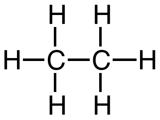
Chapter 2
Alkanes

This chapter is concerned with the chemistry of alkanes. Alkanes are hydrocarbons. Hydrocarbons are molecules that contain only C and H.

There are two main classes of hydrocarbons: (1) aliphatic and (2) aromatic.

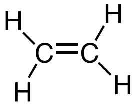
(1) Aliphatic hydrocarbons have three main groups:
a. Alkanes: contain only carbon-carbon single bonds.
b. Alkenes: have carbon-carbon double bonds
c. Alkynes: have carbon-carbon triple bonds

(2) Aromatic hydrocarbons (also called arenes) have conjugated, circular double bonds that have special properties. These are derivatives of benzene.



H_3C-CH_3

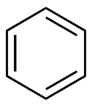
ethane (alkane)



ethene (alkene)

$H-C\equiv C-H$

ethyne (alkyne)

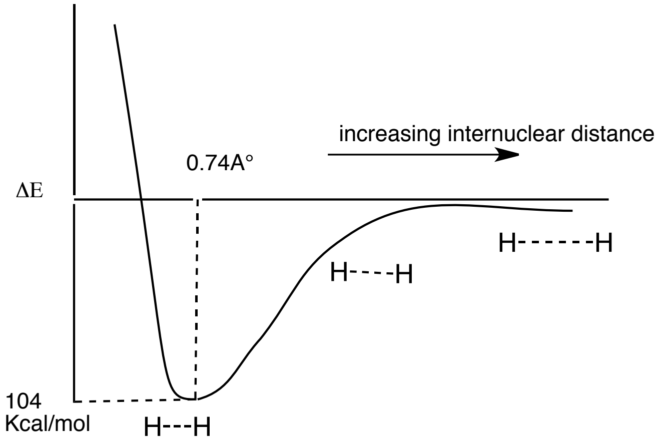


benzene (aromatic)

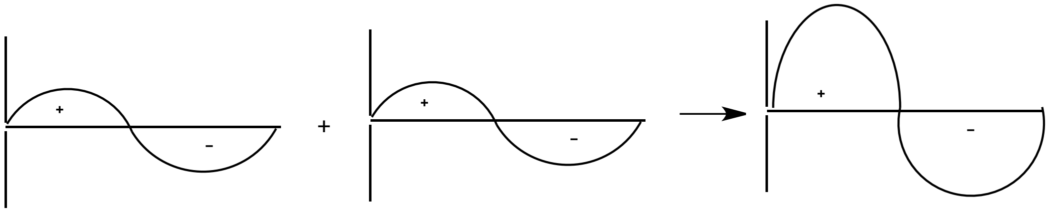
Electron Waves and Chemical Bonds

Electrons have both particle and wave properties. Chemical bonding between atoms can be thought of as the interaction of two waves. There are two widely used theories of chemical bonding: (1) the valence bond model and (2) molecular orbital theory. For simple molecules the theories are similar.

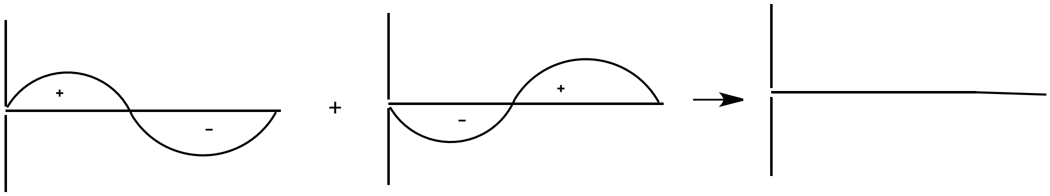
Consider the bonding between two hydrogen atoms and what happens as the distance between them begins to decrease. There are three types of interactions: (i) electron-electron repulsion (minus charge repelling minus charge) (ii) electron-nucleus attraction (minus charge attracting the positive charge of the nucleus)) and (iii) nucleus-nucleus repulsion (positive charge repelling positive charge). All of these forces increase as the distance between the two nuclei decreases. The electrons are mobile and can maximize their attractive forces while minimizing their repulsive forces. As the nuclei get to bonding distance the attractive forces are at a maximum and there is a potential energy minimum. This occurs at 0.74 A°. If the two nuclei approach closer than this the repulsive forces between the two positively charged nuclei begin to dominate.



