrate* A–Z, often involving formation of a

7 bond to carbon.

8   *Note 2*: *Protophilicity* is a special case of nucleophilicity, describing the relative rates

9 of reactions of a series of Lewis bases B: with a common *Brønsted acid* H–Z. The term

10 "protophilicity" is preferred over the alternative term "kinetic basicity" because *basicity*

11 refers to equilibrium constants, whereas "philicity" (like "fugality") refers to *rate*

12 *constant*s.

13   See [192,193,307].

14   See also *Brønsted basicity*, *electrophilicity*, *Lewis basicity*, *Mayr-Patz equation*,

15 *Ritchie equation*, *Swain-Scott equation*.

16   rev[3]

17

18 **n-σ* delocalization (n-σ* no-bond resonance)**

19 *Delocalization* of a lone pair (*n*) into an antibonding σ-orbital (σ*).

20   See also *anomeric effect*, *hyperconjugation*, *resonance*.

21   [3]

22

23 **octanol-water partition ratio** (K_{OW}):

24 Equilibrium concentration of a substance in octan-1-ol divided by its equilibrium

25 concentration in water.

26   *Note:* This is a measure of the *lipophilicity* of a substance. It is used in

27 pharmacological studies and in the assessment of environmental fate and transport of

28 organic chemicals.

29   See [337,338].

30   See also *partition ratio*.

31

32 **octet rule**

33 Electron-counting rule that the number of lone-pair electrons on a first-row atom plus

34 the number of electron pairs in that atom's bonds should be 8.

35

36 **onium ion**

37 (1) Cation derived by addition of a *hydron* to a mononuclear parent hydride of the

38 nitrogen, chalcogen, and halogen family, e.g., H_4N^+ ammonium ion.

39 (2) Derivative formed by substitution of the above parent ions by univalent groups, e.g.,

40 $(CH_3)_2SH^+$ dimethylsulfonium (dimethylsulfanium), $(CH_3CH_2)_4N^+$ tetraethylammonium.

1   See [97].

2   See also *carbenium ion*, *carbonium ion*.

3   rev[3]

4

5   **optical yield**

6   Ratio of the optical purity of the product to that of the *chiral* precursor or reactant.

7   *Note 1:* This should not be confused with *enantiomeric excess*.

8   *Note 2:* The optical yield is not related to the chemical yield of the reaction.

9   See [11].

10   See *stereoselectivity*.

11   [3]

12

13   **orbital (atomic or molecular)**

14   *Wavefunction* depending on the spatial coordinates of only one electron.

15   *Note:* An orbital is often illustrated by sketching contours, often very approximate, on

16   which the wavefunction has a constant value or by indicating schematically the

17   envelope of the region of space in which there is an arbitrarily fixed high probability (say

18   95 %) of finding the electron occupying that region, and affixing also the algebraic sign

19   (+ or −) of the wavefunction in each part of that region, or suggesting the sign by

20   shading.

21   *Examples:*

22

23   1s $2p_z$ sp^3 hybrid   bonding MO

24

25   See *atomic orbital*, *molecular orbital*.

26   See [8].

27   rev[3]

28

29   **orbital steering**

30   Concept expressing the principle that the energetically favourable stereochemistry of

31   approach of two reacting species is governed by the most favourable overlap of their

32   appropriate *orbital*s.

33   rev[3]

34

35   **orbital symmetry**

36   Behaviour of an *atomic orbital* or *molecular orbital* under molecular symmetry

37   operations, such that under reflection in a symmetry plane or rotation by 180° around a

1   symmetry axis the phase of the orbital is either unchanged (symmetric) or changes sign

2   (antisymmetric), whereby positive and negative lobes are interchanged.

3   *Examples:*

4   (1) The orbital of an idealized single bond is σ, with cylindrical symmetry.

5   (2) A p-orbital or π-bond orbital has π symmetry, i.e., it is antisymmetric with respect

6   to reflection in a plane passing through the atomic centres with which it is associated.

7   (3) The *HOMO* of 1,3-butadiene (illustrated below by its component atomic orbitals)

8   is antisymmetric with respect to 180º rotation about an axis through the C2–C3 bond

9   and perpendicular to the molecular plane.

16   See [107,123].

17   See also *conservation of orbital symmetry*, *sigma*, *pi*.

18   rev[3]

20   **order of reaction**

21   Exponent α, independent of concentration and time, in the differential rate equation

22   (*rate law*) relating the macroscopic (observed, empirical, or phenomenological) rate of

23   reaction v to c_A the concentration of one of the chemical species present, as defined by

$$\alpha = \left(\frac{\partial \ln\{v\}}{\partial \ln\{c_A\}} \right)_{[B]\ldots}$$

26   The argument in the ln function should be of dimension 1. Thus, reduced quantities

27   should be used, i.e., the quantity divided by its unit, $\{v\} = v/(\text{mol dm}^{-3}\text{ s}^{-1})$ and $\{c_A\} =$

28   $c_A/(\text{mol dm}^{-3})$.

29   *Note 1:* A rate equation can often be expressed in the form $v = k\,[A]^{\alpha}[B]^{\beta}\ldots$,

30   describing the dependence of the rate of reaction on the concentrations [A], [B],...,

31   where exponents α, β, ... are independent of concentration and time and k is

32   independent of [A], [B], ... In this case the reaction is said to be of order α with respect

33   to A, of order β with respect to B,..., and of (total or overall) order $n = \alpha + \beta + \ldots$. The

34   exponents α, β,... sometimes called "partial orders of reaction", can be positive or

35   negative, integral, or rational nonintegral numbers.

36   *Note 2:* For an *elementary reaction* a partial order of reaction is the same as the

37   stoichiometric number. The overall order is then the same as the *molecularity*. For

38   stepwise reactions there is no general connection between stoichiometric numbers and

1   partial orders. Such reactions may have more complex rate laws, so that an apparent
2   order of reaction may vary with the concentrations of the *chemical species* involved and
3   with the progress of the reaction: in such cases it is not useful to speak of orders of
4   reaction, although apparent orders of reaction may be deducible from initial rates.

5   *Note 3:* In a *stepwise reaction,* orders of reaction may in principle be assigned to the
6   elementary steps.

7   *Note 4:* For chemical rate processes occurring in systems for which concentration
8   changes are not measurable, as in the case of a dynamic equilibrium $aA \rightleftarrows pP$, and if a
9   *chemical flux* ϕ_{-A} is found experimentally (e.g., by NMR *line-shape analysis*) to be
10 related to the concentration of A and to concentrations of other species B, ..., by the
11 equation

13      $\phi_{-A} = k[A]^{\alpha}[B]^{\beta} ...$

15 then the reaction is of order α with respect to A... and of total (or overall) order
16 $(=\alpha + \beta +...)$.

17 *Note 5:* If the overall rate of reaction is given by

19      $v = k[A]^{\alpha}[B]^{\beta}$

21 but [B] remains constant in any particular sample (but can vary from sample to sample),
22 then the order of the reaction in A will be α, and the rate of disappearance of A can be
23 expressed in the form

25      $v_A = k_{obs}[A]^{\alpha}$

27 The proportionality factor k_{obs} is called the "observed rate coefficient" and is related to
28 the *rate constant k* by

30      $k_{obs} = k[B]^{\beta}$

32   *Note 6:* For the frequent case where $\alpha = 1$, k_{obs} is often referred to as a "pseudo-first-
33 order rate coefficient".

34   See [13].
35   See also *kinetic equivalence*, *rate coefficient*, *rate constant*.
36   rev[3]

1 **organocatalysis**

2 *Catalysis* by small organic molecules, as distinguished from catalysis by (transition)

3 metals or enzymes.

4   *Note 1:* Frequently used organocatalysts are secondary amines (covalent catalysis

5 by generation of enamines or of iminium ions as *reactive intermediates*) and thioureas

6 (hydrogen-bonding catalysis).

7   *Note 2*: Organocatalysts are often employed for *enantioselectivity*.

8   *Note 3*: The mechanisms employed by organocatalysts are examples of *general acid*

9 *catalysis*, *general base catalysis*, *nucleophilic catalysis*, *specific acid catalysis*, *specific*

10 *base catalysis*.

11   See [339,340,341,342].

12

13 **outer-sphere electron transfer**

14 Feature of an *electron transfer* between redox centres not sharing a common atom or

15 group.

16   *Example:*

17         $MnO_4^- + Mn^*O_4^{2-} \rightleftarrows MnO_4^{2-} + Mn^*O_4^-$

18   *Note 1:* In the *transition state* the interaction between the relevant electronic orbitals

19 of the two centres is weak (below 20 kJ mol^{-1}), and the electron(s) must tunnel through

20 space.

21   *Note 2:* If instead the donor and the acceptor exhibit a strong electronic coupling,

22 often through a *ligand* that bridges both, the reaction is described as *inner-sphere*

23 *electron transfer*.

24   *Note 3:* These two terms derive from studies of metal complexes, and for organic

25 reactions the terms "nonbonded' and 'bonded" electron transfer are often used.

26   See [9,182,343].

27   rev[3]

28

29 **oxidation**

30 (1) Removal of one or more electrons from a *molecular entity*.

31 (2) Increase in the *oxidation number* of an atom within a *substrate*, see [344].

32 (3) Gain of oxygen and/or loss of hydrogen by an organic substrate.

33   *Note 1:* All oxidations meet criterion (2) and many meet criterion (3), but this is not

34 always easy to demonstrate. Alternatively, an oxidation can be described as the

35 *transformation* of an organic substrate by removal of one or more electrons from the

36 substrate, often accompanied by gain or loss of water, *hydrons*, and/or hydroxide, or by

37 *nucleophilic* substitution, or by *molecular rearrangement*.

38   *Note 2:* This formal definition allows the original idea of oxidation (combination with

39 oxygen), together with its extension to removal of hydrogen, as well as processes

40 closely akin to this type of transformation (and generally regarded in organic chemistry

1 to be oxidations and to be effected by "oxidizing agents") to be descriptively related to
2 definition (1). For example the oxidation of methane to chloromethane may be
3 considered as

4 $\quad$ $CH_4 - 2e^- - H^+ + HO^- = CH_3OH$ $\qquad$ (oxidation),

5 followed by

6 $\quad$ $CH_3OH + HCl$ $\qquad$ $= CH_3Cl + H_2O$ $\quad$ (neither oxidation nor reduction)

7 $\quad$ rev[3]

8

9 **oxidation number**

10 oxidation state

11 Number assigned to a carbon atom in a _covalent_ organic compound according to

12

13 $\quad$ $N_{Ox} = N_X + N_O + N_N - N_H - N_M$

14

15 where N_X, N_O, N_N, N_H, and N_M are the numbers of bonds to halogen, oxygen (or sulfur),
16 nitrogen, hydrogen, and a metal, respectively.

17 $\quad$ _Examples:_

18

19 $\quad$ CH_3MgBr (-4), CH_3CH_3 (-3), $CH_2=CH_2$ (-2), CH_3OH (-2), CH_2Cl_2 (0),
20 $\quad$ CH_3**C**$H=O$ (+1), HCN (+2), CCl_4 (+4).

21

22 $\quad$ _Note 1:_ This assignment is based on the convention that each attached atom more
23 electronegative than carbon contributes +1, while each atom less electronegative
24 (including H) contributes -1, and an attached carbon contributes zero.

25 $\quad$ _Note 2:_ Oxidation numbers are not significant in themselves, but changes in oxidation
26 number are useful for recognizing whether a reaction is an oxidation or a reduction or
27 neither.

28 $\quad$ _Note 3_: A different system is used for transition-metal species [345].

29 $\quad$ See also _electronegativity_, _oxidation_.

30 $\quad$ rev[3]

31

32 **oxidative addition**

33 _Insertion_ of the metal of a metal complex into a _covalent bond_ involving formally an
34 overall two-electron loss on one metal or a one-electron loss on each of two metals,
35 i.e.,

36 $\quad$ $L_nM^m + XY \rightarrow L_nM^{m+2}(X)(Y)$

37 or $\quad$ $2 L_nM^m + XY \rightarrow L_nM^{m+1}(X) + L_nM^{m+1}(Y)$

38 $\quad$ rev[3]

39

1
2
3　　1　**oxidative coupling**
4
5　　2　Coupling of two *molecular entities* through an oxidative process, usually catalysed by a
6　　3　transition-metal compound.
7
8　　4　　　*Example* (where the oxidant can be O_2 or Cu(II) or others):
9
10　　5
11
12　　6
13　　7　rev[3]
14
15　　8
16
17　　9　**parallel effect**
18　　10　Change of the position of the *transition state* upon stabilization or destabilization of a
19　　11　structure (or structures) along the assumed *minimum-energy reaction path*.
20
21　　12　　　See *Hammond postulate*, *More O'Ferrall - Jencks diagram*.
22　　13
23　　14　**parallel reaction**
24
25　　15　　　See *composite reaction*.
26　　16　　　[3]
27　　17
28
29　　18　**paramagnetism**
30　　19　Property of substances having a magnetic susceptibility greater than 0, whereby they
31　　20　are drawn into a magnetic field.
32
33　　21　　　See also *diamagnetism*.
34　　22　　　[3]
35　　23
36
37　　24　**partial rate factor** p_f^Z, m_f^Z
38　　25　*Rate constant* for substitution at one specific site in an *aromatic* compound divided by
39　　26　the rate constant for substitution at one position in benzene.
40
41　　27　　　*Note 1:* The partial rate factor p_f^Z for para-substitution in a monosubstituted benzene
42　　28　C_6H_5Z is related to the rate constants $k(C_6H_5Z)$ and $k(C_6H_6)$ for the total reactions (i.e.,
43　　29　at all positions) of C_6H_5Z and benzene, respectively, and f_{para} (the fraction of para-
44　　30　substitution in the total product formed from C_6H_5Z, usually expressed as a percentage)
45　　31　by the relation
46　　32

47
48　　33
49

$$p_f^Z \;=\; \frac{6k(C_6H_5Z)}{k(C_6H_6)}\, f_{para}$$

50　　34
51　　35　Similarly for meta-substitution:
52　　36
53
54
55　　37

$$m_f^Z \;=\; \frac{6k(C_6H_5Z)}{2k(C_6H_6)}\, f_{meta}$$

56
57
58
59
60

The symbols f_p^Z, f_m^Z, f_o^Z are also in use.

Note 2: The term applies also to the *ipso* position, and it can be extended to other substituted *substrate*s undergoing parallel reactions at different sites with the same reagent according to the same *rate law*.

See [262,346,347].

