Chemistry Definitions

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Topic 1: Stoichiometry

Avogadro's constant: The number of particles (atoms or molecules) in one mole of any pure substance. [6.022×10^{23}]

Compound: A term used generally to indicate a definite combination of elements into a more complex structure (a molecule) but it is also applied to systems with non-stoichiometric proportions of elements

Constitution: The number and type of atoms in a molecule.

Element: A substance, which cannot be further subdivided by chemical methods.

IUPAC Nomenclature: Standardized system of nomenclature promoted by the International Union of Pure and Applied Chemistry.

Steric hindrance: Strain in a molecule produced by repulsion of groups adjacent or close to one another. Hindrance increases as size and bulk increase; the phenomenon of physical blockage of a particular site within a molecule by the presence of local atoms or groups of atoms. [As a consequence of steric hindrance, a reaction at a particular site will be impeded.]

Topic 2 and 12: Atomic Structure

Atomic orbital: The energy levels of electrons in an atom, which may be described in terms of the four quantum numbers.

Disproportionation: A process in which a compound of one oxidation state changes to compounds two or more oxidation states [E.g. $2Cu^{+}$ --> Cu + Cu^{2+}]

Electronic configuration: The particular order in which electrons are arranged in an atom or molecule. [Used in a distinct and different sense from stereochemical configuration.]

HOMO: The highest occupied molecular orbital of a molecule, ion or atom.

LUMO: The lowest unoccupied molecular orbital in a molecule or ion.

Mass spectrometry: A form of spectrometry in which, generally, high energy electrons are bombarded onto a sample and this generates charged fragments of the parent substance; these ions are then focused by electrostatic and magnetic fields to give a spectrum of the charged fragments.

Microwave spectroscopy: The interaction of electromagnetic waves with wavelengths in the range 10-2 to 1 meter. [This energy range corresponds to rotational frequencies and hence microwave spectroscopy is useful in studying the structure of materials (generally gases) and in their characterization.]

Molecular orbitals: The electron orbitals belonging to a group of atoms forming a molecule.

Nuclear magnetic resonance (NMR) spectroscopy: A form of spectroscopy which depends on the absorption and emission of energy arising from changes in the spin states of the nucleus of an atom. [For aggregates of atoms, as in molecules, the local chemical environment causes minor variations in these energy changes. The energy changes used are in the radio frequency range of the electromagnetic spectrum and depend upon the magnitude of an applied magnetic field.]

Polarity: Charge separation due to asymmetric distribution of electrons.

Radical: A term applied to an atom or molecule having one or more free valences.

Spectrometer: An instrument that measures the spectrum of a sample. [For example a mass spectrometer]

s orbital: A spherically symmetrical electron orbital centered on the nucleus.

Topic 3 and 13: Periodicity

Anion: Negatively-charged ion.

Cation: Positively-charged ion.

Electronic transition: In an atom or molecule the electrons have certain allowed energies only (orbitals). If an electron passes from one orbital to another an electronic transition occurs and there is the emission or absorption of energy corresponding to the difference in energy of the two orbitals.

Electronegativity: Ability of an atom to attract electrons, resulting in polarized bonds.

Molecule: The smallest particle of matter that can exist in a free state. In the case of ionic substances, such as sodium chloride, the molecule is considered as a pair of ions, NaCl.

Unsaturated compound: Compound with double or triple bonds.

Topic 4 and 14: Bonding

Angle strain: Occurs in molecules when bond angles are forced from their ideal values.

Bond energy: The energy required to break a particular bond by a homolytic process.

Co-ordinate bond: The linkage of two atoms by a pair of electrons both electrons being provided by one of the atoms (the donor). [Coordinate bonds are covalent bonds.]

Covalent bonding: Bonding in which the half-filled orbitals of atoms overlap such that both constituents share the resulting electron pair.

Delocalization of electrons: Distribution of electron density over several atoms because of conjugation of pi bonds.

Dipole moment: Measure of the net polarity of a bond or molecule.

Double bond: Some atoms can share two pairs of electrons to form a double bond (two covalent bonds). Formally the second (double) bond arises from the overlap of p orbitals from two atoms, already united by a sigma bond, to form a **p-** bond.

Electrovalent (ionic) bond: Bonding by electrostatic attraction.