There are two ways that waves can add to reinforce each other: constructive interference in which the two waves add in the same phases and destructive interference in which the two waves add out-of-phase and cancel each other.



Constructive interference - the waves add to each other



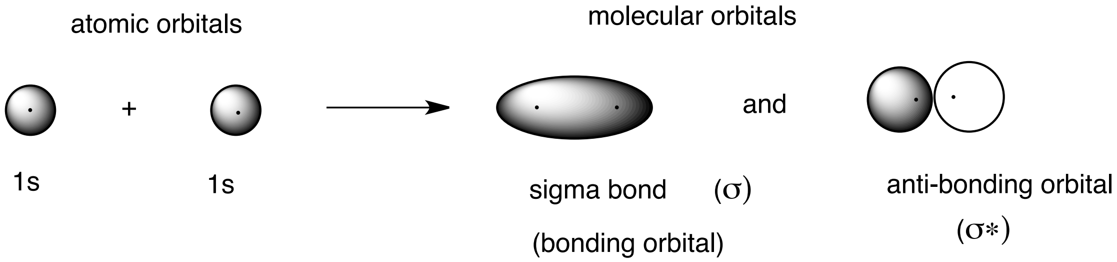
Destructive interference - the waves cancel each other out

Electron waves in atoms are characterized by their wave function, which is a mathematical description of the shape of the wave. This is called the orbital and defines where most of the electron density is to be found. The valence bond model constructs the bond from the overlap of the available orbitals of each bonding atom. These are the familiar 1s, 2s, 2p orbitals. The molecular orbital theory is more complicated in that it constructs new orbitals from the available atomic orbitals. These new orbitals are called molecular orbitals and spread over the entire new molecule.

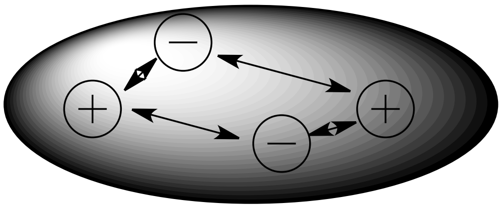
For bonding in the simple H_2 case both theories give a similar picture.

Bonding in Hydrogen: Valence Bond Model

We have an in-phase overlap of a half-filled 1s orbital of one atom with a half-filled 1s orbital of the other. These combine to form a sigma bond. The

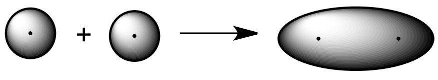


The energy of the system is lowered because now each electron is attracted by two protons, one in each hydrogen nucleus, and each proton is now attract by two electrons.

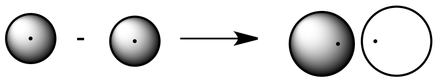


Molecular Orbital Model

In the molecular orbital model, the two 1s wave functions are combined (in a process called linear combination of atomic orbitals) to give two new molecular orbitals. There are two ways that the orbitals (or wave functions) can be combined. They can be added constructively to give a σ orbital that is bonding. In the bonding σ orbital most of the electron density of the two bonding electrons is concentrated between the two nuclei. This bonding orbital will be lower in energy than two separated hydrogen 1s orbitals. The other way they can be combined is by subtraction. Their signs will be opposite. This will result in destructive overlap with no electron density between the two nuclei. This orbital will be anti-bonding and will be higher in energy than two separated 1s orbitals. This anti-bonding orbital is typically called a σ^* orbital (sigma star orbital).