See also *selectivity*.

rev[3]

partition ratio (partition constant, distribution ratio) *P*

Concentration of a substance in one phase divided by its concentration in another phase, at equilibrium.

Example, for an aqueous/organic system the partition ratio (or distribution ratio *D*) is given by

$$P = c_{org}(A)/c_{aq}(A)$$

Note 1: The most common way of applying *P* in *correlation analysis* or *quantitative structure-activity relationships* is as lg *P*.

Note 2: The parameter *P* is extensively used as an indicator of the capacity of a molecular entity to cross biological membranes by passive diffusion.

Note 3: The term *partition coefficient* is in common usage in toxicology but is not recommended for use in chemistry and should not be used as a synonym for partition constant, partition ratio, or distribution ratio.

See [167,232].

See also *Hansch constant, octanol-water partition ratio*.

pericyclic reaction

Chemical reaction in which *concerted* reorganization of bonding takes place throughout a cyclic array of continuously bonded atoms.

Note 1: It may be viewed as a reaction proceeding through a fully *conjugated* cyclic transition state.

Note 2: The term embraces a variety of processes, including *cycloaddition, cheletropic reaction, electrocyclic reaction* and *sigmatropic rearrangement*, etc. (provided they are *concerted*).

See also *pseudopericyclic*.

[3]

permittivity, relative ε_r

dielectric constant (obsolete)

1 Measure of the reduction of the magnitude of the potential energy of interaction between
2 two charges on going from vacuum to a condensed medium, expressed as the ratio of
3 the former to the latter.
4   *Note*: The term dielectric constant is obsolete. Moreover, the dielectric constant is
5 not a constant since it depends on frequency.
6   See [12].
7

perpendicular effect
9 Change of the position of the transition state upon stabilization or destabilization of a
10 structure (or structures) that lies off the assumed *minimum-energy reaction path*.
11   See *anti-Hammond effect*, *Hammond postulate*, *More O'Ferrall - Jencks diagram*.
12   rev[3]
13

persistence
15 Characteristic of a *molecular entity* that has an appreciable *lifetime* (minutes or
16 nanoseconds or other, depending on context).
17   *Note 1*: Dilute solution or inert solvent may be required for persistence.
18   *Note 2*: Persistence is a kinetic or reactivity property, whereas, in contrast, stability
19 (being *stable*) is a thermodynamic property.
20   See [348].
21   See also *transient*.
22   rev[3]
23

pH-rate profile
25 Plot of observed *rate coefficient*, or more usually the decadic logarithm of its numerical
26 value, against solution pH, other variables being kept constant.
27   [3]
28

phase-transfer catalysis
30 Enhancement of the rate of a reaction between *chemical species* located in different
31 phases (immiscible liquids or solid and liquid) by addition of a small quantity of an agent
32 (called the phase-transfer *catalyst*) that extracts one of the reactants, most commonly
33 an anion, into the other phase so that reaction can proceed.
34   *Note 1*: These catalysts are often *onium ion*s (e.g., tetraalkylammonium ions) or
35 complexes of inorganic cations (e.g., as *crown ether* complexes).
36   *Note 2*: The catalyst cation is not consumed in the reaction although an anion
37 exchange does occur.
38   *Example:*
39   $CH_3(CH_2)_7Cl$ in decane + aqueous Na^+CN^- + catalytic $PhCH_2N(CH_2CH_3)_3^+$
40   = $CH_3(CH_2)_7CN$ + aqueous Na^+Cl^-

1   rev[3]

2

phenonium ion
    See *bridged carbocation*.
    [3]

photochromism
Reversible transformation of a *molecular entity* between two forms, A and B, having different absorption spectra, induced in one or both directions by absorption of electromagnetic radiation.
    Note 1: The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (photochromism of type T) or photochemically (photochromism of type P).
    Note 2: The spectral change is typically, but not necessarily, of visible colour.
    Note 3: An important parameter is the number of cycles that a photochromic system can undergo.
    See [9].

photolysis
Bond cleavage induced by ultraviolet, visible, or infrared radiation.
    Example:
        $Cl_2 \rightarrow 2\ Cl^{\bullet}$
    Note: The term is used incorrectly to describe irradiation of a sample without any bond cleavage, although in the term "flash photolysis" this usage is accepted.
    See [9].
    [3]

photostationary state
Steady state reached by a chemical system undergoing photochemical reaction, such that the rates of formation and disappearance are equal for each of the transient *molecular entities* formed.
    See [9].

pi-adduct
    See *π-adduct*.

pi-bond
    See *σ, π*.

polar aprotic solvent
See *dipolar non-HBD solvent*.
[3]

polar effect
All the interactions whereby a *substituent* on a reactant molecule RY modifies the electrostatic forces operating at the reaction centre Y, relative to the reference standard R_oY.
Note 1: These forces may be governed by charge separations arising from differences in the *electronegativity* of atoms (leading to the presence of dipoles), by the presence of monopoles, or by electron *delocalization*.
Note 2: It is distinguished from a *steric effect*.
Note 3: Sometimes, however, the term polar effect is taken to refer to the influence, other than steric, that non-conjugated substituents exert on reaction rates or equilibria, thus excluding effects of electron delocalization between a substituent and the molecular framework to which it is attached.
See also *electronic effects (of substituents)*, *field effect*, *inductive effect*.
[3]

polar solvent
Liquid composed of molecules with a significant dipole moment, capable of dissolving ions or other molecules with significant dipole moments.
See *polarity*.
rev[3]

polarity (of a bond**)**
Characteristic of a bond between atoms of different *electronegativity*, such that the electrons in that bond are not shared equally.

polarity (of a solvent**)**
Overall solvation capability (solvation power) of a solvent toward solutes, which depends on the action of all possible intermolecular interactions between solute ions or molecules and solvent molecules, excluding interactions leading to definite chemical alterations of the ions or molecules of the solute.
Note: Quantitative measures of solvent polarity include relative *permittivity* (dielectric constant) and various spectroscopic parameters.
See [17].
See *solvent parameter*.
rev[3]

1 **polarizability**

2 α

3 (SI unit: C m^2 V^{-1})

4 electric polarizability

5 Induced dipole moment, $\mu_{induced}$, divided by applied electric field strength **E**

6 $\quad \alpha = \mu_{induced}/\boldsymbol{E}$

7 *Note 1*: The polarizability represents the ease of distortion of the electron cloud of a

8 *molecular entity* by an electric field (such as that due to the proximity of a charged

9 species).

10 *Note 2*: Polarizability is more often expressed as polarizability volume, with unit cm^3,

11 where ε_0 is the *permittivity* of vacuum:

12

13 $\quad \alpha \,/\text{cm}^3 \;=\; \dfrac{10^6}{4\pi\varepsilon_0}\,\dfrac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}E}$

14

15 *Note 3*: In general, polarizability is a tensor that depends on direction, for example,

16 depending on whether the electric field is along a bond or perpendicular to it, and the

17 induced dipole may not even be along the direction of the electric field. However, in

18 ordinary usage the term refers to the mean polarizability, the average over three

19 rectilinear axes of the molecule.

20 rev[3]

21

22 **polydent**

23 polydentate

24 See *ambident*.

25 [3]

26

27 **potential-energy profile**

28 Curve describing the variation of the potential energy of a system of atoms as a function

29 of a single coordinate.

30 *Note 1*: For an *elementary reaction* the relevant coordinate is the *reaction coordinate*,

31 which is a measure of progress along the *minimum-energy reaction path* (MERP) from

32 a saddle point on a *potential-energy surface* in each direction toward adjacent energy

33 minima. For a stepwise reaction it is the succession of reaction coordinates for the

34 successive individual reaction steps. For a reaction involving a *bifurcation* each branch

35 requires a different reaction coordinate and has its own profile.

36 *Note 2*: A profile constructed as a function of an arbitrary internal coordinate (for

37 example, a bond distance) is not guaranteed to pass through a saddle point on the

38 corresponding potential-energy surface; in order to do so, it must be smooth,

1 continuous, and follow the path of lowest energy connecting the reactant and product
2 energy minima.
3 *Examples:* (one-step reaction, two-step reaction)
4

5 reaction coordinate   reaction coordinate
6

7 See [349].
8 See also *Gibbs energy diagram*, *potential-energy surface*.
9 rev[3]

10

11 **potential-energy surface** (**PES**)
12 Surface describing the variation within the *Born-Oppenheimer approximation* of the
13 potential energy of a system of atoms as a function of a set of internal coordinates.
14 *Note 1*: A minimum on a PES is characterized by positive curvature in all directions
15 and corresponds to a structure that is stable with respect to small displacements away
16 from its equilibrium geometry; for this structure (a reactant, *intermediate* or product) all
17 vibrational frequencies are real. A saddle point is characterized by positive curvature in
18 all directions except for one with negative curvature and corresponds to a transition
19 structure, for which one vibrational frequency is imaginary. A local maximum is
20 characterized by negative curvatures in two (or more) directions and has two (or more)
21 imaginary frequencies; it is sometimes called a second-order (or higher-order) saddle
22 point.
23 *Note 2*: It is usual to select only two coordinates in order to represent the surface,
24 with potential energy as the third dimension, or alternatively as a two-dimensional
25 contour map. For example, a PES for a simple reacting triatomic system A–B + C →
26 A + B–C, could be constructed using the A$\cdots$B and B$\cdots$C distances as two internal
27 coordinates; the third independent coordinate could be the ABC angle or the A$\cdots$C
28 distance, and its value could either be kept fixed or else be relaxed to minimize the
29 energy at each point on the (A$\cdots$B, B$\cdots$C) surface.
30 *Note 3*: The path of steepest-descent from a saddle point in each direction towards
31 adjacent energy minima defines a *minimum-energy reaction path* (MERP) that is
32 equivalent to the energetically easiest route from reactants to products. The change in
33 potential energy along this path across the PES defines a *potential-energy profile* for

the *elementary reaction*. Progress along this path is measured by the value of the *reaction coordinate*.

Note 4: In general there is neither a unique set of internal coordinates nor a unique choice of two coordinates with which to construct a PES of reduced dimensionality. Consequently there is no guarantee of a smooth and continuous PES containing a saddle point connecting reactant and product minima.

See [8,73,350,351].

See: *bifurcation*, *minimum-energy reaction path*, *potential-energy profile*, *reaction coordinate*, *transition structure*.

rev[3]

potential of mean force (PMF)

Free energy as a function of a set of coordinates, the negative gradient of which gives the average force acting on that configuration averaged over all other coordinates and momenta within a statistical distribution. If the averaging is performed within a canonical ensemble (constant volume, temperature, and number of particles) the PMF is equivalent to the Helmholtz energy, but if it is performed within an isobaric-isothermal ensemble (constant pressure, temperature, and number of particles) the PMF is equivalent to the Gibbs energy.

Note 1: Commonly, the PMF acting upon a selected geometric variable and averaged over the coordinates and momenta of all other geometric variables is evaluated for a succession of constrained values of the selected variable, thereby generating (generically) a *free-energy* profile with respect to the selected *reaction coordinate* (e.g., a bond distance or angle, or a combination of internal coordinates); specifically this is either a Helmholtz-energy or a Gibbs-energy profile, depending upon the choice of ensemble for the statistical averaging within a computational simulation.

Note 2: Selection of two geometric variables as reaction coordinates allows a free-energy surface to be computed as a two-dimensional PMF.

Note 3: Molecular simulations often yield Helmholtz energies, not Gibbs energies, but for condensed phases the difference is usually neglected.

See: *free energy*, *reaction coordinate*.

pre-association

Step on the *reaction path* of some *stepwise reaction*s in which the *molecular entity* C forms an encounter pair or *encounter complex* with A prior to the reaction of A to form product.

Example:

1

2   *Note 1*: In this mechanism the *chemical species* C may but does not necessarily
3   assist the formation of B from A, which may itself be a *bimolecular* reaction with some
4   other reagent.
5   *Specific example* (aminolysis of phenyl acetate)*:*
6

7
8
9   *Note* 2: Pre-association is important when B is too short-lived to permit B and C to
10   come together by diffusion. In the specific example, $T^{\pm}$ would dissociate faster than
11   general acid HA can diffuse to it. Experimentally, the Brønsted α is > 0, which is
12   inconsistent with *rate-limiting* diffusion and *hydron* transfer.
13   See [352].
14   See also *Brønsted relation*, *microscopic diffusion control*, *spectator mechanism*.
15   rev[3]
16

precursor complex
18   See *encounter complex*.
19   [3]
20

pre-equilibrium
22   prior equilibrium
23   Rapid reversible step preceding the *rate-limiting step* in a *stepwise reaction*.
24   *Example:*

25
26
27   See also *kinetic equivalence*, *steady state*.

1 [3]

2

3 **pre-exponential factor**

4 See *energy of activation*, *entropy of activation*.

5 [3]

6

7 **principle of nonperfect synchronization**

8 Consideration applicable to reactions in which there is a lack of synchronization

9 between bond formation or bond rupture and other changes that affect the stability of

10 products and reactants, such as *resonance*, *solvation*, electrostatic, *hydrogen bonding*

11 and *polarizability* effects.

12 *Note*: The principle states that a product-stabilizing factor whose development lags

13 behind bond changes at the *transition state*, or a reactant-stabilizing factor whose loss

14 is ahead of bond changes at the transition state, increases the *intrinsic barrier* and

15 decreases the *rate constant* of a reaction. For a product-stabilizing factor whose

16 development is ahead of bond changes, or a reactant-stabilizing factor whose loss lags

17 behind bond changes, the opposite relations hold. The reverse effects are observable

18 for factors that destabilize a reactant or product.

19 See [108].

20 See also *imbalance*, *synchronous*.

21

22 **prior equilibrium**

23 See *pre-equilibrium*.

24 [3]

25

26 **product-determining step**

27 Step of a *stepwise reaction* in which the product distribution is determined.

28 *Note*: The product-determining step may be identical to, or may occur later than, the

29 *rate-determining step* in the reaction.

30 [3]

31

32 **product-development control**

33 Case of *kinetic control* in which the *selectivity* of a reaction parallels the relative

34 (thermodynamic) stabilities of the products.

35 *Note*: Product-development control arises because whatever effect stabilizes or

36 destabilizes a product is already operative at the *transition state*. Therefore it is usually

37 associated with a transition state occurring late on the *minimum-energy reaction path*.