Hybridization: The process whereby atomic orbitals of different type but similar energies are combined to form a set of equivalent hybrid orbitals. These hybrid orbitals do not exist in the atoms but only in the formation of molecular orbitals by combining atomic orbitals from different atoms.

Hydrogen bonding: Weak electrostatic interaction between a hydrogen atom bonded to an electronegative atom, such as N, O, or F, and the lone pairs of other electronegative atom

Inductive effect: An electron-withdrawing or electron-attracting effect transmitted through sigma bonds in response to a dipole.

Ionic bond: Bond between compounds with very different electron affinities, involving the transfer of an electron to the more electronegative atom; e.g., LiF.

Peptide bond: Amide between the nitrogen of the amino group of one amino acid and the carbon of the carbonyl group of another amino acid. Characterized by partial double-bond character and thus imparts rigidity to peptide chains.

Pi (p) bond: Covalent bond formed by parallel overlap, (side-ways overlap), of two unhybridized atomic p-orbitals, as in a carbon-carbon double bond.

Polar covalent bond: Bond formed by the sharing of electrons between two atoms of different electronegatives, resulting in the attraction of electrons toward the more electronegative atom.

Protonation: Acceptance of a proton by an electron-pair donor.

Resonance: Delocalization of electrons within a compound. Such compounds may be represented by various electron configurations, and have a true electron configuration somewhere between the various possibilities. Because the electrons are spread out over the molecule, the structure gains added stability.

Ring strain: Tension experienced by cyclic compounds due to the bending and stretching of bonds in order to fulfill geometric (angular) and steric requirements.

Sigma (s) bond: Head-to-head overlap, (overlap across the bond nuclear axis), of hybridized or s orbitals from separate atoms to form a bonding orbital.

Valence bond theory: The wave mechanical basis of resonance theory.

van der Walls forces: Weak intermolecular interactions such as dipole-dipole interactions, hydrogen bonding, and London force

Topic 5 and 15: Energetics

Electron affinity: Measurable energy change accompanying the addition of an electron to an atom.

Endothermic: A reaction in which heat is absorbed.

Energy diagram (or reaction energy diagram): A graph of the energy of a reaction against the progress of the reaction.

Enthalpy: A thermodynamic state function, generally measured in kilojoules per mole. In chemical reactions the enthalpy change (? H) is related to changes in the free energy (? G) and entropy (? S) by the equation: ? G = ? H - T? S

Entropy: A thermodynamic quantity, which is a measure of the degree of disorder within any system. [The greater the degree of order the higher the entropy; for an increase in entropy, S is positive. Entropy has the units of joules per degree K per mole.]

Free energy (? G): A thermodynamic state function; the free energy change (? G) in any reaction is related to the enthalpy and entropy:

? G = ? H - T? S

Inhibitor: A general term for any compound, which will inhibit (slow down) a reaction. [Inhibitors can be used to slow down or stop free radical chain reactions.]

Mechanism: Pathway by which a reaction occurs, describing all reactants, intermediates, and products and the conditions that must be present for the reaction to take place.

Rate-determining step: Slowest step in a multistep reaction. The rate of the reaction is dependent only on this step.

Reactive intermediates: Reaction molecules or molecule pieces that are formed during a reaction and quickly proceed to subsequent steps of the reaction sequence.

Topic 6 and 16: Kinetics

Activation energy: Energy barrier that must be overcome in order for a reaction to occur. The activation energy required determines the rate of the reaction at a particular temperature.

Chain reaction: A reaction involving several steps, each leading to a reactive substance that is necessary for the next step to occur. For example, in a free-radical reaction, each step after initiation of the radical that makes the reaction continue.

E1 (Unimolecular elimination): Elimination reaction whose kinetics are first-order. The rate-limiting step is the departure of a leaving group, which produces a carbocation; a base then abstracts a proton to form a double bond.

E2 (Bimolecular elimination): Elimination reaction whose kinetics are second-order. A base removes a proton and the leaving group simultaneously departs, forming a double bond.

First-order reaction: Reaction whose rate depends on the concentration of only one reactant (Rate = k [reactant]).

Half-life, t1/2: The time taken for the concentration of a substance in a reaction to reduce to half its original value.
[Used in first order reactions and as a measure of the rate of radioactive decay.]

