

Molecular Geometry

VSEPR electron pairs in the valence shell of an atom repel one another and will arrange themselves to be as far apart as possible, minimizing the repulsive interactions between them

electron domain a lone pair or a bond, regardless of whether the bond is single, double, or triple

electron domain geometry (EG) arrangement of electron domains (bonds and lone pairs) around the central atom

molecular geometry (MG) arrangement of bonded atoms

when there are no lone pairs on any of the the central atoms, MG is the same as EG.

bond angle angle between two adjacent bonds in a molecule or polyatomic ion

AB5 molecules contain 2 bond angles because positions occupied by bonds in a trigonal bipyramid are not all equal.

1) equatorial: 3 bonds arranged in a trigonal plane
2) axial: 2 bonds that form an axis perpendicular to the trigonal plane

Valence Bond Theory

valence bond theory bonds form between atoms when atomic orbitals overlap, thus allowing the atoms to share valence electrons.

Valence Bond Theory (cont)

each of the overlapping atomic orbitals must contain a single, unpaired electron. the two electrons shared by the bonded atoms must have opposite spins.

the nuclei of both atoms are attracted to the shared pair of electrons.

the mutual attraction for the shared electrons holds the atoms together.

valence bond theory explains why covalent bonds form. a covalent bond will form between two atoms if the potential energy of the resulting molecule is lower than the combined potential energies of the isolated atoms.

formation of a covalent bond gives off energy; energy must be supplies to a molecule to break covalent bonds.

summary of valence bond theory: a bond forms when slightly occupied atomic orbitals on two atoms overlap. the two electrons shared in the region of orbital overlap must be of opposite spin. formation of a bond results in a lower potential energy for the system.

Intermolecular Forces

intermolecular forces electr-ostatic attractions between opposite charges or partial charges. particles in the condensed phases (solids and liquids) are held together by intermolecular forces.

van der waals forces intermole- cular forces acting between atoms or molecules in a pure substance. include dipole-dipole interactions (which include hydrogen bonding) and dispersion forces.

dipole - dipole interactions attractive forces that act between polar molecules. partial positive charge on one molecule is attracted to the partial negative charge on the neigh-oring molecule. the larger the dipole, the larger the attractive force.

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Not published yet.

Last updated 12th December, 2022.

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Intermolecular Forces (cont)

hydrogen bonding is a strong type of dipole-dipole interaction that occurs in molecules containing hydrogen bonded to a small, highly electronegative atom, such as nitrogen, oxygen, or fluorine.

within a series of hydrogen compounds of group 14, the boiling point increases with increasing molar mass.

for groups 15-17, the same trend is observed for all but the smallest member of each series, which has an irregularly high boiling point.

Intermolecular Forces (cont)

magnitude of dispersion forces depends on how the electrons are distributed in the molecule. The boiling point of a nonpolar molecule acquires an instantaneous dipole, it is polarized.

in small molecules, the electrons are relatively close to the nuclei and cannot move about freely. Thus, the electron distribution is not easily polarized.

Intermolecular Forces (cont)

the more if a valence compound is polar, a dipole has, the more easily it is polarized.

if a molecule is polar with a hydrogen bonded to fluorine, nitrogen, or oxygen, dipole-dipole (including hydrogen) and dispersion forces are acting on it.

dispersion forces

attractive forces that act between all nonpolar and polar.

forces between an instantaneous dipole (fleeting, temporary dipole) and induced dipoles (instantaneous dipoles can induce neighboring dipoles).

when a nonpolar molecule acquires an instantaneous dipole, it is polarized.

in larger instantaneous dipoles, larger induced dipoles, and larger intermolecular forces overall.

ion-dipole interactions

attraction between ions and polar molecules in solutions.

magnitude depends on the charge and size of the ion dipole moment and size of the polar molecule.

cation: interaction more strong with dipole: anions because they tend to be smaller ion with higher charge and smaller size will interact more strong with molecule



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Not published yet.
Last updated 12th December, 2022.
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Intermolecular Forces (cont)

strongest force to weakest force: ion-dipole, hydrogen, dipole-dipole, dispersion

Hybridization of Multiple Bonds

sigma bonds first bond formed and stronger than pi bonds shared electron density concentrated directly along the internuclear axis overlap of hybrid orbitals that point directly toward each other

pi bonds second bond formed and weaker than sigma bonds form when parallel unhybridized p orbitals sideways overlap. electron density concentrated above and below plane of molecule.

singly occupied p orbitals give rise to multiple bonds. one sigma and one pi bond together constitute a double bond. one sigma and two pi bonds together constitute a triple bond.

Hybridization of Multiple Bonds (cont)

pi bonds restrict the rotation of a molecule in a way that sigma bonds do not overall. double bonds consist of one sigma bond and one pi bond; the pi bond restricts rotation about the sigma bond, making the molecules rigid, planar, and not interchangeable.