38 See also *steric-approach control*, *thermodynamic control*.

39 [3]

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1 **promotion**

2   See *pseudo-catalysis*.

3   [3]

4

5 **propagation**

6   See *chain reaction*.

7   [3]

8

9 **propargylic substitution**

10   See *allylic substitution reaction*.

11

12 **protic**

13   See *protogenic*.

14   [3]

15

16 **protic solvent**

17 Solvent that is capable of acting as a *hydrogen-bond* donor.

18   See *HBD solvent*.

19

20 **protofugality**

21 special case of *nucleofugality*, describing the relative rates of transfer of a proton (more

22 generally: *hydron*) from a series of *Brønsted acids* H–X to a common *Brønsted base*.

23   *Note:* This term has the advantage over the commonly used "kinetic acidity" that

24 philicity and fugality are associated with kinetics, while acidity and basicity are

25 associated with thermodynamics.

26   See [194].

27   See also *Brønsted acidity, nucleofugality, protophilicity*.

28

29 **protogenic** (solvent)

30 HBD (hydrogen bond donor) solvent.

31 Capable of acting as a proton (*hydron*) donor.

32   *Note 1*: Such a solvent may be a strong or weak *Brønsted acid*.

33   *Note 2*: The term is preferred to the synonym *protic* or to the more ambiguous

34 expression acidic.

35   See *protophilic solvent*.

36   [3]

37

38 **protolysis**

39 proton (*hydron*)-transfer reaction.

1   *Note*: Because of its misleading similarity to *hydrolysis*, *photolysis*, etc., this use is
2   discouraged.
3   See also *autoprotolysis*.
4   rev[3]
5

proton affinity
7   Negative of the enthalpy change in the gas phase reaction between a proton (more
8   appropriately *hydron*) and the *chemical species* concerned, usually an electrically
9   neutral or anionic species, to give the *conjugate acid* of that species.
10   *Note 1*: For an anion A$^-$, the proton affinity is the negative of the enthalpy of the
11   heterolytic dissociation (in the gas phase) of the *Brønsted acid* HA.
12   *Note 2*: Proton affinity is often, but unofficially, abbreviated as PA.
13   *Note 3:* Affinity properly refers to Gibbs energy.
14   See also *gas phase basicity, gas phase acidity*.
15   See [2]. See also [213,353].
16   rev[3]
17

protonation
19   Attachment of the ion $^1H^+$ (of relative atomic mass $\approx$ 1).
20   See also *hydronation*.
21

proton–transfer reaction
23   Chemical reaction, the main feature of which is the intermolecular or intramolecular
24   transfer of a proton (*hydron*) from one binding site to another.
25   *Example:*
26       $CH_3COOH + (CH_3)_2C=O \rightarrow CH_3CO_2^- + (CH_3)_2C=OH^+$
27   *Note*: In the detailed description of proton-transfer reactions, especially of rapid
28   proton transfers between electronegative atoms, it should always be specified whether
29   the term is used to refer to the overall process (including the more-or-less *encounter-*
30   *controlled* formation of a hydrogen-bonded complex and the separation of the products)
31   or just to the proton-transfer event (including solvent rearrangement) by itself.
32   See also *autoprotolysis*, *microscopic diffusion control*, *tautomerism*.
33   [3]
34

protophilic (solvent)
36   See *HBA (hydrogen bond acceptor) solvent*.
37   rev[3]
38

39

40

protophilicity

Special case of *nucleophilicity*, describing the relative rates of reactions of a series of *Lewis base*s with a common *Brønsted acid*. This term has the advantage over the commonly used "kinetic basicity" that philicity and fugality are associated with kinetics, while acidity and basicity are associated with thermodynamics.

See [194].

See also *Brønsted basicity, nucleophilicity, protofugality*.

prototropic rearrangement (prototropy)

See *tautomerization*.

[3]

pseudo-catalysis

Increase of the rate of a reaction by an acid or base present in nearly constant concentration throughout a reaction in solution (owing to buffering or to the use of a large excess), even though that acid or base is consumed during the process, so that the acid or base is not a *catalyst* and the phenomenon strictly cannot be called *catalysis* according to the established meaning of these terms in chemical kinetics.

Note 1: Although the *mechanism* of such a process is often closely related to that of a catalysed reaction, it is recommended that the term pseudo-catalysis be used in these and analogous cases. 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 the hydrolysis of an amide should be described as pseudo-catalysis because the acid pseudo-catalyst is stoichiometrically consumed during the reaction through formation of an ammonium ion.

Note 2: 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*.

Note 3: The terms acid- and base-promoted, acid- and base-accelerated, and acid- and base-induced are sometimes used for reactions that are pseudo-catalysed by or bases. However, the term promotion also has a different meaning in other chemical contexts.

rev[3]

pseudo-first-order rate coefficient

See *order of reaction, rate coefficient*.

[3]

1 **pseudopericyclic**

2 *Feature of a concerted transformation* in which the primary changes in bonding occur

3 within a cyclic array of atoms but in which one (or more) nonbonding and bonding

4 *atomic orbital*s interchange roles.

5   *Examples:* enol-to-enol *tautomerism* of 4-hydroxypent-3-en-2-one (where the

6 electron pairs in the O–H bond and in the lone pair on the other O are in σ orbitals

7 whereas the other three electron pairs are in π orbitals) and hydroboration (where the

8 B uses an sp^2 bonding orbital and a vacant p orbital)

9

10
11

12   *Note:* Because the atomic orbitals that interchange roles are orthogonal, such a

13 reaction does not proceed through a fully *conjugated transition state* and is thus not a

14 pericyclic reaction. It is therefore not governed by the rules that express *orbital*

15 *symmetry* restrictions applicable to pericyclic reactions.

16   See [354,355].

17   See also *coarctate*.

18   rev[3]

19

20 **push-pull conjugation**

21 Feature of an extended conjugated π system bearing an electron donor group at one

22 end and an electron acceptor group at the other end.

23   See [356].

24   See also *cross-conjugation*.

25

26 **pyrolysis**

27 *Thermolysis*, usually associated with exposure to a high temperature.

28   See also *flash vacuum pyrolysis*.

29   [3]

30

31 **π-adduct (pi-adduct)**

32 *Adduct* formed by electron-pair donation from a π *orbital* into a σ* orbital, or from a σ

33 orbital into a π* orbital, or from a π orbital into a π* orbital.

1   *Example:*

2

3   *Note*: Such an adduct has commonly been known as a π *complex*, but, as the
4   bonding is not necessarily weak, it is better to avoid the term complex, in accordance
5   with the recommendations in this Glossary.
6   See also *coordination*.
7   [3]

8

9   **π-bond** (pi bond)
10   Interaction between two atoms whose p *orbital*s overlap sideways.
11   *Note:* The designation as π is because the p orbitals are antisymmetric with respect
12   to a defining plane containing the two atoms.
13   See *sigma, pi.*
14   rev[3]

15

16   **π-complex**
17   See *π-adduct.*
18   [3]

19

20   **π-electron acceptor**
21   *Substituent* capable of electron withdrawal by resonance (e.g., NO_2).
22   See *electronic effect, polar effect, π-electron donor, σ-constant.*
23   rev[3]

24

25   **π-electron donor**
26   *Substituent* capable of electron donation by resonance (e.g., OCH_3).
27   See *electronic effect, polar effect, π-electron acceptor, σ-constant.*
28   rev[3]

29

30   **quantitative structure-activity relationship** (QSAR)
31   Regression model to correlate biological activity or chemical reactivity with predictor
32   parameters based on measured or calculated features of molecular structure.
33   See [357,358].
34   See also *correlation analysis*.

1 rev[3]

2

3 **quantitative structure-property relationship** (QSPR)

4 Regression model to correlate chemical properties such as boiling point or

5 chromatographic retention time with predictor parameters based on measured or

6 calculated features of molecular structure.

7 See [359].

8 See also *correlation analysis*.

9

10 **quantum yield**

11 Number of defined events that occur per photon absorbed by the system.

12 *Note 1:* The integral quantum yield Φ is the number of events divided by the number

13 of photons absorbed in a specified wavelength range.

14 *Note 2:* For a photochemical reaction $\Phi(\lambda)$ is the amount of reactant consumed or

15 product formed divided by the number of photons absorbed at wavelength λ.

16 *Note 3:* The differential quantum yield for a homogeneous system is

17

18 $$\Phi(\lambda) = \frac{\left|\frac{dx}{dt}\right|}{q_{p,\lambda}[1 - 10^{A(\lambda)}]}$$

19

20 where $|dx/dt|$ is the rate of change of a quantity x that measures the progress of a

21 reaction, $q_{p,\lambda}$ is the spectral photon flux (mol or its non-SI equivalent einstein) incident

22 per unit time at wavelength λ, and $A(\lambda)$ is the decadic absorbance at the excitation

23 wavelength λ.

24 *Note 4:* When the quantity x is an amount concentration, it is convenient to use in

25 the denominator the rate (in moles) of photons absorbed per volume.

26 See [9,10].

27 rev[3]

28

29 **radical**

30 free radical (obsolete)

31 *Molecular entity* possessing an unpaired electron.

32 *Examples:* $\cdot CH_3$, $\cdot SnR_3$, $Cl\cdot$

33 *Note 1*: In these formulae the dot, symbolizing the unpaired electron, should be

34 placed so as to indicate the atom of highest spin density, if possible.

35 *Note 2*: Paramagnetic metal ions are not normally regarded as radicals. However, in

36 the *isolobal* analogy the similarity between certain paramagnetic metal ions and radicals

37 becomes apparent.

Note 3: Depending upon the core atom that possesses the highest spin density, the radicals can be described as carbon-, oxygen-, nitrogen-, or metal-centred radicals.

Note 4: If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed σ or π radicals.

Note 5: The term radical has also been used to designate a *substituent* group within a molecular entity, as opposed to "free radical", which is now simply called radical. The bound entities may be called *groups* or substituents, but should no longer be called radicals.

See [40,97].

See also *diradical*.

rev[3]

radical combination

Formation of a *covalent bond* by reaction of one *radical* with another.

See *colligation*.

rev[3]

radical ion

Radical that carries a net electric charge.

Note 1: A positively charged radical is called a radical cation (e.g., the benzene radical cation $C_6H_6^{•+}$); a negatively charged radical is called a radical anion (e.g., the benzene radical anion $C_6H_6^{•-}$ or the benzophenone radical anion $Ph_2C–O^{•-}$).

Note 2: 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 $^{•}+$ or $^{•}-$, as suggested by the name radical ion. However, the usage in mass spectrometry is to place the charge symbol before the dot [7].

Note 3: In the first edition of this Glossary it was recommended to place the charge designation directly above the dot. This format is now discouraged because of the difficulty of extending it to ions bearing more than one charge and/or more than one unpaired electron.

[3]

radical pair

geminate pair

Two *radical*s in close proximity in solution, within a solvent *cage*.

Note 1: The two radicals may be formed simultaneously by some *unimolecular* process, e.g., peroxide decomposition or *photolysis*, or they may have come together by diffusion.

Note 2: 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*.

See [9,40].

[3]

radiolysis

Cleavage of one or several *bond*s resulting from exposure to high-energy radiation.

Note: The term is also often used loosely to specify the method of irradiation (e.g., pulse radiolysis) used in any radiochemical reaction, not necessarily one involving bond cleavage.

[3]

rate coefficient

Empirical constant k in the equation for the rate of a reaction that is expressible by an equation of the form

$$v = k[A]^a[B]^b....$$

Note 1: It is recommended that the term *rate constant* be confined to reactions that are believed to be *elementary reactions*.

Note 2: When a rate coefficient relates to a reaction occurring by a composite mechanism, it may vary not only with temperature and pressure but also with the concentration of reactants. For example, in the case of a *unimolecular* gas reaction the rate at sufficiently high pressures is given by

$$v = k[A]$$

whereas at low pressures the rate expression is

$$v = k'[A]^2$$

Similarly, for a second-order reaction, the rate is given by

$$v = k_2[A][B]$$

But under conditions where [B] remains constant at $[B]_0$, as when B is a *catalyst* or is present in large excess,

1    $v = k_2[A][B]_0 = k[A]$

2

3   where the rate coefficient $k = k_2[B]_0$, which varies with $[B]_0$.

4   Such a rate coefficient k, which varies with the concentration [B], is called a first-

5   order rate coefficient for the reaction, or a *pseudo first-order rate constant* even though

6   it is not a rate constant.

7   *Note*: *Rate constant* and *rate coefficient* are often used as synonyms, see [12],

8   section 2.12, p.63.

9   See [13].

10   See *order of reaction.*

11   rev[3]

12

13   **rate constant**

14   *k*

15   Term generally used for the *rate coefficient* of a reaction that is believed to be an

16   *elementary reaction*. See [13].

17   *Note 1*: In contrast to a rate coefficient, a rate constant should be independent of

18   concentrations, but in general both rate constant and rate coefficient vary with

19   temperature.

20   *Note 2*: Rate constant and rate coefficient are often used as synonymous, see [12],

21   section 2.12, p.63.

22   See *order of reaction*.

23   rev[3]

24

25   **rate-controlling step**

26   See *rate-determining states, rate-limiting step*.

27   rev[3]

28

29   **rate law**

30   empirical differential rate equation

31   Expression for the *rate of reaction* in terms of concentrations of *chemical species* and

32   constant parameters (normally *rate coefficients* and partial *orders of reaction*) only.

33   For examples of rate laws see the equations under *kinetic equivalence*, and under

34   *steady state*.

35   [3]

36

37   **rate-limiting step**

38   rate-controlling step

39   rate-determining step

Step in a multistep reaction that is the last step in the sequence whose *rate constant* appears in the rate equation.

See [13].

Example: Two-step reaction of A with B to give *intermediate* C, which then reacts further with D to give products:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \text{ (Step 1)}$$

$$C + D \xrightarrow{k_2} \text{products (Step 2)}$$

If [C] reaches a *steady state*, then the observed rate is given by

$$v = -d[A]/dt = k_1 k_2 [A][B][D]/(k_{-1} + k_2[D])$$

Case 1: If $k_2[D] >> k_{-1}$, then the observed rate simplifies to

$$v = -d[A]/dt = k_1[A][B]$$

Because k_2 disappears from the rate equation and k_1 is the last rate constant to remain, step (1) is said to be rate-limiting.

Case 2: If $k_2[D] << k_{-1}$, then the observed rate is given by

$$v = k_1 k_2 [A][D]/k_{-1} = K k_2 [A][B][D]$$

where K, equal to k_1/k_{-1}, is the *equilibrium* constant for the *pre-equilibrium* (Step 1). Because k_2 remains in the rate equation, Step 2 is said to be rate-limiting. Notice that in this case, where Step 2 involves another reactant D, which step is rate-limiting can depend on [D]: Step 1 at high [D] and Step 2 at low [D].