Heat of reaction: The amount of heat absorbed or evolved when specified amounts of compounds react under constant pressure. [Expressed as kilojoules per mole. For exothermic reactions the convention is that the enthalpy change (heat of reaction) is negative.]

Kinetics: The study of the rate of reactions.

Kinetic order of reaction: Sum of the exponents of all the reactant present in a rate equation.

Melting point: Temperature at which the solid and liquid phases of a compound are in equilibrium.

Transition state: The point of highest energy on an energy against reaction coordinate curve. [By definition the transition state is the least stable point (peak) on a reaction path; a reaction path may involve more than one transition states.

Topic 7 and 17: Equilibrium

Boiling point: Temperature at which the vapor pressure of a liquid is equal to atmospheric pressure, and the liquid and gas phases are in equilibrium.

Catalyst: Any material that reduces the activation energy of a reaction and thus increases its forward and reverse reaction rates. Catalysts are neither altered nor consumed during a reaction.

Equilibrium constant: According to the law of mass action, for any reversible chemical reaction:

$$aA + bB \rightarrow cC + dD,$$

the equilibrium constant (K)is defined as:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Reversible process: A process in which the forward reaction can reach equilibrium with the reverse reaction.

Topic 8 and 18: Acids and Bases

Acid: An agent able to produce positively charged hydrogen ions (H^+). [Since the hydrogen ion is a bare proton, it usually exists in a solvated form, such as $(H_3O)^+$.

Base: A base is a substance that can combine with a proton.

Lewis acid: Electron-pair acceptor, e.g., BF_3 or $AlCl_3$.

Lewis base: Electron-pair donor, e.g., $:NH_3$.

Salts: Positive and negative ions linked by electrostatic attraction. A salt is the neutralization product of an acid and a base.

Topic 9 and 19: Oxidation and Reduction

Oxidation: Loss of electrons; a chemical process in which the proportion of electronegative substituents in a compound is increased, or the charge is made more positive, or the oxidation number is increased.

Radical: A term applied to an atom or molecule having one or more free valencies.

Reduction: Gain of electrons; Chemical processes in which the proportion of more electronegative substituents is decreased, or the charge is made more negative, or the oxidation number is lowered.

Topic 10 and 20: Organic Chemistry

Achiral: A molecule that does not possess optical activity.

Activating group: Activating group make an aromatic ring more susceptible to electrophilic substitution. Activating groups, except for alkyl groups, have at least one pair of nonbonding electrons on the atom directly attached to the ring; these electrons stabilize the carbocation intermediate. Activating groups direct substituents to the *ortho* and *para* positions. Typical examples are -NH_2, -OH, -CH_3, and -OCH_3.

Addition reaction: Reaction in which an electrophile and then a nucleophile add to a p – bond, resulting in a more saturated compound.

Alcohols (aka: alkanols): Compounds of the general formula ROH, containing an -OH group.

Aldehydes: Compounds of the general formula RCHO.

Aliphatic compounds: Nonaromatic hydrocarbons.

Alkanes: The simplest organic molecules, consisting only of carbon and hydrogen and containing only single bonds. The general formula for alkanes is C_nH_{2n+2}. Also called ***paraffins***.

Alkaloid: Organic substances occurring naturally, which are basic, forming salts with acids. The basic group is usually an amino function.

Alkenes: Hydrocarbons with at least one carbon-carbon double bond, (C=C). Their general formula is C_nH_{2n}. Also called ***olefins***.

Alkynes: Hydrocarbons with at least one carbon-carbon triple bond, (C=C). Their general formula is C_nH_{2n-2}.

Allyl group: A group containing 3 carbon atoms and a double bond [C1=C2-C3], where C3 is called the allyliuc position or allylic carbon atom].

Allylic rearrangement: The migration of a double bond in a 3-carbon system from carbon atoms one and two to carbon atoms two and three.

Alpha carbon: A carbon adjacent to a carbon containing the functional group under consideration.

Alpha hydrogen: The hydrogen bonded to an alpha carbon, which is usually affected by the nearby group. For instance, a hydrogen alpha to a carbonyl group is more acidic than other carbon-bonded hydrogens, because of the resonance stabilization effect of the carbonyl on the resulting carbanion.