Deviation from Ideal Bond Angles

lone pairs take up more space than bonding pairs. a lone pair on the central atom is attracted only to the nucleus of that atom. a bonding pair is simultaneously attracted to the nuclei of both the bonding atoms. lone pairs have more freedom to spread out and greater capacity to repel other electron domains.

sigma bonds and contribute less to the overall bond strength than sigma bonds.

Deviation from Ideal Bond Angles (cont)

multiple bonds repel more strongly than single bonds because they contain more electron density. multiple bonds are shorter than single bonds.

Bonding Theory

in species that can be represented by two or more resonance structures, the pi bonds are delocalized, meaning that they are spread out over the molecule and not constrained to just two atoms. localized bonds are those constrained to two atoms.

Hybridization of Atomic Orbitals

hybridization atomic orbitals mix to form hybrid orbitals.

hybrid orbitals orbitals formed by hybridization of some combination of s, p, or d atomic orbitals.

each sp hybrid orbital has one small lobe and one large lobe. they are oriented in opposite directions with a 180 degree angle between them.

number of electron domains is equal to the number of hybrid orbitals which is also equal to the number of atomic orbitals needed to mix.



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Not published yet.
Last updated 12th December, 2022.
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Hybridization of Atomic Orbitals (cont)

elements in the third period of the periodic table and beyond do not obey the octet rule because they have d orbitals that can hold additional electrons.

in molecules where there are more than 4 electron domains on the central atom, include d orbitals in hybridization.

sp^3d have shapes similar to sp , sp^2 , and sp^3 orbitals - one large lobe and one small lobe.

do not use hybrid orbitals to predict molecular geometries but to explain geometries that are already known.

Molecular Geometry and Polarity

polar molecule a bond between two atoms of different electronegativities

a molecule bonded with a highly electronegative element will be polar. highly electronegative elements: fluorine, nitrogen, oxygen, or chlorine

if the central atom has lone pairs, molecule is most likely polar

if vectors cancel each other, molecule is nonpolar. if vectors do not cancel each other (are not equal) the molecule is polar.

structural isomers molecules that have the same chemical formula but have different arrangement of atoms

Molecular Orbital Theory

molecular orbital theory atomic orbitals involved in bonding combine to form new molecular orbitals that are associated with the whole molecule rather than individual atoms. molecular orbital theory predicts that the more effective the interaction or overlap of the atomic orbitals, the lower the energy resulting bonding molecular orbitals will be and the higher in energy the resulting antibonding molecular orbitals will be.

Molecular Orbital Theory (cont)

molecular orbitals that result from the interaction of atomic orbitals of bonding atoms.

similar to atomic orbitals - they have specific shapes and energies and can accommodate a maximum of two electrons.

two electrons residing in the same molecular orbital must have opposite spins.

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Not published yet.

Last updated 12th December, 2022.

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Molecular Orbital Theory (cont)

number of molecular orbitals produced is equal to the number of atomic orbitals that combined.

bonding molecular orbital lower in energy than the atomic orbitals that combined to produce it. concentrated between the nuclei, along the internuclear axis. result from the interaction of atomic orbitals that are in phase.

antibonding molecular orbital higher in energy than the atomic orbitals that combined to produce it. most of its electron density is located outside the internuclear region. result from the interaction of atomic orbitals that are out of phase.

Molecular Orbital Theory (cont)

sigma molecular orbitals lie along the internuclear axis bonding molecular orbitals are designated sigma_{1s}; antibonding orbital is designated sigma_{1s}*

bond order indicated how stable a molecule is higher bond order, the more stable the molecule; higher bond order, shorter bond length. bond order = # electrons in bonding molecular orbitals - # electrons in antibonding molecular orbitals/2

Molecular Orbital Theory (cont)

pi molecular orbitals regions of electron density affect both nuclei but do not lie along the internuclear axis. 2px orbitals lie along the x-axis and 2py and 2pz orbitals are aligned parallel to each other and combine to form pi molecular orbitals. combine to form sigma molecular orbitals.

molecular orbitals resulting from the combination of p atomic orbitals are higher in energy than the molecular orbitals resulting from the combination of s atomic orbitals. px orbitals, which lie along the internuclear axis, overlap most effectively, giving the lowest-energy bonding molecular orbital and the highest-energy antibonding molecular orbital.



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Last updated 12th December, 2022.

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Hybridization Chart

Number of Electron Domains on Central Atom	2	3	4	5	6
hybrid orbitals	sp	sp ²	sp ³	sp ³ d	sp ³ d ²
geometry	linear	trigonal planar	tetrahedral	trigonal bipyramidal	octahedral



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