Specific example: Acid-catalyzed bromination of a methyl ketone
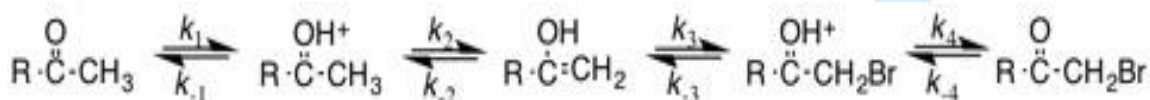
where $k_1 = k_1'[H+]$, $k_{-2} = k_{-2}'[H+]$, $k_3 = k_3'[Br_2]$, $k_{-3} = k_{-3}'[Br^-]$.

According to the *steady-state* approximation,

$$v = k_{obs}[RCOCH_3] = k_1 k_2 k_3 k_4 [RCOCH_3]/\{k_2 k_3 k_4 + k_{-1}k_3 k_4 + k_{-1}k_{-2}(k_{-3} + k_4)\}.$$

1　or　$k_{obs} = k_1 k_2 k_3 k_4 / \{k_2 k_3 k_4 + k_{-1} k_3 k_4 + k_{-1} k_{-2}(k_{-3} + k_4)\}$.

2

3　If $k_4 \gg k_{-3}$, k_{-3} can be ignored in the parentheses, so that k_{obs} simplifies to
4　$k_1 k_2 k_3 k_4 / \{k_2 k_3 k_4 + k_{-1} k_3 k_4 + k_{-1} k_{-2} k_4\}$. Then if $k_3 \gg k_{-2}$, k_{obs} simplifies further to
5　$k_1 k_2 k_3 k_4 / \{k_2 k_3 k_4 + k_{-1} k_3 k_4\}$, where $k_3 k_4$ cancels and k_{obs} becomes $k_1 k_2 / \{k_{-1} + k_2\}$, so that
6　k_2 is the last rate constant remaining in k_{obs}. The second step is rate-limiting, and the
7　rate is independent of k_3 or of $[Br_2]$.
8　　*Note 1*: Although the expressions rate-controlling, rate-determining, and rate-limiting
9　are often regarded as synonymous, rate-limiting is to be preferred, because in Case 2
10　all three rate constants enter into the rate equation, so that all three are rate-controlling
11　and rate-determining, but the first step is not rate-limiting.
12　　*Note 2:* If the concentration of any intermediate builds up to an appreciable extent,
13　then the steady-state approximation no longer holds, and the reaction should be
14　analyzed as though that intermediate is the reactant.
15　　*Note 3:* It should be noted that a *catalytic cycle* does not have a rate-determining
16　step. Instead, under steady-state conditions, all steps proceed at the same rate
17　because the concentrations of all intermediates adjust so as to offset the differences in
18　the corresponding rate constants [360].
19　　See also *Gibbs energy diagram*, *microscopic diffusion control*, *mixing control*.
20　　rev[3]
21

22　**rate of reaction**
23　*v*
24　(unit: mol dm^{-3} s^{-1} or mol L^{-1} s^{-1})
25　For the general *chemical reaction*
26

27　　　$a\,A + b\,B \;=\; p\,P + q\,Q\,...$
28

29　occurring under constant-volume conditions, without an appreciable build-up of reaction
30　*intermediate*s, the rate of reaction v is defined as
31

32　　$$v \;=\; -\,\frac{1}{a}\,\frac{d[A]}{dt} \;=\; -\,\frac{1}{b}\,\frac{d[B]}{dt} \;=\; -\,\frac{1}{p}\,\frac{d[P]}{dt} \;=\; -\,\frac{1}{q}\,\frac{d[Q]}{dt}$$

33

34　where symbols inside square brackets denote concentrations (conventionally
35　expressed in unit mol dm^{-3}). The symbols R and r are also used instead of v. It is
36　recommended that the unit of time be the second.
37　　*Example:*
38

39　　　$Cr_2O_7^{2-} + 3\,(CH_3)_2CHOH + 8\,H^+ = 2\,Cr^{3+} + 3\,(CH_3)_2C{=}O + 7\,H_2O$

1

$$v = -\frac{d[Cr_2O_7^{2-}]}{dt} = -\frac{1}{3}\frac{d[(CH_3)_2CHOH]}{dt} = \frac{1}{2}\frac{d[Cr^{3+}]}{dt} = \frac{1}{3}\frac{d[(CH_3)_2C=O]}{dt}$$

Note: For a *stepwise reaction* this definition of rate of reaction 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) or rate of appearance of P (i.e., d[P]/dt) be used, depending on the particular *chemical species* that is actually observed. In some cases reference to the *chemical flux* observed may be more appropriate.

See [13].

See also *chemical relaxation*, *lifetime*, *order of reaction*.

rev[3]

reaction coordinate

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 as a measure of the progress along a *minimum-energy reaction path*.

Note 1: The term "reaction coordinate" is often used to refer to a geometric variable itself (typically a bond distance or bond angle, or a combination of distances and/or angles) as well as (or instead of) the value of that variable. Although strictly incorrect, this usage is very commonly encountered.

Note 2: In cases where the location of the transition structure is unknown, an internal coordinate of the system (e.g., a geometric variable or a bond order, or an energy gap between reactant-like and product-like valence-bond structures) is often selected as a reaction coordinate. A *potential-energy profile* obtained by energy minimization over other coordinates for a succession of fixed values of an arbitrary reaction coordinate is not guaranteed to pass through the *transition structure* unless it is a continuous function of that reaction coordinate. Similarly, a free-energy profile obtained as a *potential of mean force* with respect to an arbitrary reaction coordinate is not guaranteed to pass through the lowest-energy *transition state*.

Note 3: "Reaction coordinate" is sometimes used as an undefined label for the horizontal axis of a *potential-energy profile* or a *Gibbs energy diagram*.

See [349,361].

See also *Gibbs energy diagram*, *potential-energy profile*, *potential-energy surface*.

rev[3]

reaction path

(1) Synonym for *mechanism*.

1   (2) Trajectory on the *potential-energy surface*.

2   rev[3]

3

4   **reaction step**

5   *Elementary reaction* constituting one of the stages of a *stepwise reaction* in which a
6   reaction *intermediate* (or, for the first step, the reactants) is converted into the next
7   reaction intermediate (or, for the last step, the products) in the sequence of
8   intermediates between reactants and products.

9   [3]

10

11   **reactive intermediate**

12   intermediate

13

14   **reactivity (n.), reactive (adj.)**

15   Kinetic property of a *chemical species* by which (for whatever reason) it has a different
16   rate constant for a specified *elementary reaction* than some other (reference) species.

17   *Note 1*: The term has meaning only by reference to some explicitly stated or implicitly
18   assumed set of conditions. It is not to be used for reactions or reaction patterns of
19   compounds in general.

20   *Note 2*: Term also used more loosely as a phenomenological description not
21   restricted to elementary reactions. When applied in this sense, the property under
22   consideration may reflect not only rate constants but also equilibrium constants.

23   See also *stable*, *unreactive*, *unstable*.

24   [3]

25

26   **reactivity index**

27   Numerical quantity derived from quantum-mechanical model calculations or from a
28   *linear Gibbs-energy relationship (linear free-energy relationship)* that permits the
29   prediction or correlation of relative reactivities of different molecular sites.

30   *Note:* Many indices are in use, based on a variety of theories and relating to various
31   types of reaction. The more successful applications have been to the *substitution*
32   reactions of *conjugated* systems, where relative reactivities are determined largely by
33   changes of π-electron energy and π-*electron density*.

34   rev[3]

35

36   **reactivity-selectivity principle** (RSP)

37   Idea that the more *reactive* a reagent is, the less *selective* it is.

38   *Note*: There are many examples in which the RSP is followed, but there are also
39   many counterexamples. Although the RSP is in accord with intuitive feeling, it is now

1 clear that selectivity can decrease, increase, or remain constant as *reactivity* increases,
2 so that the RSP is unreliable as a guide to reactivity.
3   See [126,346,362,363,364,365].
4   rev[3]
5

6 **rearrangement**
7   See *degenerate rearrangement*, *molecular rearrangement*, *sigmatropic*
8 *rearrangement*.
9   [3]
10

11 **reduction**
12 (1) Transfer of one or more electrons to a *molecular entity*, usually inorganic.
13 (2) Decrease in the *oxidation number* of any atom within any *substrate* [344].
14 (3) Loss of oxygen or halogen and/or gain of hydrogen of an organic *substrate*.
15   See *oxidation*.
16   rev[3]
17

18 **reductive elimination**
19 Reverse of *oxidative addition*.
20   [3]
21

22 **regioselectivity** (*n.*)**, regioselective** (*adj.*)
23 Property of a reaction in which one position of *bond* making or breaking occurs
24 preferentially over all other possible positions.
25   *Note 1:* The resulting regioisomers are *constitutional isomers*.
26   *Note 2*: Reactions are termed completely (100 %) regioselective if the discrimination
27 is complete, or partially (*x* %) if the product of reaction at one site predominates over
28 the product of reaction at other sites. The discrimination may also be referred to semi-
29 quantitatively as high or low regioselectivity.
30   *Note 3*: Historically the term was restricted to *addition reaction*s of unsymmetrical
31 reagents to unsymmetrical alkenes.
32   *Note 4*: In the past, the term regiospecificity was proposed for 100 % regioselectivity.
33 This terminology is not recommended, owing to inconsistency with the terms
34 *stereoselectivity* and *stereospecificity*.
35   See [366,367].
36   See also *chemoselectivity*.
37   rev[3]
38

39 **Reichardt E_T parameter**
40   See *Dimroth-Reichardt $E_T(30)$ parameter*.

1

2 **relaxation**

3 Passage of a system that has been perturbed from *equilibrium,* by radiation excitation
4 or otherwise, toward or into thermal equilibrium with its environment.

5 See [9].

6 See also *chemical relaxation*.

7 rev[3]

8

9 **reorganization energy**

10 Gibbs energy required to distort the reactants (and their associated solvent molecules)
11 from their relaxed nuclear configurations to the relaxed nuclear configurations of the
12 products (and their associated solvent molecules).

13 *Note 1:* This approach was originally formulated for one-electron transfer reactions,
14 $A + D \rightarrow A^{-\cdot} + D^{+\cdot}$, in the framework of the *Marcus equation*, assuming weak coupling
15 between the reactants [368].

16 *Note 2:* Reorganization energy is not the same as distortion energy, which is the
17 energy required to distort the reactants to the nuclear configuration of the *transition*
18 *state*.

19 *Note 3:* This approach has been extended to enzyme-catalysed reactions [369].

20 *Note 4:* Marcus theory has been shown to be valid for some complex reactions
21 (*cycloaddition*, S_N2), even though the weak-coupling assumption is clearly not valid. In
22 these cases the reorganization energy (in terms of activation strain) is counteracted by
23 stabilizing interactions (electrostatic and orbital) [166].

24 See also *distortion interaction model*, *intrinsic barrier*, *Marcus equation*.

25 rev[3]

26

27 **resonance**

28 Representation of the electronic structure of a *molecular entity* in terms of contributing
29 *Lewis structure*s.

30 *Note 1*: Resonance means that the *wavefunction* is represented by mixing the
31 wavefunctions of the contributing Lewis structures.

32 *Note 2*: The contributing Lewis structures are represented as connected by a double-
33 headed arrow ($\leftrightarrow$), rather than by the double arrow ($\rightleftarrows$) representing *equilibrium*
34 between species.

35 *Note 3:* This concept is the basis of the quantum-mechanical valence-bond methods.
36 The resulting stabilization is linked to the quantum-mechanical concept of *resonance*
37 *energy*. The term resonance is also used to refer to the *delocalization* phenomenon
38 itself.

39 *Note 4:* This term has a completely different meaning in physics.

40 See [75,370].

1   See also [371].

2   rev[3]

3

4   resonance effect

5   Experimentally observable influence (on reactivity, etc.) of a _substituent_ through

6   electron _delocalization_ to or from the substituent.

7   See [126,173,191].

8   See also _inductive effect_.

9   rev[3]

10

11   resonance energy

12   Difference in potential energy between the actual _molecular entity_ and the contributing

13   _Lewis structure_ of lowest potential energy.

14   _Note_: The resonance energy cannot be measured experimentally, but only

15   estimated, since contributing Lewis structures are not observable molecular entities.

16   See _resonance_.

17   rev[3]

18

19   resonance form

20   resonance structure, contributing structure, canonical form

21   One of at least two _Lewis structure_s,with fixed single, double, and triple bonds, that is

22   a contributing structure to the valence-bond _wavefunction_ of a molecule that cannot be

23   described by a single Lewis structure.

24   _Note 1_: Although the valence-bond wavefunction is a linear combination of the

25   wavefunctions of the individual resonance forms, the coefficients and the relative

26   contributions of the various resonance forms are usually kept qualitative. For example,

27   the major resonance forms for the conjugate base of acetone are $CH_2=C(CH_3)–O^-$ and

28    $H_2C^-–C(CH_3)=O$, with the former contributing more.

29   _Note 2:_ Resonance forms are connected by a double-headed arrow ($\leftrightarrow$). This must

30   not be confused with the double arrow connecting species in _equilibrium_ ($\rightleftharpoons$).

31   See also _delocalization_, _Kekulé structure_, _resonance_.

32

33   resonance hybrid

34   _Molecular entity_ whose electronic structure is represented as the superposition of two

35   or more _resonance form_s (or _Lewis structure_s) with different formal arrangements of

36   electrons but identical arrangements of nuclei.

37   _Note 1:_ Whereas each contributing resonance form represents a localized

38   arrangement of electrons which, considered by itself, would imply different bond lengths

39   (say) for formal single and double bonds, _resonance_ between two or more contributors

40   requires each to have the same geometry, namely that of the resulting hybrid, which

represents a delocalized arrangement of electrons. A particular bond in the hybrid may have a length that is, loosely, an "average" of formal single-bond and double-bond values implied by its contributing individual resonance forms, but the hybrid does not oscillate among these as if they were in *equilibrium*.

Note 2: The resonance forms are connected by a double-headed arrow (↔), rather than by the double arrow (⇌) representing equilibrium between species.

retrocycloaddition
deprecated
Cycloelimination.
[3]

Ritchie equation
Linear Gibbs-energy relation (linear free-energy relation)

$$\lg \{k_N\} = \lg \{k_0\} + N_+$$

applied to the reactions between nucleophiles and certain large and relatively stable organic cations, e.g., arenediazonium, triarylmethyl, and aryltropylium cations, in various solvents, where $\{k_N\}$ is the (reduced) second-order *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 (reduced) first-order rate constant for the same cation with water in water, and N_+ is a parameter characteristic of the nucleophilic system and independent of the *electrophilic* reaction partner.