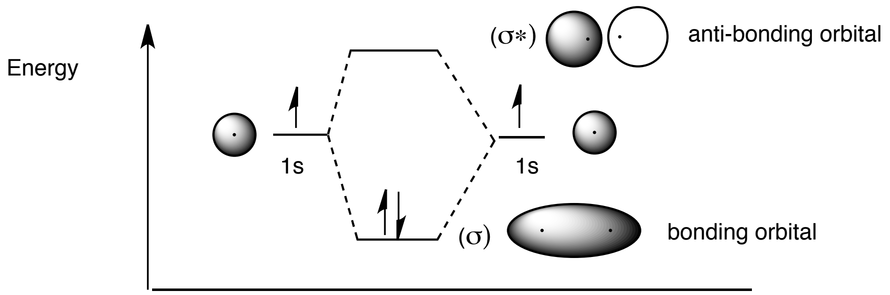


σ orbital



σ* orbital

Electrons are then put into the lowest energy orbitals first. The two electrons in H_2 go into the low energy bonding orbital.

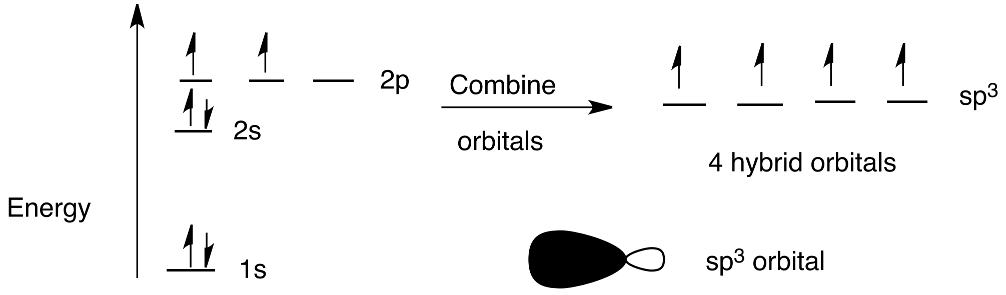


For a simple molecule like H_2, there is not much difference between the valence bond picture of bonding and the molecular orbital picture but differences do become apparent when the molecules become larger.

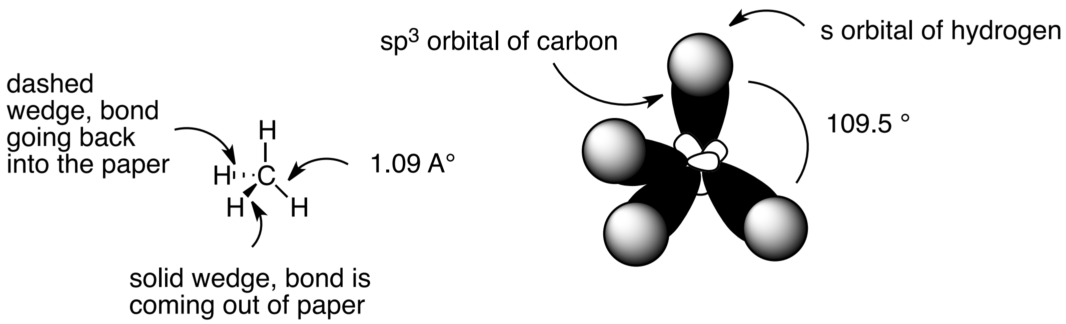
Alkanes: Methane, Ethane Propane

Alkanes have the general formula C_nH_{2n+2}.

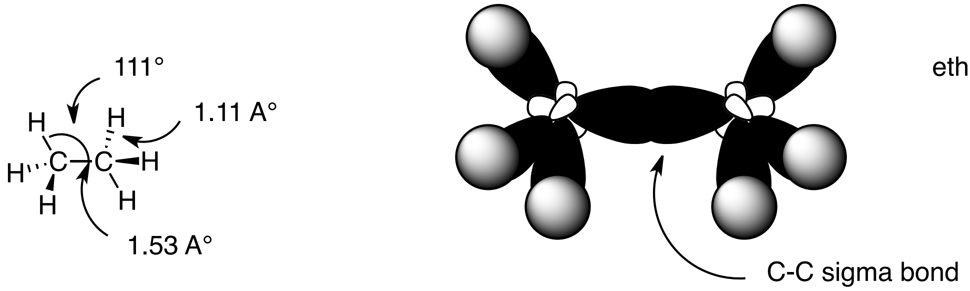
Methane, with the formula CH_4, is the simplest alkane. All four bonds are the same, oriented in a tetrahedral array. This is the shape that keeps the four substituents as far apart as possible so as to minimize repulsion between the electrons in the four C-H bonds. In order to form four equal bonds from we need to use the concept of hybridization. Look at the electronic structure of carbon.