Amides: Compounds of the general formula $RCONH_2$, RCONHR, or $RCONR_2$.

Amines: Compounds of the general formula RNH_2(primary), R_2NH(secondary), or R_3N(tertiary).

Amino acids: Compounds of the general formula $NH_2CRHCOOH$, The 20 amino acids found in nature are the building blocks of proteins.

Anhydrides: Compounds of the general formula RCO_2COR. They are the dimeric products of two carboxylic acids, or acids derivatives, that have lost water or hydrogen halides.

Aromatic compounds (Arenes): Cyclic compounds that fulfil the following criteria:

1) 4n + 2 pi electrons (Hückel's Rule).
2) Every atom of the ring is associated with at least one pi orbital.
3) Planar configuration.

Association: A term applied to the combination of molecules of a substance with one another to form more complex systems. E.g. CH_3COOH

Asymmetry: A term applied an object or molecule that does not possess symmetry.

Base peak: The most intense peak in a mass spectrum.

Beta carbon: A carbon two carbons away from the functional group under consideration.

Carbanion: Carbon atom that possesses a formal negative charge (has an extra electron).

Carbonium: Carbon atom that possesses a formal positive charge (lacks an electron).

Carbohydrates: Compounds of the general formula $C_m(H_2O)_n$.

Carbonyl group: C=O group found in aldehydes, ketones, and carboxylic acids, among others.

Carboxylic acids: Compounds of the general formula RCOOH. The hydrogen is acidic due to resonance stabilization of the conjugate base.

Catalytic cracking: The method for producing gasoline from heavy petroleum distillates.
[Generally the catalysts are mixtures of silica and alumina or synthetic conjugates such as the zeolites.]

Catalytic reforming: The process of improving the octane number of straight-run gasoline by increasing the proportion of aromatic and branched chain alkanes.
[Catalysts employed are either molybdenum aluminium oxides or platinum based.]

Chair conformation: The most stable conformation of cyclohexane, in which all C-C bonds are 109.5^0 and all the substituents on alternating carbons are staggered.

Chiral center: Atom, usually carbon, with four different substituents attached to it.

Chiral molecule: A molecule not superimposable on its mirror image and that exhibits optical activity. A chiral center is usually but not necessarily present.

Cis isomers: Configuration about a double bond in which the two largest groups are on the same side of the molecule. (See **Geometric isomers**).

Condensation reaction: Combination of two or more molecules, often with the loss of a small molecule such as water or alcohol; e.g., aldol condensation.

Conformation: Orientation of atoms in a molecule, which can be altered by rotation about a C-C single bond.

Conjugated dienes: Dienes whose two C-C double bonds are separated by one single bond and that are therefore subject to electron delocalization.

Cycloalkanes: Saturated cyclic hydrocarbons of the formula C_nH_{2n}.

Deactivating groups: Substituents which, when attached to benzene rings, make the ring less susceptible to electrophilic attack. These are compounds that withdraw electrons from the aromatic ring, destabilizing the carbocation intermediate. Examples include $-NO_2$, -COOH, -CHO, and halogens. Most are *meta* directors, except for the halogens, which are *ortho/para* directors.

Decarboxylation: A reaction resulting in the loss of a molecule of CO_2.

Dehydration: A reaction resulting in a net loss of H_2O, often observed in the elimination reactions of alcohols.

Dextrorotatory: Term used to describe the rotation of plane-polarized light by an optically active molecule in a clockwise or positive (+) direction.

Diastereomers: Stereoisomers that are not mirror images of each other, e.g., the S, R and R, R forms of tartaric acid.

Dienes: Compounds containing two double bonds.

Diols: Compounds with two alcohol groups. Germinal (*gem*) diols have the two -OH groups on the same carbon atom; vicinal (*vic*) diols, also known as glycols, have the two -OH groups on adjacent carbons.

Electrophiles: Species that “love” electrons and therefore seek them out. They often are positively-charged and seek electrons in order to fill their outer shells. Many typical electrophiles are Lewis acids.

Electrophilic addition: Addition of an electrophile to an electron rich species. A typical example is the addition of Br_2 to an alkene.

Electrophilic aromatic: Substitution of an electrophile into the electron-rich p-system of substitution an aromatic compound. Typically, a Lewis acid is used as a catalyst.