The discrepancy between second-order and first-order rate constants must be reconciled by writing the equation with arguments of the logarithms of dimension 1, i.e., by using reduced rate constants (as denoted by the curly brackets in the defining equation):

$$\lg [k_N/(dm^3 \, mol^{-1}s^{-1})] = \lg (k_0/s^{-1}) + N_+$$

Note 1: 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 decadic log (lg) units. The equation thus involves a gigantic breakdown of the *reactivity-selectivity principle*.

Note 2: The Ritchie equation is a special case of the more general *Mayr-Patz equation*.

See [193,372,373]. See also [125,374].

rev[3]

1 **ρ-value (rho-value)**

2 Quantitative measure of the susceptibility of the _rate constant_ or _equilibrium_ constant

3 of an organic reaction to the influence of _substituent_ groups, usually on an _aromatic_

4 ring.

5   _Note 1_: Defined by Hammett to describe the effects of substituents at the _meta-_ and

6 _para_-positions on rate or equilibrium of a reaction on the side chain of a substituted

7 benzene, the empirical equation has the general form

8

9      $\lg(k_X/k_H)$ or $\lg(K_X/K_H) = \rho\sigma_X$

10

11 in which σ_X is a constant characteristic of the substituent X and of its position in the

12 reactant molecule.

13   _Note 2_: More generally (not only for aromatic series), ρ-values (modified with

14 appropriate subscripts and superscripts) are used to designate the susceptibility to

15 substituent effects of reactions of families of organic compounds, as given by the

16 modified set of σ-constants in an empirical correlation.

17   _Note 3_: Reactions with a positive ρ-value are accelerated (or the equilibrium

18 constants are increased) by substituents with positive σ-constants. Since the sign of σ

19 was defined so that substituents with a positive σ increase the acidity of benzoic acid,

20 such substituents are generally described as attracting electrons away from the

21 aromatic ring. It follows that reactions with a positive ρ-value involve a _transition state_

22 (or reaction product) with an increased _electron density_ at the _reactive_ site of the

23 substrate.

24   See also _Hammett equation_, _σ-constant_, _Taft equation_.

25   rev[3]

26

27 **$\rho\sigma$-equation (rho-sigma equation)**

28   See _Hammett equation_, _ρ-value_, _σ-constant_, _Taft equation_.

29   [3]

30

31 **salt effect**

32   See _kinetic electrolyte effect_.

33   [3]

34

35 **saturation transfer**

36   See _magnetization transfer_.

37   rev[3]

38

39 **Saytzeff rule**

40 Preferential removal of a hydrogen from the β carbon that has the fewest hydrogens in

1   dehydrohalogenation of secondary and tertiary haloalkanes.

2   *Note 1*: The rule was originally formulated by A. Saytzeff (Zaitsev) to generalize the

3   orientation in *β-elimination* reactions of haloalkanes. It has been extended and

4   modified, as follows: When two or more olefins can be produced in an *elimination*

5   reaction, the thermodynamically most *stable* alkene will predominate.

6   *Note 2*: Exceptions to the Saytzeff rule are exemplified by the *Hofmann rule*.

7   See [375].

8   See also *Markovnikov rule*.

9   [3]

10

11   **scavenger**

12   Substance that reacts with (or otherwise removes) a trace component (as in the

13   scavenging of trace metal ions) or traps a *reactive intermediate*.

14   See also *inhibition*.

15   [3]

16

17   **selectivity**

18   Discrimination shown by a reagent in competitive attack on two or more *substrate*s or

19   on two or more positions or diastereotopic or enantiotopic faces of the same substrate.

20   *Note 1*: Selectivity is quantitatively expressed by the ratio of *rate constant*s of the

21   competing reactions, or by the decadic logarithm of such a ratio.

22   *Note 2*: In the context of *aromatic substitution* (usually *electrophilic*, for

23   monosubstituted benzene derivatives), the selectivity factor S_f (expressing

24   discrimination between *p*- and *m*-positions in PhZ) is defined as

25

26     $S_f = \lg (p_f^Z/m_f^Z)$

27

28   where the *partial rate factors* p_f^Z and m_f^Z express the *reactivity* of para and meta

29   positions in the aromatic compound PhZ relative to that of a single position in benzene.

30   See [347].

31   See also *isoselective relationship*, *partial rate factor*, *regioselectivity*,

32   *stereoselectivity*.

33   rev[3]

34

35   **self-assembly**

36   Process whereby a system of single-molecule components spontaneously forms an

37   organized structure, owing to *molecular recognition*.

38

39   **shielding**

40   Extent to which the effective magnetic field is reduced for a nucleus in a molecule

1   immersed in an external magnetic field, relative to that experienced by a bare nucleus
2   in that field.

3   *Note 1*: The reduction is due to the circulation of the electrons around the observed
4   and the neighbouring nuclei. The external field induces a magnetic moment that is
5   oriented in the opposite direction to the external field, so that the local field at the central
6   nucleus is weakened, although it may be strengthened at other nuclei (deshielding).

7   *Note 2*: This phenomenon is the origin of the structural dependence of the resonance
8   frequencies of the nuclei.

9   See also *chemical shift*.

10   [3]

11

12   **shift reagent**
13   Paramagnetic substance that induces an additional change of the NMR resonance
14   frequency of a nucleus near any site in a molecule to which the substance binds.
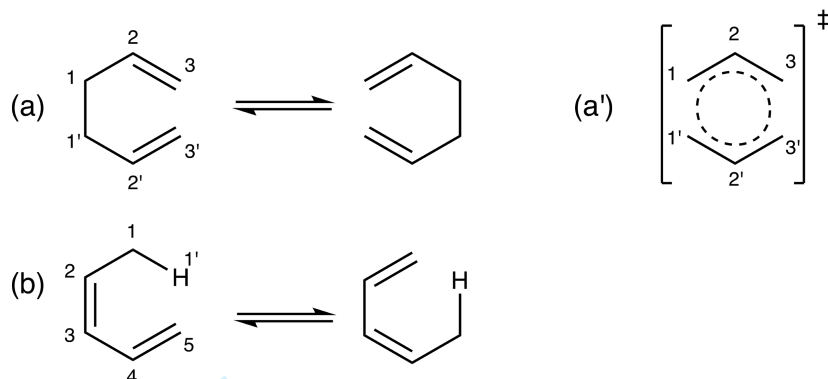
15   See *chemical shift.*

16

17   **sigma, pi**
18   See σ, π
19   rev[3]

20

21   **sigmatropic rearrangement**
22   *Molecular rearrangement* that involves both the creation of a new σ *bond* between
23   atoms previously not directly linked and the breaking of an existing σ bond.

24   *Note 1*: There is normally a concurrent relocation of π bonds in the molecule
25   concerned, but neither the number of π bonds nor the number of σ bonds changes.

26   *Note 2*: The *transition state* of such a reaction may be visualized as an *association*
27   of two fragments connected at their termini by two partial σ bonds, one being broken
28   and the other being formed as, for example, the two allyl fragments in (a'). Considering
29   only atoms within the (real or hypothetical) cyclic array undergoing reorganization, if the
30   numbers of these in the two fragments are designated i and j, then the rearrangement
31   is said to be a sigmatropic change of order [i,j] (conventionally $i \leq j$). Thus rearrangement
32   (a) is of order [3,3], whereas rearrangement (b) is a [1,5]sigmatropic shift of hydrogen.
33   (By convention the square brackets [...] here refer to numbers of atoms, in contrast with
34   current usage in the context of *cycloaddition.*)

1
2
3   The descriptors a and s (*antarafacial* and *suprafacial*) may also be annexed to the
4   numbers *i* and *j*; (b) is then described as a [1$_s$,5$_s$] sigmatropic rearrangement, since it is
5   suprafacial with respect to both the hydrogen atom and the pentadienyl system:
6

7
8
9   See also *cycloaddition*, *tautomerization*.
10   rev[3]
11

12 **silylene**
13 (1) Generic name for H$_2$Si**:** and substitution derivatives thereof, containing an
14 electrically neutral bivalent silicon atom with two non-bonding electrons. (The definition
15 is analogous to that given for *carbene*.)
16 (2) The silanediyl group (H$_2$Si<), analogous to the methylene group (H$_2$C<).
17   [3]
18

19 **single-electron transfer mechanism (SET)**
20 Reaction *mechanism* characterized by the transfer of a single electron between two
21 species, occurring in one of the steps of a multistep reaction.
22   [3]
23

24 **single-step reaction**
25 one-step reaction
26 Reaction that proceeds through a single *transition state* (or no transition state).
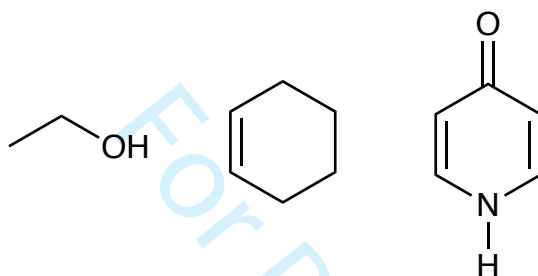27   [3]
28

29

1 **skeletal formula**

2 bond-line formula

3 Two-dimensional representation of a _molecular entity_ in which bonds are indicated as
4 lines between vertices representing octet carbon atoms with attached hydrogens
5 omitted and in which other atoms are represented by their chemical symbols.

6 _Examples:_ ethanol, cyclohexene, 4-pyridone

7

8
9

10 See _line formula_.

11

12 **Slater-type orbital (STO)**

13 Function centred on an atom for which the radial dependence has the form $\phi(r) \propto r^{n-1}$
14 $\exp(-\zeta r)$, used to approximate _atomic orbital_s in the LCAO-MO method.

15 _Note 1_: n is the effective principal quantum number and ζ is the orbital exponent
16 (screening constant) derived from empirical considerations.

17 _Note 2_: The angular dependence is usually introduced by multiplying the radial
18 function by a spherical harmonic $Y_{1m}(\theta,\phi)$.

19 _Note 3_: Owing to difficulties in computing the integrals of STOs analytically for
20 molecules with more than two atoms they are often replaced by linear combinations of
21 _Gaussian orbitals_.

22 See [8].

23 rev[3]

24

25 **solvation**

26 Stabilizing interaction between a solute (or solute moiety) and the solvent.

27 _Note_: Such interactions generally involve electrostatic forces and _van der Waals_
28 _forces_, as well as chemically more specific effects such as _hydrogen bond_ formation.

29 See also _cybotactic region_.

30 [3]

31

32 **solvatochromic relationship**

33 _Linear Gibbs-energy relationship (linear free-energy relationship)_ based on
34 _solvatochromism_.

1 See also *Dimroth-Reichardt E_T parameter*, *Kamlet-Taft solvent parameters*.

2 [3]

3

solvatochromism

5 Pronounced change in position and sometimes intensity of an electronic absorption or

6 emission band, accompanying a change in the *polarity* of the *medium*.

7 *Note*: Negative (positive) solvatochromism corresponds to a *hypsochromic shift*

8 (*bathochromic shift*) with increasing solvent polarity.

9 See [9,17,376].

10 See also *Dimroth-Reichardt E_T parameter*, *Z-value*.

11 [3]

12

solvatomers

14 *Isomers* that differ in their solvation environment.

15 *Note 1:* Because the solvation environment fluctuates rapidly, solvatomers

16 interconvert rapidly.

17 *Note 2:* Species that differ in the type of solvent molecules should not be called

18 solvatomers, because they are not isomers.

19

solvent parameter

21 Quantity that expresses the capability of a solvent for interaction with solutes, based on

22 experimentally determined physicochemical quantities, in particular: relative

23 *permittivity*, refractive index, *rate constant*s, Gibbs energies and enthalpies of reaction,

24 and ultraviolet-visible, infrared, and NMR spectra.

25 *Note 1*: Solvent parameters are used in *correlation analysis* of solvent effects, either

26 in single-parameter or in multiple-parameter equations.

27 *Note 2:* Solvent parameters include those representing a bulk property, such as

28 relative *permittivity* (dielectric constant) as well as those that describe a more localized

29 solute/solvent interaction, such as hydrogen-bonding acceptance or donation and

30 Lewis acid/base adduct formation.

31 See [17,377].

32 See also: *acceptor number*, *Catalán solvent parameters*, *Dimroth-Reichardt E_T*

33 *parameter*, *Grunwald-Winstein equation*, *Kamlet-Taft solvent parameters*, *Laurence*

34 *solvent parameters*, *Koppel-Palm solvent parameters*, *linear solvation energy*

35 *relationship*, *Z-value*.

36 rev[3]

37

solvolysis

39 Reaction with solvent.

40 *Note 1*: Such a reaction generally involves the rupture of one or more *bond*s in the

1 solute. More specifically the term is used for *substitution*, *elimination*, and *fragmentation*
2 reactions in which a solvent species serves as *nucleophile* or *base*.
3   *Note 2:* A solvolysis can also be classified as a *hydrolysis*, alcoholysis, or
4 ammonolysis, etc., if the solvent is water, alcohol, or ammonia, etc.
5   *Note 3:* Often a solvolysis is a *nucleophilic substitution* (usually S_N1, accompanied
6 by E1 *elimination*), where the nucleophile is a solvent molecule.
7   rev[3]
8

9 **SOMO**
10 **S**ingly **O**ccupied **M**olecular **O**rbital (such as the half-filled *HOMO* of a radical).
11   See also *frontier orbitals*.
12   [3]
13

14 **special salt effect**
15 Steep increase of the rate of certain solvolysis reactions observed at low concentrations
16 of some non-common-ion salts.
17   *Note*: The effect is attributed to trapping of an intimate *ion pair* that would revert to
18 reactant in the absence of the salt.
19   See also *kinetic electrolyte effect*.
20   rev[3]
21

22 **specific catalysis**
23 Acceleration of a reaction by a unique *catalyst*, rather than by a family of related
24 substances.
25   *Note*: The term is most commonly used in connection with specific hydrogen-ion or
26 hydroxide-ion (*lyonium ion* or *lyate ion*) catalysis.
27   See also *general acid catalysis*, *general base catalysis*, *pseudo-catalysis*.
28   [3]
29

30 **spectator mechanism**
31 *Pre-association* mechanism in which one of the *molecular entities*, C, is already present
32 in an encounter pair with A during formation of B from A, but does not assist the
33 formation of B, e.g.,
34

35 $$A \; + \; C \underset{}{\overset{\text{Pre-association}}{\rightleftharpoons}} \; (A \cdots\cdots C) \xrightarrow{\hspace{1.5cm}} (B \cdots\cdots C) \xrightarrow{\text{rapid}} \; \text{Product}$$
   encounter   encounter
   complex   complex
36

37   *Note*: The formation of B from A may itself be a bimolecular reaction with some other
38 reagent. Since C does not assist the formation of B, it is described as being present as

1 a spectator.