There are three 2p orbitals and one 2s orbitals available for bonding. The 1s orbital is too low in energy and need not be considered. These four orbitals are combined to give four sp^3 orbitals that are oriented in a tetrahedral fashion.

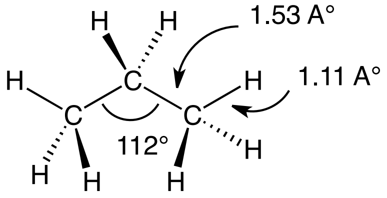


To form a new C-C single bond as in ethane, C_2H_6, we need to have the end-to-end overlap of two sp^3 orbital on each carbon. This forms a sigma bond in which the electron density of the two electrons formed in the bond is largely confined between the two carbon atoms.



ethane, C_2H_6

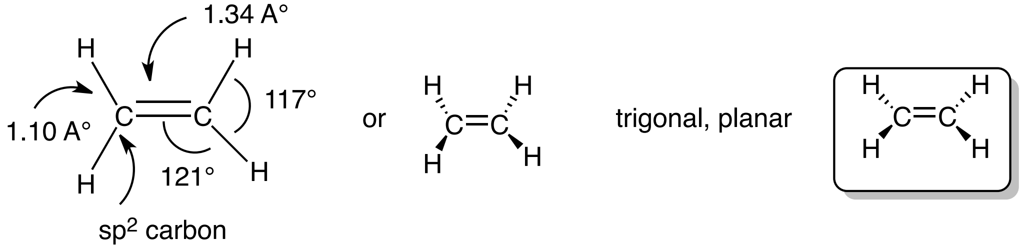
Propane has the formula C_3H_8 ($CH_3CH_2CH_3$)



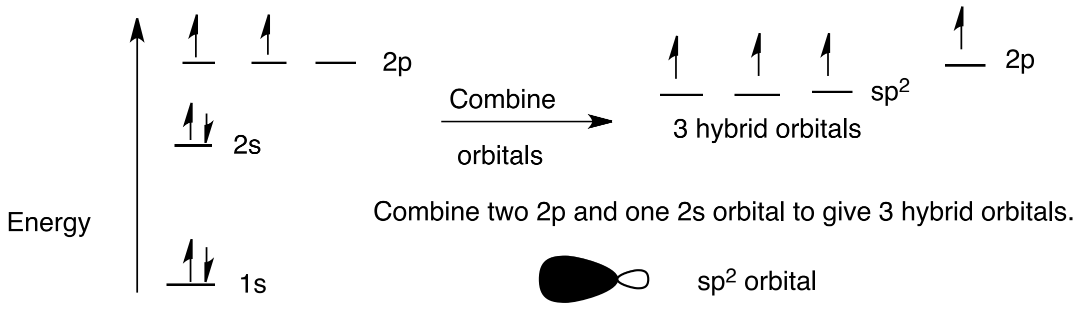
propane

Ethene, Hybridization and Bonding

Ethene (or ethylene) is trigonal and planar with sp^2 hybridized carbons.