Electrophilic substitution: An overall reaction in which an electrophile binds to a substrate with the expulsion of another electrophile. [The most common example is the electrophilic substitution of a proton by another electrophile, such as a nitronium ion, on an aromatic substrate such as benzene.

Enantiomers: Stereoisomers that are non-superimposable mirror images of one another. For example, if there is one chiral center then the R and S isomers are enantiomers.

Enzyme: A naturally occurring substance able to catalyse a chemical reaction.

Esterification: The formation of an ester by reaction of an alcohol with an acid.

Esters: Compounds of the general formula RCOOR.

Ethers: Compounds of the general formula ROR′

Fatty acid: Long-chain aliphatic carboxylic acids derived from the hydrolysis of fats.

Free radical: Highly reactive species possessing an unpaired electron.

Free radical substitution: Chain-reaction in which a radical abstracts a substituent from a molecule (usually hydrogen) and replaces it with another substituent, often a halogen, forming the product and a free radical. Three steps characterize free-radical substitutions: initiation, propagation, and termination.

Geometric isomers: Compounds that differ only in the geometry of the groups on the same carbon and is a hydrate of an aldehyde or ketone.

Halogenation: Reaction in which a halogen atom is incorporated into a substrate through and addition, free-radical, or substitution reaction.

Heat of combustion: Amounts of heat released when a compound is burned. For the combustion of a hydrocarbon:

$$C_nH_m + O_2 \longrightarrow n\,CO_2 + \frac{m}{2} H_2O$$

Heterogeneous reaction: A reaction, which occurs between substances, which are mainly present in different phases. [For example, between a gas and a liquid.]

Heterolytic reaction: A reaction in which a covalent bond is broken with unequal sharing of electrons from the bond.

Homolytic reaction: A reaction in which a covalent bond is broken with equal sharing of the electrons from the bond.

Hydroboration: The cis-addition of B-H bonds across double (or triple) carbon-carbon bonds.

Hydrogenolysis: The cleaving of a chemical bond by hydrogen. [Generally carried out in the presence of a hydrogenation catalyst.]

Hydrocarbons: Organic compounds containing only carbon and hydrogen.

Hydrogenation: Reaction in which hydrogen is added to an unsaturated compound, usually performed with a catalyst.

Hydrolysis: The addition of the elements of water to a substance, often with the partition of the substance into two parts, such as in the hydrolysis of an ester to an acid and an alcohol.

Infrared spectroscopy: The study of the absorption of infrared light by substances. [Since this corresponds to vibrational (and some rotational) changes, infrared spectroscopy provides valuable information about the structure of a substance. Detailed correlation tables exist relating infrared bands (absorbances) to functional groups.]

Initiation reaction: A reaction generating a free radical, e.g.: Br_2 —> 2Br·

Isomers: Compounds with the same molecular formulas but different structures. See *Structural Isomers; Geometric Isomers; Stereoisomers.*

Ketones: Compounds of the general formula RCOR.

Leaving group: Group that is replaced in a substitution reaction, which must be weaker nucleophiles than the species which will replace them. The best leaving groups from the most stable anions in solution.

Levorotatory: Term used to describe the rotation of plane-polarized light by an optically active molecule in a counterclockwise or negative (-) direction.

Markonikov's Rule: The rule stating that the addition of a protic acid (HX) to an alkene occurs such that the proton attaches to the carbon atom with the smallest number of alkyl groups, producing the most stable carbocation.

***Meso* compounds:** Compounds with at least two chiral centers, but with a plane of symmetry resulting in a mirror image that is superimposable on the original molecule.

***Meta* compounds:** In disubstituted benzene rings, the configuration in which the two functional groups are oriented in the 1,3 or 1,5 positions on the ring.

Micelles: Clusters of molecules possessing hydrophilic ionic heads facing the surface of a sphere where they can interact with water, and possessing hydrophobic hydrocarbon tails in the interior. Soap forms micelles, facilitating the dissolution of oils and fats.

Nucleophile: Species that is a "nucleus lover" and thus tends to donate an electron pair to an electrophile.

Olefins: Another name for alkenes.

Optically active: Term describing compounds that can rotate the plane of polarized light.

***Ortho* configuration:** In disubstituted benzene rings, the configuration in which the two functional groups are oriented in the 1,2 or 1,6 positions on the ring.