2   See also *microscopic diffusion control*.

3   [3]

4

5 **spin adduct**

6   See *spin trapping*.

7   [3]

8

9 **spin counting**

10   See *spin trapping*.

11   [3]

12

13 **spin density**

14 Unpaired *electron density* at a position of interest, usually at carbon, in a *radical* or a

15 *triplet state*.

16   *Note*: Spin density is often measured experimentally by electron paramagnetic

17 resonance/electron spin resonance (EPR/ ESR) spectroscopy through hyperfine

18 splitting of the signal by neighbouring magnetic nuclei.

19   See also *radical centre*.

20   [3]

21

22 **spin label**

23 *Stable* paramagnetic *group* (typically an *aminoxy* radical, $R_2NO^\bullet$) that is attached to a

24 part of a *molecular entity* whose chemical environment may be revealed by its electron

25 spin resonance (ESR) spectrum.

26   *Note*: When a paramagnetic molecular entity is used without covalent attachment to

27 the molecular entity of interest, it is frequently referred to as a spin probe.

28   [3]

29

30 **spin trapping**

31 Formation of a more *persistent* radical from interaction of a *transient radical* with a

32 diamagnetic reagent.

33   *Note 1*: The product radical accumulates to a concentration where detection and,

34 frequently, identification are possible by EPR/ESR spectroscopy.

35   *Note 2*: The key reaction is usually one of *attachment*; the diamagnetic reagent is

36 said to be a spin trap, and the persistent product radical is then the spin *adduct*. The

37 procedure is referred to as spin trapping, and is used for monitoring reactions involving

38 the intermediacy of *reactive* radicals at concentrations too low for direct observation.

39 Typical spin traps are *C*-nitroso compounds and nitrones, to which reactive radicals will

40 rapidly add to form *aminoxy* radicals.

1   *Example:*

2

3   *Note 3*: A quantitative development in which essentially all reactive radicals
4   generated in a particular system are intercepted has been referred to as spin counting.
5   *Note 4*: Spin trapping has also been adapted to the interception of radicals generated
6   in both gaseous and solid phases. In these cases the spin adduct is in practice
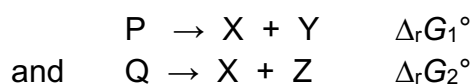7   transferred to a liquid solution for EPR/ESR observation.
8   [3]
9

10   **stable**
11   Having a lower standard Gibbs energy, compared to a reference *chemical species*.
12   *Note 1*: Quantitatively, in terms of Gibbs energy, a chemical species A is more stable
13   than its isomer B if $\Delta_r G°$ is positive for the (real or hypothetical) reaction A → B.
14   *Note 2*: For the two reactions
15

16   P → X + Y $\Delta_r G_1°$
17   and   Q → X + Z $\Delta_r G_2°$
18

19   if $\Delta_r G_1° > \Delta_r G_2°$, then P is more stable relative to its product Y than is Q relative to Z.
20   *Note 3*: Both in qualitative and quantitative usage the term stable is therefore always
21   used in reference to some explicitly stated or implicitly assumed standard.
22   *Note 4*: The term should not be used as a synonym for *unreactive* or less *reactive*
23   since this confuses thermodynamics and kinetics. A relatively more stable chemical
24   species may be more reactive than some reference species towards a given reaction
25   partner.
26   See also *inert*, *unstable*.
27   [3]
28

29   **stationary state**
30   (1) (in quantum mechanics): *Wavefunction* whose probability density $|\Psi|^2$ remains
31   constant and whose observable properties do not evolve with time.
32   (2) (in kinetics): See *steady state*.
33   [3]
34

35   **steady state (or stationary state)**
36   (1) Approximation that the kinetic analysis of a complex reaction involving *unstable*

intermediates in low concentration can be simplified by setting the rate of change of each such *intermediate* 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, if X is an *unstable* intermediate in the reaction sequence:

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X$$

$$X + C \xrightarrow{k_2} D$$
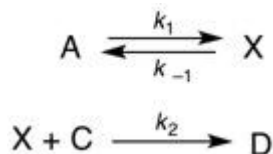
Since [X] is negligibly small, d[X]/dt, the rate of change of [X], can be set equal to zero. The steady state approximation then permits solving the following equation

$$d[X]/dt = k_1[A] - k_{-1}[X] - k_2[X][C] = 0$$

to obtain the steady-state [X]:

$$[X] = k_1[A]/(k_{-1} + k_2[C])$$

whereupon the rate of reaction is expressed:

$$d[D]/dt = k_2[X][C] = k_1k_2[A][C]/(k_{-1} + k_2[C])$$

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].

(2) Regime in a stirred flow reactor such that all concentrations are independent of time. See [13].

[3]

stepwise reaction

Chemical reaction with at least one reaction *intermediate* and involving at least two consecutive *elementary reaction*s.

See also *composite reaction, reaction step*.

[3]

stereoelectronic

Pertaining to the dependence of the properties (especially energy or *reactivity*) of a *molecular entity* or of a *transition state* on the relative disposition of electron pairs owing to the nuclear geometry.

Note: Stereoelectronic effects are ascribed to the differing overlaps of *atomic orbital*s in different *conformation*s.

1 See [11].

2 [3]

3

stereogenic centre

5 Atom within a molecule bearing groups such that interchanging any two of them leads

6 to a _stereoisomer_ of the original molecule.

7 See [11,378].

8

stereoisomers

10 _Isomers_ that have the same bonds (_connectivity_) but differ in the arrangement of their

11 atoms and cannot be interconverted by rapid rotation around single bonds.

12 See [11].

13

stereoselectivity (stereoselective)

15 Preferential formation in a _chemical reaction_ of one _stereoisomer_ over another.

16 _Note 1_: When the stereoisomers are _enantiomer_s, the phenomenon is called

17 enantioselectivity and is quantitatively expressed by the enantiomeric excess or

18 enantiomeric ratio; when they are _diastereoisomers_, it is called _diastereoselectivity_ and

19 is quantitatively expressed by the diastereomeric excess or diastereomeric ratio.

20 _Note 2_: Reactions are termed 100 % stereoselective if the preference is complete,

21 or partially (_x_ %) stereoselective if one product predominates. The preference may also

22 be referred to semiquantitatively as high or low stereoselectivity

23 See [11,140].

24 [3]

25

stereospecificity (stereospecific)

27 Property of those _chemical reaction_s in which different stereoisomeric reactants are

28 converted into different stereoisomeric products.

29 _Example:_ electrocyclization of _trans,cis,trans_-octa-2,4,6-triene produces _cis_-5,6-

30 dimethylcyclohexa-1,3-diene, whereas c_is,cis,trans_-octa-2,4,6-triene produces racemic

31 _trans_-5,6-dimethylcyclohexa-1,3-diene.

32

1
2

3   *Note 1*: A stereospecific process is necessarily *stereoselective* but not all
4   stereoselective processes are stereospecific. Stereospecificity may be total (100 %) or
5   partial.

6   *Note 2*: The term is also applied to situations where reaction can be performed with
7   only one stereoisomer. For example the exclusive formation of racemic *trans*-1,2-
8   dibromocyclohexane upon bromination of cyclohexene is a stereospecific process,
9   even though the analogous reaction with (*E*)-cyclohexene has not been performed.

10   *Note 3:* Stereospecificity does NOT mean very high stereoselectivity. This usage is
11   unnecessary and is strongly discouraged.

12   See [11,140].

13   For the term stereospecific polymerization see [379].

14   rev[3]

15

steric-approach control

17   Situation in which the *stereoselectivity* of a reaction under *kinetic control* is governed
18   by steric hindrance to attack of the reagent, which is directed to the less hindered face
19   of the molecule.

20   *Note*: Partial bond making at the *transition state* must be strong enough for steric
21   control to take place, but the transition state should not be so close to products that the
22   steric demand of the reagent at the transition state is the same as the steric demand of
23   the group as present in the product.

24   An example is LiAlH$_4$ reduction of 3,3,5-trimethylcyclohexan-1-one, where steric
25   hindrance by an axial methyl directs hydride addition to the equatorial position, even
26   though the more stable product has the H axial and the OH equatorial.

27   See also *product-development control*.

28   rev[3]

29

30

31

steric effect

Consequences for molecular geometry, thermochemical properties, spectral features, solvation, or reaction rates resulting from the fact that atoms repel each other at close distance. The repulsion is due to the quantum-mechanical Pauli exclusion principle. Substitution of hydrogen atoms by groups with a larger van der Waals radius may lead to situations where atoms or groups of atoms repel each other, thereby affecting distances and angles.

Note 1: It is in principle difficult to separate the steric effect from other electronic effects.

Note 2: For the purpose of *correlation analysis* or *linear Gibbs-energy relations* (*linear free-energy relation*s) various scales of steric parameters have been proposed, notably *A values*, Taft's E_S and Charton's *v* scales.

Note 3: A steric effect on a rate process may result in a rate increase (steric acceleration) or a decrease (steric retardation) depending on whether the transition state or the reactant state is more affected by the steric effect.

Note 4: Bulky groups may also attract each other if at a suitable distance.

See [290,380].

See *Taft equation, van der Waals forces*.

rev[3]

steric hindrance

Steric effect whereby the crowding of substituents around a reaction centre retards the attack of a reagent.

rev[3]

stopped flow

Technique for following the kinetics of reactions in solution (usually in the millisecond time range) in which two, or more, 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 a method with a rapid response (e.g., optical absorption spectroscopy).

See *mixing control*.

rev[3]

strain

Feature of a *molecular entity* or *transition structure* for which the energy is increased because of unfavourable non-bonded (steric) interactions, bond lengths, bond angles, or dihedral angles (torsional strain), relative to a standard.

Note 1: The strain energy is quantitatively defined as the standard enthalpy of a

1 structure relative to that of a strainless structure (real or hypothetical) made up from the
2 same atoms with the same types of bonding.
3   For example, the enthalpy of formation of cyclopropane is +53.6 kJ mol^{-1}, whereas
4 the hypothetical enthalpy of formation based on three "normal" methylene groups, from
5 acyclic models, is -62 kJ mol^{-1}. On this basis cyclopropane is destabilized by ca. 115 kJ
6 mol^{-1} of strain energy.
7   See *molecular mechanics*.
8   [3]
9

10 **structural isomers**
11 discouraged term for *constitutional isomers*.
12

13 **subjacent orbital**
14 **N**ext-to-**H**ighest **O**ccupied **M**olecular **O**rbital (NHOMO, also called HOMO–1).
15   *Note*: Subjacent and *superjacent* orbitals sometimes play an important role in the
16 interpretation of molecular interactions according to the *frontier orbital* approach.
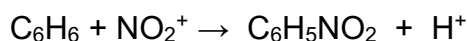17   See [381].
18   [3]
19

20 **substituent**
21 Any atom or *group* of bonded atoms that can be considered to have replaced a
22 hydrogen atom (or two hydrogen atoms in the special case of bivalent groups) in a
23 parent *molecular entity* (real or hypothetical).
24   [3]
25

26 **substitution**
27 *Chemical reaction*, elementary or stepwise, of the form A–B + C → A–C + B, in which
28 one atom or group in a molecular entity is replaced by another atom or group.
29   *Examples*
30       $CH_3Cl + HO^- \rightarrow CH_3OH + Cl^-$
31       $C_6H_6 + NO_2^+ \rightarrow C_6H_5NO_2 + H^+$
32   *Note:* A substitution reaction can be distinguished as an *electrophilic substitution* or
33 a *nucleophilic substitution*, depending on the nature of the reactant that is considered
34 to react with the *substrate*.
35   rev[3]
36

37 **substrate**
38 *Chemical species*, the reaction of which with some other chemical reagent is under
39 observation (e.g., a compound that is transformed under the influence of a catalyst).

1   *Note*: The term should be used with care. Either the context or a specific statement
2   should always make it clear which chemical species in a reaction is regarded as the
3   substrate.
4   See also *transformation*.
5   [3]

7   **successor complex**
8   *Chemical species* formed by the transfer of an electron or of a hydrogen (atom or ion)
9   from a donor D to an acceptor A after these species have diffused together to form the
10 precursor or *encounter complex*:

$$A + D \longrightarrow (A \; D) \longrightarrow (A^{\cdot-} \; D^{\cdot+})$$

$$A + DH \longrightarrow (A \; DH) \longrightarrow (AH^{\cdot-} \; D^{\cdot+}) \; or \; (AH^{+} \; D^{-})$$

11
12 rev[3]

14 **suicide inhibition**
15 See *mechanism-based inhibition*.
16 [3]

18 **superacid**
19 Medium having a high *acidity*, generally greater than that of 100 % sulfuric acid. The
20 common superacids are made by dissolving a powerful *Lewis acid* (e.g., SbF_5) in a
21 suitable *Brønsted acid*, such as HF or HSO_3F.
22 *Note 1*: An equimolar mixture of HSO_3F and SbF_5 is known by the trade name Magic
23 Acid.
24 *Note 2*: An uncharged gas-phase substance having an endothermicity (enthalpy) of
25 deprotonation (dehydronation) lower than that of H_2SO_4 is also called a superacid.
26 Nevertheless such a superacid is much less acidic in the gas phase than similar cationic
27 acids.
28 See [18,382,383,384].
29 See *acidity, superbase*.
30 rev[3]

32 **superbase**
33 Compound having a very high *basicity*.
34 Examples include amide bases such as LDA, potassium *tert*-butoxide +
35 organolithium, some phosphazenes.
36 See *superacid*.
37 See [385].
38 rev[3]
39

1   1   **superjacent orbital**

2   2   **S**econd **L**owest **U**noccupied **M**olecular **O**rbital (SLUMO).

3   3   *Note*: *Subjacent* and superjacent orbitals sometimes play an important role in the

4   4   interpretation of molecular interactions according to the *frontier orbital* approach.
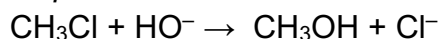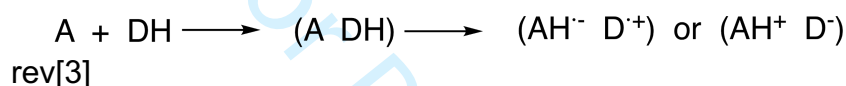
5   5   See [381].