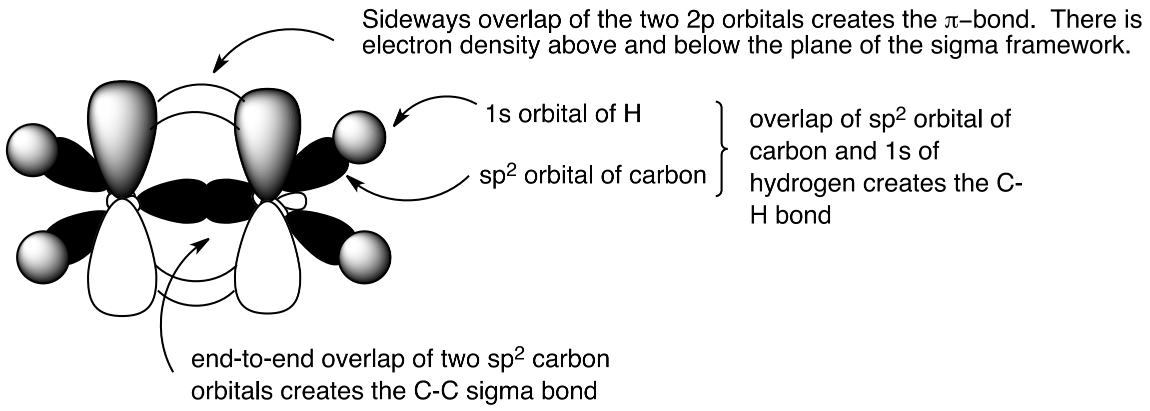


To form the three hybrid orbitals that are trigonal planar, combine two 2p orbitals with one 2s orbital to give three new orbitals that are intermediate in energy between the 2s and 2p orbitals. These are the sp^2 orbitals. They are similar in shape to the sp^3 orbitals but are slightly smaller due to the greater percentage of p character (33.3% p character in sp^2 versus 25% p character in sp^3 orbitals). This leave one 2p orbital unchanged. This will be use to form π–bond.



Combine two 2p and one 2s orbital to give 3 hybrid orbitals.

The carbon-carbon double bond is made up of two different types of bonds. There is a sigma bond made up of end-to-end overlap of two sp^2 orbitals, one on each carbon. The main portion of electron density in this bond is between the two nuclei. The second bond is the π–bond. It is made up of overlap of the two 2p orbitals, one on each carbon. In the π–bond the main portion of the electron density is above and below the plane of the sigma framework. The π–bond is not nearly as strong as the sigma bond and as we will see in subsequent chapters, it is quite reactive as a nucleophile.

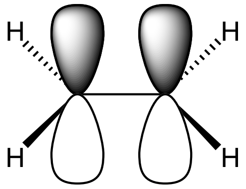


Sideways overlap of the two 2p orbitals creates the π–bond. There is electron density above and below the plane of the sigma framework.

overlap of sp^2 orbital of carbon and 1s of hydrogen creates the C-H bond

end-to-end overlap of two sp^2 carbon orbitals creates the C-C sigma bond

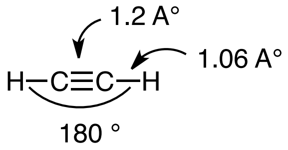
Note that all the six atoms of ethene, the two carbons and four hydrogens, lie in the same plane and the π–bond, made up of sideways-overlap between the two 2p orbitals, lies perpendicular to this plane.



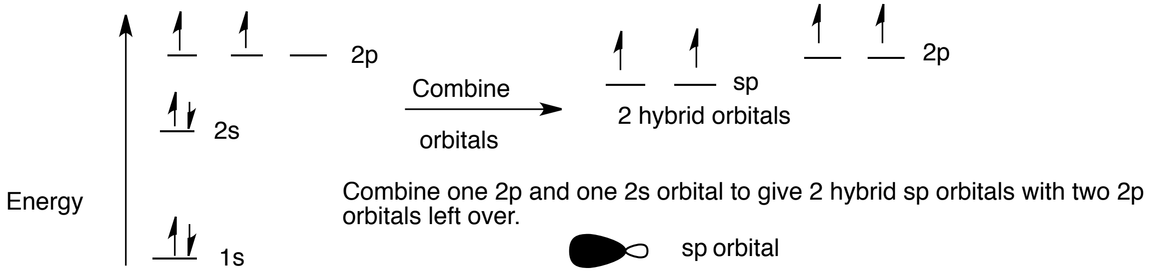
Another view of ethylene showing only the sigma framework and the π-portion of the double bond.

Ethyne, Hybridization and Bonding

Ethyne or acetylene has a triple bond. It is linear with two sp hybridized carbons.