***Para* configuration:** In disubsituted benzene rings, the configuration in which the two functional groups are oriented in the 1,4 positions on the ring.

Peptides: Molecules that consist of two or more amino acids linked to each other by peptide bonds.

Photochemical reaction: A chemical reaction brought about by the action of light.

Polarimeter: An instrument used to measure the amount of rotation of plane-polarized light by a compound, generally prepared in a solution.

Polarized light: Light in which all electric fields vibrate in one plane.

Primary amine: An amine with two hydrogen and one hydrocarbon substituents, i.e., RNH_2.

Primary (1^0) atom: A carbon atom attached to only one other carbon atom, or a hydrogen atom or other group attached to such a carbon.

Propagation: Series of events immediately following initiation in a chain reaction. A reactive intermediate reacts with a stable molecule to form another reactive intermediate, thereby continuously regenerating the reacting species. This enables the reaction to continue until completion.

Proteins: Long-chain polypeptides with high molecular weights.

Racemic mixture: A 50:50 mixture of the (+) and (-) enantiomers of an optically-active substance.

Rearrangement: Shifting of substituents with their electrons to a new location on the same molecule, leaving behind a more stable molecule, e.g., methyl and hydride shifts.

Resolution: The separation of a racemate into its two enantiomers by means of some chiral agency.

Saponification: Hydrolysis of an ester with a base, forming a carboxylic acid salt.

Saturated hydrocarbon: A hydrocarbon with only single bonds.

Secondary amine: An amine with one hydrogen and two hydrocarbon substituents, i.e., R_2NH.

Secondary atom: A carbon atom attached to two other carbon atoms, or a hydrogen atom or other group attached to such a carbon.

S_N1: Unimolecular nucleophilic substitution. It is characterized by two steps:
1) dissociation of a molecule into a carbocation and a leaving group;
2) combination of a nucleophile with the carbocation. No inversion of a configuration occurs, but a loss of stereochemistry does occur, because of the formation of a planar intermediate.

S_N2: Bimolecular nucleophilic substitution. It occurs in one step, involving two principal reactants. A strong nucleophile pushes into a molecule, dislodging a leaving group. These reactions are characterized by an inversion of absolute configuration.

Spectrophotometer: An instrument that measures the degree of absorption (or emission) of electromagnetic radiation by a substance. The measuring system generally includes a photomultiplier. [U.v., i.r., visible, and microwave regions of the electromagnetic spectrum may be measured in this way.]

Stereochemistry: The study of the spatial arrangements of atoms in molecules and complexes.

Stereoisomers: Isomeric compounds that possess the same atomic connectivity but differ in their spatial orientation.

Stereospecific reactions: Reactions in which bonds are broken and made at a particular carbon atom and which lead to a single stereoisomer. If the configuration is altered in the process the reaction is said to involve inversion of configuration; if the configuration remains the same the transformation occurs with retention of configuration.

Structural isomers: Compounds with the same molecular formula but different connections between atoms.

Substitution reactions: Reactions in which one atom or group of atoms is replaced by another atom or group of atoms. [See electrophilic substitutions and nucleophilic substitutions.]

Termination: The step in a chain-reaction in which two reactive species join together to form a nonreactive species.

Tertiary atom: A carbon atom attached to three other carbons, or a hydrogen atom or other group attached to such a carbon.

Tertiary anime: An amine with three hydrocarbon substituents, i.e., R_3N.

Twist boat conformation: Intermediate between the two chair conformations in cyclohexane; similar to the boat conformation except it is more stable, because the twist relieves eclipsing.

Ultraviolet light: Radiation of an energy range than that of visible light but lower than that of ionizing radiations such as X-rays. Many substances absorb ultraviolet light, leading to electronic excitation. [This process is useful both as a means for characterizing materials and for stimulating chemical reactions (photochemical reactions.)]
Vinyl group: The ethenyl group, -CH=CH2.

Walden inversion: A Walden inversion occurs at a tetrahedral carbon atom during an S_N2 reaction when the entry of the reagent and the departure of the leaving group are synchronous. The result is an inversion of configuration at the center under attack.

Zwitterion: Neutral dipolar molecular in which the charges are separated, such as amino acids.