6

7   7   **suprafacial**

8   8   See *antarafacial*.

9   9   [3]

10

11   11   **supramolecular**

12   12   Description of a system of two or more *molecular entities* that are held together and

13   13   organized by means of intermolecular (noncovalent) binding interactions.

14   14   See [386].

15   15   [3]

16

17   17   **Swain-Lupton equation**

18   18   Dual-parameter approach to the correlation analysis of substituent effects, which

19   19   involves a field constant (F) and a resonance constant (R).

20

21   21 $\lg(k_X/k_H) \;=\; fF_X \;+\; rR_X$

22

23   23   See [191,387].

24   24   *Note 1*: The original treatment was modified later.

25   25   *Note 2*: The procedure has often been applied, but also often criticized.

26   26   See [388,389,390,391,392].

27   27   [3]

28

29   29   **Swain-Scott equation**

30   30   *Linear Gibbs-energy relation* (*linear free-energy relation*) of the form

31

32   32 $\lg(k/k_0) = sn$

33

34   34   applied to the variation of *reactivity* of a given *electrophilic* substrate towards a series

35   35   of *nucleophilic* reagents, where k_0 is a *rate constant* for reaction with water, k is the

36   36   corresponding rate constant for reaction with any other nucleophilic reagent, n is a

37   37   measure of the *nucleophilicity* of the reagent ($n = 0.0$ for water) and s is a measure of

38   38   the sensitivity of the substrate to the nucleophilicity of the reagent ($s = 1.0$ for CH_3Br).

39   39   See [192].

40   40   See also *Mayr-Patz equation, Ritchie equation*.

1   [3]

2

3   **symproportionation**

4   *comproportionation*

5   [3]

6

7   ***syn***

8   See *anti*.

9   See [11].

10   [3]

11

12   **synartetic acceleration**

13   See *neighbouring group participation*.

14   [3]

15

16   **synchronization**

17   See *principle of nonperfect synchronization*.

18   rev[3]

19

20   **synchronous**

21   Feature of a *concerted* process in which all the changes (generally bond rupture and

22   bond formation) have progressed to the same extent at the *transition state*.

23   *Note 1:* A synchronous reaction is distinguished from (1) a concerted reaction, which

24   takes place in a single kinetic step without being synchronous, (2) a reaction where

25   some of the changes in bonding take place earlier, followed by the rest, and (3) a two-

26   step reaction, which takes place in two kinetically distinct steps, via a stable

27   *intermediate*

28   *Note 2*: The progress of the bonding changes (or other primitive changes) is not

29   defined quantitatively in terms of a single parameter applicable to different bonds. The

30   concept therefore does not admit an exact definition except in the case of concerted

31   processes involving changes in two identical bonds. If the bonds are not identical, the

32   process should simply be described as concerted.

33   See [393,394,395]. For an index of synchronicity see [396].

34   See also *imbalance*.

35   rev[3]

36

37   **σ, π**

38   Symmetry designations that distinguish *molecular orbital*s as being symmetric (σ) or

39   antisymmetric (π) with respect to a defining plane containing at least one atom.
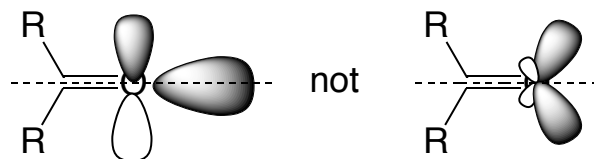
40   *Note 1*: In practice the terms are used both in this rigorous sense (for orbitals

encompassing the entire molecule) and for localized two-centre orbitals or bonds. In the case of localized two-centre bonds, a π bond has a nodal plane that includes the internuclear bond axis, whereas a σ bond has no such nodal plane. (A δ bond in organometallic or inorganic chemical species has two nodes.) *Radicals* are classified by analogy into σ and π radicals.

Note 2: Such two-centre orbitals may take part in molecular orbitals of σ or π symmetry. For example, the methyl group in propene contains three C–H bonds, each of which is of local σ symmetry (i.e., without a nodal plane including the internuclear axis), but these three σ bonds can in turn be combined to form a set of group orbitals one of which has π symmetry with respect to the principal molecular plane and can accordingly interact with the two-centre orbital of π symmetry (π bond) of the double-bonded carbon atoms, to form a molecular orbital of π symmetry. Such an interaction between the CH_3 group and the double bond is an example of *hyperconjugation*. This cannot rigorously be described as σ-π conjugation since σ and π here refer to different defining planes, and interaction between orbitals of different symmetries (with respect to the same defining plane) is forbidden.

Note 3: Conjugation between a π system and a lone pair of (for example) an ether oxygen involves a lone pair of π symmetry with respect to the defining plane. It is incorrect to consider this as an interaction between the π system and one of two identical sp^3-hybrid lone pairs, which are neither σ nor π.

Note 4: The two lone pairs on a carbonyl oxygen are properly classified as σ or π with respect to the plane perpendicular to the molecular plane (dotted line perpendicular to the plane of the page), rather than as two sp^2-hybridized lone pairs. This distinction readily accounts for the facts that there are two different lone-pair *ionization energies* and two different *n-π* *excited state*s.

See also [397].

σ-adduct

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 σ bond is formed and the original *conjugation* is disrupted.

Note 1: This has generally been called a σ complex, or a Wheland complex from

1 electrophilic addition, but adduct is more appropriate.

2 *Note* 2: The term may also be used for analogous adducts to π systems.

3 See also *Meisenheimer adduct*.

4 rev[3]

5

6 **σ-constant**

7 Substituent constant for *meta*- and *para*-substituents in benzene derivatives as defined

8 by Hammett on the basis of the *ionization* constant of a substituted benzoic acid, i.e.,

9 $\lg(K_a^X/K_a^H)$, where K_a^X is the ionization constant (acid-dissociation constant) of a *m*- or

10 *p*-substituted benzoic acid and K_a^H that of benzoic acid itself.

11 *Note 1:* A large positive σ-value implies high electron-withdrawing power by an

12 inductive and/or resonance effect, relative to H; a large negative σ-value implies high

13 electron-releasing power relative to H.

14 *Note 2:* The term is also used as a collective description for related electronic

15 substituent constants based on other standard reaction series, of which, σ^+, σ^- and σ_0

16 are typical; also for constants which represent dissected electronic effects, such as σ_I

17 and σ_R. For example, σ^- (sigma-minus) constants are defined on the basis of the

18 ionization constants of *para*-substituted phenols, where such substituents as nitro show

19 enhanced electron-withdrawing power.

20 See [124,125,126,191,226,398].

21 See also *Hammett equation*, *ρ-value*, *Taft equation*.

22 [3]

23

24 **Taft equation**

25 *Linear free-energy relation* (*linear Gibbs-energy relation*) involving the polar substituent

26 constant σ^* and the steric substituent constant E_s, as derived from reactivities of

27 aliphatic esters

28

29 $$\lg \{k\} = \lg \{k_0\} + \rho^*\sigma^* + \delta E_s$$

30

31 The argument of the lg function should be of dimension 1. Thus, the reduced rate

32 constants should be used, i.e., the *rate coefficient* divided by its units: $\{k\} = k/[k]$ and

33 $\{k_0\} = k_0/[k_0]$.

34 *Note*: The standard reaction (k_0) is the *hydrolysis* of methyl acetate, whereby E_s is

35 evaluated from the rate of acid-catalyzed hydrolysis, relative to that of methyl acetate,

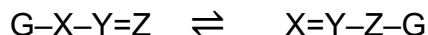36 and σ^* is evaluated from the ratio of the rates of base- and acid-catalyzed hydrolysis.

37 See [172,380,399,400].

38 See also *Hammett equation*, *ρ-value*, *σ-constant*.

39 rev[3]

40

1

2

3   1   **tautomerization**

4   2   Rapid *isomerization* of the general form

5   3   G–X–Y=Z ⇌ X=Y–Z–G

6   4   where the isomers (called *tautomers*) are readily interconvertible.
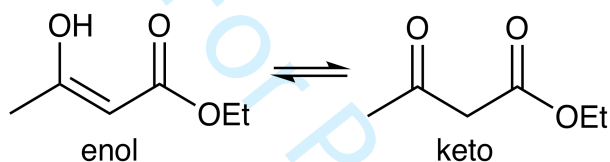
7

8   5   *Note 1*: The atoms of the groups X,Y, Z are typically any of C, H, N, O, or S, and G

9   6   is a group that becomes an *electrofuge* or *nucleofuge* during isomerization.

10   7   *Note 2*: The commonest case, when the electrofuge is H^+, is also known as a

11

12   8   *prototropic rearrangement*.
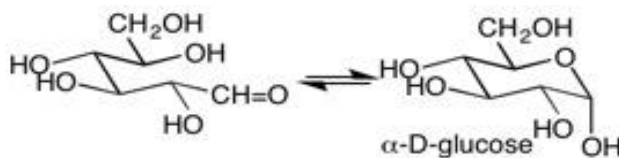
13   9   *Examples*:

14   10

15

16

17

18

19

20   enol   keto

21

22

23

24

25

26

27   11

28   12

29

30   13   *Note 3*: The group Y may itself be a three-atom (or five-atom) chain extending the

31   14 conjugation, as in

32   15

33

34

35

36   16

37   17

38

39   18   *Note 4*: Ring-chain tautomerization is the case where addition across a double bond

40   19 leads to ring formation, as in

41   20

42

43

44

45

46

47   α-D-glucose

48   21

49

50   22   *Note 5*: *Valence tautomerization* is the case of rapid isomerization involving the

51   23 formation and rupture of single and/or double bonds, without *migration* of atoms: for

52   24 example

53

54

55

56

57

58

59

60

See [346,401].

See also *ambident*, *fluxional*, *sigmatropic rearrangement*, *valence tautomerization*.
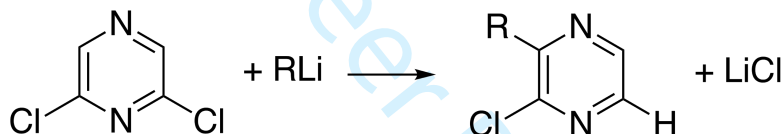
rev[3]

tautomers

Constitutional isomers that can interconvert more or less rapidly, often by *migration* of a *hydron*.

See *tautomerization*.

tele-substitution

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.

Example

See also *cine-substitution*.
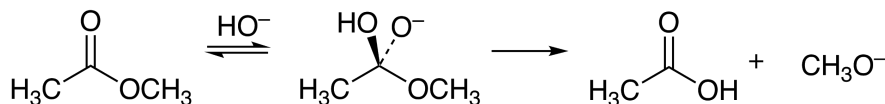
See [402,403].

rev[3]

termination

Step(s) in a *chain reaction* in which *reactive intermediate*s are destroyed or rendered inactive, thus ending the chain.

[3]

tetrahedral intermediate

Reaction *intermediate* in which the bond arrangement around an initially double-bonded carbon atom (typically a carbonyl carbon) has been transformed from tricoordinate to tetracoordinate (with a *coordination number* of 4).

Example:

rev[3]

1 **thermodynamic control (of product composition)**

2 equilibrium control

3 Conditions (including reaction times) that lead to reaction products in a proportion

4 specified by the *equilibrium* constant for their interconversion.

5   See also *kinetic control*.

6   rev[3]

7

8 **thermolysis**

9 Uncatalysed cleavage of one or more *covalent bond*s resulting from exposure of a

10 *molecular entity* to a raised temperature, or a process of which such cleavage is an

11 essential part.

12   See also *pyrolysis*.

13   [3]

14

15 **through-conjugation**

16 Phenomenon whereby electrons can be delocalized from any of three (or more) groups

17 to any other.

18   *Example:* *p*-XC_6H_4Y, where an electron pair can be delocalized from electron-

19 donating X not only to ring carbons but also to electron-withdrawing Y.

20   *Note 1*: This may be contrasted with *cross-conjugation.*

21   *Note 2*: In Hammett-type correlations (*linear Gibbs-energy relationship*s) this

22 situation can lead to exalted substituent constants σ^+ or σ^-, as in solvolysis of *p*-

23 $CH_3OC_6H_4C(CH_3)_2Cl$ or acidity of *p*-nitrophenol, respectively.
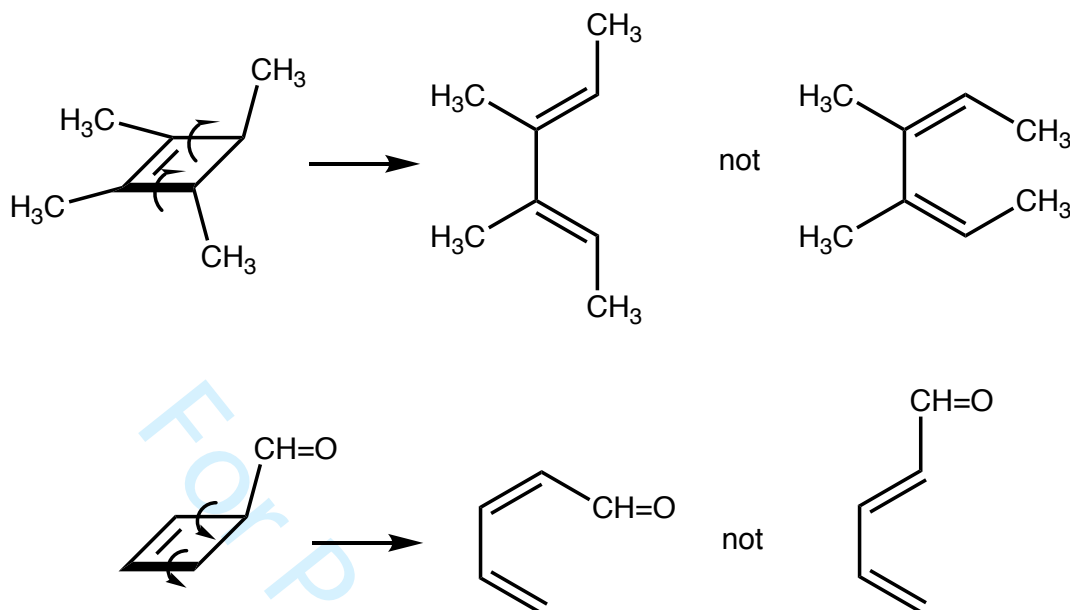
24

25 **TICT**

26   See *twisted intramolecular charge transfer*.

27

28 **torquoselectivity**

29 Preference for inward or outward rotation of substituents in *conrotatory* or *disrotatory*

30 *electrocyclic* ring-opening and ring-closing reactions, often owing to a preference for

31 electron donors (especially including large groups) to rotate outward and acceptors to

32 rotate inward.