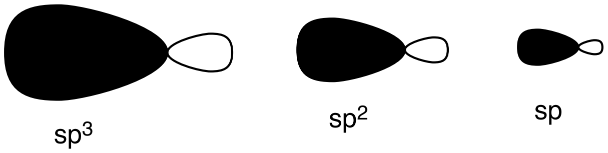


To form two identical carbon orbitals that are oriented in a linear fashion, one 2p and one 2s orbital are combined to give two sp hybrid orbitals.



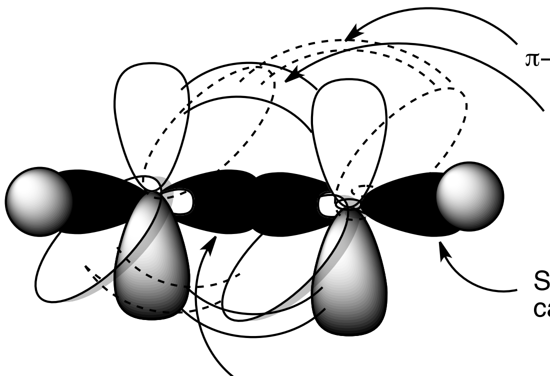
Combine one 2p and one 2s orbital to give 2 hybrid sp orbitals with two 2p orbitals left over.

The sp orbital is similar in shape to the sp^3 and sp^2 orbitals but it is smaller, with the bulk of the electron density closer to the nucleus. Therefore an electron in an sp orbital is more tightly held than an electron in an sp^2 orbital, which in turn is more tightly held than an electron in an sp^3 orbital.



Relative sizes oof the hybrid orbitals.

The sigma framework of ethyne is linear. The C-C single bond is made up of end-to-end overlap of two carbon sp bonds and the two C-H sigma bonds are made up of overlap of a carbon sp bond and a 1s orbital of hydrogen. The sp hybridization leaves two 2p orbitals on each carbon. These 2p orbitals are mutually perpendicular. They overlap to form two mutually perpendicular π–bonds.



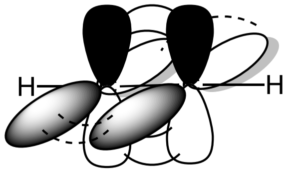
π–bond formed from overlap of two 2p orbitals

Second π–bond formed from overlaps of the other pair of 2p orbitals.

The two π–bonds are mutually perpendicular.

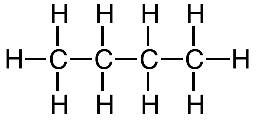
Sigma C-H bond formed from overlaps of carbon sp orbital and 1s orbital of hydrogen.

Sigma C-C bond from end-to-end overlap of two carbon sp orbitals.

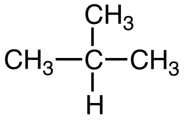


Another picture, showing the sigma framework and the two mutually perpendicular π–bonds. One π–bond is in the plane of hte page and the other π–bond is coming out of the page, perpendicular to the first one.

Butane has the formula C_4H_{10}. Butane can exist in two different forms called isomers. Isomers are molecules that have the same formula but have one or more properties that are different. There are several types of isomers possible. Isomers in which the atoms are connected together in different ways are called constitutional isomers.



This is sometimes called n-butane where n = normal or unbranched.



$CH_3-C(CH_3)(H)-CH_3$

isobutane

Methane, ethane, propane and butane are all gases are room temperature.

CH_4	CH_3CH_3	$CH_3CH_2CH_3$	$CH_3CH_2CH_2CH_3$	$(CH_3)_3CH$
methane	ethane	propane	n-butane	isobutane
b.p. -160 °C	b.p. -89°C	b.p. -42 °C	b. p. -0.4 °C	b.p. -10.2 °C

Note the regular increase in boiling point as the number of carbons increases.

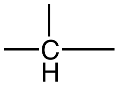
Note also:

$—CH_3$

methyl group

$—CH_2—$

methylene group

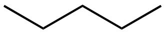


$-\overset{|}{\underset{H}{C}}-$

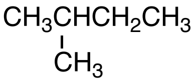
methine group

Pentane, C_5H_{12}, has three possible constitutional isomers. Note the zigzag shape for n-pentane.

n-pentane $CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$ or

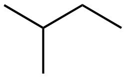


isopentane

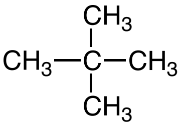


$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2CH_3$

or $(CH_3)_2CHCH_2CH_3$ or

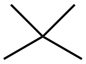


neopentane

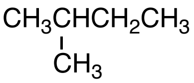


$CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3$

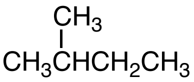
or $(CH_3)_4C$ or



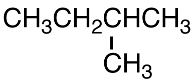
The number of isomers increases rapidly as the number of carbon atoms increases. For example, C_6H_{14} has 5 isomers, C_7H_{16} has 9 isomers and $C_{40}H_{82}$ has 62,491,178,805,831 isomers!!! There is no simple way to tell how many isomers are possible for a given number of carbons. The best way to find all the isomers is to draw out the straight chain isomer first and then systematically branch the carbon atoms. The key thing is the way the carbons are connected (the connectivity). For example, all of the following molecules are actually the same.



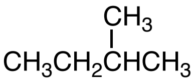
$CH_3\underset{\substack{|\\CH_3}}{C}HCH_2CH_3$



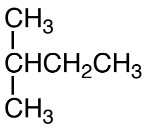
$CH_3\overset{\substack{CH_3\\|}}{C}HCH_2CH_3$



$CH_3CH_2\underset{\substack{|\\CH_3}}{C}HCH_3$



$CH_3CH_2\overset{\substack{CH_3\\|}}{C}HCH_3$

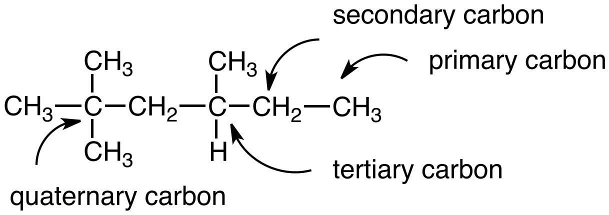


$\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}HCH_2CH_3$

Types of Carbons

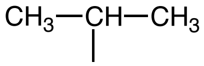
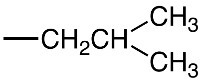
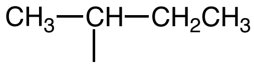
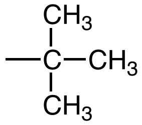
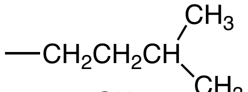
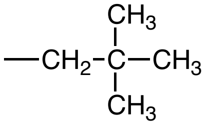
Carbons are classified according to the number of other carbons attached to the carbon in question.

- Primary (1°) carbons have one other carbon attached.
- Secondary (2°) carbons have two other carbons attached.
- Tertiary (3°) carbons have three other carbons attached.
-Quaternary carbons have four other carbons attached.



IUPAC Nomenclature

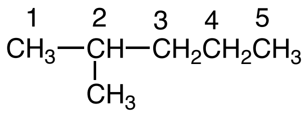
The International Union of Pure and Applied Chemistry has devised a systematic set of rules for naming compounds. The rules are somewhat arbitrary but they are internally consistent and each compound has its own unique name. We need to learn these rules, first for alkanes, and then for other functional groups as we proceed through the course. The rules for alkanes provide the foundation for the rules to follow.

Number of carbons	formula	alkane	alkyl group	representation
C1	CH_4	methane	methyl	$—CH_3$
C2	CH_3CH_3	ethane	ethyl	$—CH_2CH_3$
C3	$CH_3CH_2CH_3$	propane	propyl	$—CH_2CH_2CH_3$
			isopropyl	 $CH_3—\underset{\vert}{CH}—CH_3$
C4	$CH_3(CH_2)_2CH_3$	butane	butyl	$—CH_2CH_2CH_2CH_3$
			isobutyl	 $—CH_2CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$
			sec-butyl	 $CH_3—\underset{\vert}{CH}—CH_2CH_3$
			tertiary-butyl	 $—\overset{CH_3}{\underset{CH_3}{C}}—CH_3$
C5	$CH_3(CH_2)_3CH_3$	pentane	pentyl	$—CH_2CH_2CH_2CH_2CH_3$
			isopentyl	 $—CH_2CH_2CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$
			neopentyl	 $—CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}—CH_3$
C6	$CH_3(CH_2)_4CH_3$	hexane	hexyl	
C7	$CH_3(CH_2)_5CH_3$	heptane	heptyl	
C8	$CH_3(CH_2)_6CH_3$	octane	octyl	
C9	$CH_3(CH_2)_7CH_3$	nonane	nonyl	
C10	$CH_3(CH_2)_8CH_3$	decane	decyl	