33   See [404,405].

1

2   rev[3]

3

4   **transferability**

5   Assumption that a chemical property associated with an atom or group of atoms in a

6   molecule will have a similar (but not identical) value in other circumstances.

7   *Examples*: equilibrium bond length, bond force constant, NMR chemical shift.

8   [3]

9

10   **transformation**

11   Conversion of a *substrate* into a particular product, irrespective of the specific reagents

12   or *mechanisms* involved.

13   *Example*: transformation of aniline (C$_6$H$_5$NH$_2$) into *N*-phenylacetamide

14   (C$_6$H$_5$NHCOCH$_3$), which may be effected with acetyl chloride or acetic anhydride or

15   ketene.

16   *Note:* A transformation is distinct from a reaction, the full description of which would

17   state or imply all the reactants and all the products.

18   See [406].

19   [3]

20

21   **transient (chemical) species**

22   Short-lived reaction *intermediate*.

23   *Note 1*: Transiency can be defined only in relation to a time scale fixed by the

24   experimental conditions and by the limitations of the technique employed in the

25   detection of the intermediate. The term is a relative one.

Note 2: 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*.

[3]

transition dipole moment

Vector quantity describing the oscillating electronic moment induced by an electromagnetic wave, given by an integral involving the dipole moment operator **m** and the ground- and excited-state *wavefunction*s:

$$\boldsymbol{M} = \int \Psi_{exc}\, \mathbf{m}\, \Psi_{gnd}\, d\tau$$

Note: The magnitude of this quantity describes the allowedness of an electronic transition. It can often be separated into an electronic factor and a nuclear-overlap factor known as the Franck-Condon factor.

See [9].

transition state

State of a molecular system from which there are equal probabilities of evolving toward states of lower energy, generally considered as reactants and products of an *elementary reaction*.

Note 1: The transition state corresponds to the maximum along the minimum-Gibbs-energy path connecting reactants and products.

Note 2: The transition state can be considered to be a *chemical species* of transient existence.

Note 3: The term transition-state structure refers to a structure inferred from kinetic and stereochemical investigations; it does not necessarily coincide with a transition state or with a *transition structure*, which corresponds to a saddle point on a *potential-energy surface*, although it may represent an average structure.

Note 4: The assembly of atoms at the transition state has also been called an *activated complex*, although it is not a *complex* according to the definition in this Glossary.

Note 5: There are also reactions, such as the gas-phase *colligation* of simple *radical*s or the reactions of some *reactive intermediate*s in solution, that do not require activation and do not involve a transition state.

Note 6: Ultrafast spectroscopy permits observation of transition states in some special cases.

See [349,407].

1   See also *Gibbs energy of activation*, *potential-energy profile*, *reaction coordinate*,
2 *transition structure*.
3   rev[3]
4

5 **transition-state analogue**
6 Species designed to mimic the geometry and electron density of the *transition state* of
7 a reaction, usually enzymatic.
8   *Note*: A transition-state analogue is usually not a substrate for the enzyme, but rather
9 an inhibitor.
10   rev[3]
11

12 **transition structure**
13 *Molecular entity* corresponding to a saddle point on a *potential-energy surface*, with one
14 negative force constant and its associated imaginary frequency.
15   *Note 1*: Whereas the *transition state* is not a specific molecular structure, but a set
16 of structures between reactants and products, a transition structure is one member of
17 that set with a specific geometry and energy.
18   Note 2: Although the saddle point coincides with the potential-energy maximum
19 along a *minimum-energy reaction path*, it does not necessarily coincide with the
20 maximum of Gibbs energy for an ensemble of *chemical species*.
21   *Note 3:* The term transition-state structure is not a synonym for transition structure.
22   See [349,408].
23   See also *activated complex*, *transition state*.
24   rev[3]
25

26 **transition vector**
27 Normal mode of vibration of a *transition structure* corresponding to the single imaginary
28 frequency and tangent to the *intrinsic reaction coordinate* at the saddle point.
29 Sometimes called the reaction-coordinate vibrational mode.
30   *Note*: Infinitesimal motion along the transition vector in the two opposite senses
31 determines the initial direction leading either toward reactants or toward products.
32   *Note 2*: The term "transition coordinate" was used in the 1994 Glossary of Terms in
33 Physical Organic Chemistry in the sense defined here for transition vector, but
34 apparently this usage was unique in the literature at that time and has not been
35 generally adopted since.
36   See [349,409].
37   See *reaction coordinate*, *transition state*.
38

39

40

transport control

    See *encounter-controlled rate, microscopic diffusion control*.

    [3]

trapping

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.

    See also *scavenger*.

    [3]

triplet state

State having a total electron spin quantum number of 1.

    See [9].

tunnelling

Quantum-mechanical phenomenon by which a particle or a set of particles penetrates a barrier on its *potential-energy surface* without having the energy required to surmount that barrier.

    Note 1: In consequence of Heisenberg's Uncertainty Principle, a molecular entity has a nonzero probability of adopting a geometry that is classically forbidden because it corresponds to a potential energy greater than the total energy.

    Note 2: Tunnelling is often considered to be a correction to an (over)simplified version of transition-state theory.

    Note 3: Because the rate of tunnelling increases with decreasing mass, it is significant in the context of *isotope effect*s, especially of hydrogen isotopes.

    See [410,411].

    rev[3]

twisted intramolecular charge transfer (TICT)

Feature of an excited electronic state formed by intramolecular electron transfer from an electron donor (D) to an electron acceptor (A), where interaction between electron and hole is restricted because D^+ and A^- are perpendicular to each other.

    See [412].

umpolung

Process by which the nucleophilic or electrophilic property of a functional group is reversed.

    Note: Umpolung is often achieved by temporary exchange of heteroatoms N or O by others, such as P, S, or Se, as in the conversion of electrophilic RCH=O to $RCH(SR')_2$

1 and then with base to nucleophilic RC(SR')$_2^-$. Also the transformation of a haloalkane
2 RX into a Grignard reagent RMgCl is an umpolung.
3   See [413].
4   rev[3]
5

6 **unimolecular**
7 Feature of a reaction in which only one *molecular entity* is involved.
8   See *molecularity*.
9   rev[3]
10

11 **unreactive**
12 Failing to react with a specified *chemical species* under specified conditions.
13   *Note*: The term should not be used in place of *stable*, which refers to a
14 thermodynamic property, since a relatively more stable species may nevertheless be
15 more *reactive* than some reference species towards a given reaction partner.
16   [3]
17

18 **unstable**
19 Opposite of *stable*, i.e., the *chemical species* concerned has a higher molar Gibbs
20 energy than some assumed standard.
21   *Note*: The term should not be used in place of *reactive* or transient, although more
22 reactive or *transient species* are frequently also more unstable.
23   rev[3]
24

25 **upfield**
26 superseded but still widely used to mean shielded.
27   See *chemical shift*.
28   [3]
29

30 **valence**
31 Maximum number of single bonds that can be commonly formed by an atom or ion of
32 the element under consideration.
33   *Note*: Often there is a most common maximum for a given element, and atoms in
34 compounds where this number is exceeded, such as pentacoordinate carbocations
35 ("carbonium ions") and iodine(III) compounds, are called *hypervalent*.
36   rev[3]
37

38 **valence isomer**
39 *Constitutional isomer* related to another by *pericyclic reaction*.

1   *Examples*: Dewar benzene, prismane, and benzvalene are valence isomers of
2   benzene.
3   *Note*: Valence isomers are separable, as distinguished from valence tautomers,
4   which interconvert rapidly. See *valence tautomerization*.
5   rev[3]
6

valence tautomerization

8   Rapid isomerization involving the formation and rupture of single and/or double bonds,
9   without *migration* of atoms.
10   *Example:*

11

12   See *tautomerization*.
13   rev[3]
14

van der Waals forces

16   Attractive or repulsive forces between *molecular entities* (or between groups within the
17   same molecular entity) other than those due to *bond* formation or to the electrostatic
18   interaction of ions or of ionic *group*s with one another or with neutral molecules.
19   *Note 1*: The term includes dipole-dipole, dipole-induced dipole, and London
20   (instantaneous induced dipole-induced dipole) forces, as well as quadrupolar *forces.*
21   *Note 2*: The term is sometimes used loosely for the totality of nonspecific attractive
22   or repulsive intermolecular forces.
23   *Note 3*: In the context of molecular mechanics, van der Waals forces correspond only
24   to the London dispersion forces plus the Pauli repulsion forces. Interactions due to the
25   average charge distribution (and not to fluctuations around the average or to induced
26   dipoles), including dipole-dipole, ion-ion and ion-dipole forces, are called Coulombic
27   forces.
28   See [290,414].
29   See also *dipole-dipole interaction*, *dipole-induced dipole forces, London forces.*
30   rev[3]
31

volume of activation, $\Delta^{\ddagger}V$

33   Quantity derived from the pressure dependence of the *rate constant* of a reaction,
34   defined by the equation
35

36    $\Delta^{\ddagger}V = -RT \left[\partial\ln(k/[k])/\partial p\right]_T$

37

provided that 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 argument in the lg function should be of dimension 1. Thus, the rate constant should be divided by its units, [k].

Note: The volume of activation is interpreted as the difference between the partial molar volume $^{\ddagger}V$ of the *transition state* and the sums of the partial molar volumes of the reactants at the same temperature and pressure, i.e.,

$$\Delta^{\ddagger}V = {}^{\ddagger}V - \Sigma(\rho V_R)$$

where ρ is the order in the reactant R and V_R its partial molar volume.

See [13].

See *order of reaction*.

rev[3]

water/octanol partition coefficient (partition ratio)

See *octanol-water partition ratio*

wavefunction

A mathematical expression whose form resembles the wave equations of physics, supposed to contain all the information associated with a particular atomic or molecular system. In particular, a solution of the Schrödinger wave equation, $H\psi = E\psi$, as an eigenfunction ψ of the hamiltonian operator H, which involves the electronic and/or nuclear coordinates.

Note 1: The wavefunction contains all the information describing an atomic or molecular system that is consistent with the Heisenberg Uncertainty Principle.

Note 2: When a wavefunction is operated on by certain quantum-mechanical operators, a theoretical evaluation of physical and chemical observables for that system (the most important one being energy) can be carried out.

See [8,12].

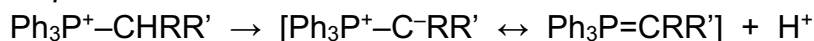**Wheland intermediate**

See *Meisenheimer adduct, σ-adduct*.

[3]

Woodward-Hoffmann rules

See *orbital symmetry*.

ylide

Chemical species that can be produced by loss of a _hydron_ from an atom directly attached to the central atom of an _onium ion_.

Example:

$$Ph_3P^+–CHRR' \rightarrow [Ph_3P^+–C^-RR' \leftrightarrow Ph_3P=CRR'] + H^+$$

See [40].

[3]

Yukawa-Tsuno equation

Multiparameter extension of the _Hammett equation_ to quantify the role of enhanced _resonance_ effects on the reactivity of _para_–substituted benzene derivatives,

$$lg \{k\} = lg \{k_o\} + \rho[\sigma^o + r(\sigma^+ - \sigma^o)]$$

or $\quad lg \{k\} = lg \{k_o\} + \rho[\sigma^o + r(\sigma^- - \sigma^o)]$

where the parameter _r_ expresses the enhancement and where σ^o is a _substituent constant_ based on reactivities of phenylacetic acids and similar substrates, where resonance interaction is weak or absent. The argument in the lg function should be of dimension 1. Thus, reduced rate constants should be used $\{k\}= k/[k]$ and $\{k_o\} = k_o/[k_o]$.

See [398,415,416].

See also _dual substituent-parameter equation_, _ρ-value_, _σ-constant_, _through-conjugation_.

rev[3]

Zaitsev rule

See _Saytzeff rule_.

[3]

zero-point energy

Extent, in consequence of Heisenberg's Uncertainty Principle, by which a particle or a set of particles has an energy greater than that of the minimum on the _potential-energy surface_.

Note 1: Because of zero-point energy a molecular entity has a nonzero probability of adopting a geometry whose energy is greater than that of the energy minimum.

Note 2: A molecular entity with zero-point energy may even adopt a geometry with a potential energy greater than its total energy, a possibility that permits _tunnelling_.

Note 3: Because the magnitude of zero-point energy increases with decreasing mass, it is significant in the context of _isotope effect_s, especially of hydrogen isotopes.

Zucker-Hammett hypothesis

1 Assumption that if lg {k_1} (= k_1/[k_1], reduced pseudo-first-order rate constant of an acid-

2 catalyzed reaction) is linear in H_o (Hammett *acidity function*), then water is not involved

3 in the *transition state* of the *rate-controlling step*, whereas if lg {k_1} is linear in lg {[H$^+$]}

4 then water is involved. The argument in the lg function should be of dimension 1. Thus,

5 reduced concentration = {[H$^+$]} should be used, i.e., concentration of protons divided by

6 its units.

7   *Note*: This has been shown to be an overinterpretation.

8   See [22,417].

9   See also *Bunnett-Olsen equation*, *Cox-Yates equation.*

10   rev[3]

11

12 **Z-value**

13 Quantitative measure of solvent polarity based on the UV-vis spectrum of 1-ethyl-4-

14 (methoxycarbonyl)pyridinium iodide.

15   See [143].

16   See *solvent parameter*.

17   rev[3]

18

19 **zwitterion**

20 Highly dipolar, net uncharged (neutral) molecule having full electrical charges of

21 opposite sign, which may be delocalized within parts of the molecule but for which no

22 uncharged canonical resonance structure can be written.

23   *Examples*: glycine (H$_3$N$^+$–CH$_2$–CO$_2^-$), betaine (Me$_3$N$^+$–CH$_2$–CO$_2^-$).

24   *Note 1*: Sometimes also referred to as inner salts or ampholytes.

25   *Note 2:* Mesoionic compounds, such as sydnones, in which both positive and

26 negative charge are delocalized, are sometimes considered as zwitterions, but species

27 with a localized nonzero formal charge, such as a nitrone, CH$_3$CH=N$^+$(–O$^-$)CH$_3$, are

28 not.

29   See [418].

30   rev[3]

31

1

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