Rules for Naming:

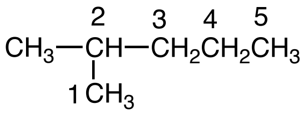
1. Pick out the longest continuous chain. This is the parent chain.

2. Identify the substituent groups.
3. Number the longest continuous chain so that the substituent at the first point of branching gets the lowest number.



$\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$

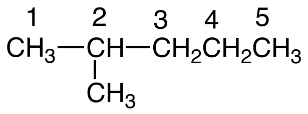
or



$CH_3-\underset{\displaystyle 1\,CH_3}{\overset{2}{C}H}-\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$

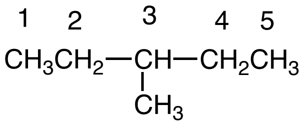
pentane

4. Write the name designating the position of the substituent by number.



$\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\overset{2}{C}H}-\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$

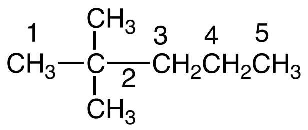
2-methylpentane



$\overset{1}{CH_3}\overset{2}{C}H_2-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{4}{C}H_2\overset{5}{C}H_3$

3-methylpentane

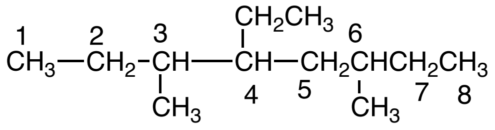
5. If a substituent occurs more than once, use di-, tri-, tetra-, etc. and repeat the number.



$\overset{1}{CH_3}-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{2}{C}}}-\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$

2,2-dimethylpentane

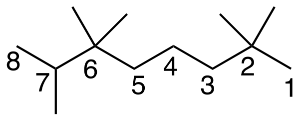
6. If there is more than one substituent, list them in alphabetical order, ignoring any prefix such as di-, tri-, etc.



$\overset{1}{CH_3}-\overset{2}{C}H_2-\underset{\displaystyle CH_3}{\overset{3}{C}H}-\overset{\displaystyle CH_2CH_3}{\underset{4}{C}H}-\underset{5}{C}H_2\underset{\displaystyle CH_3}{\overset{6}{C}H}\underset{7}{C}H_2\underset{8}{C}H_3$

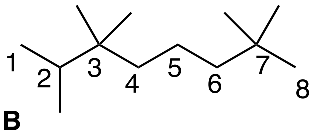
4-ethyl-3,6-dimethyloctane

7. Number the chain so as to give the lowest number at the "first point of difference" in the two possible numbering schemes.



A 2,2,6,6,7-pentamethyloctane

CORRECT

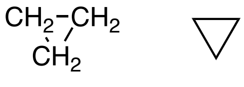


B 2,3,3,7,7-pentamethyloctane

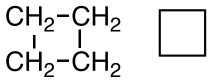
INCORRECT

A is the correct numbering since there is a '2' at the second number whereas **B** has a '3' at the second number position.

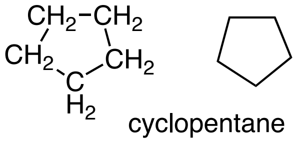
Cycloalkanes



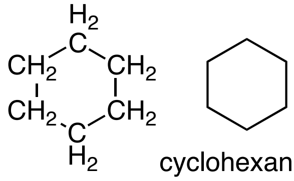
cyclopropane



cyclobutane

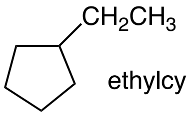


cyclopentane



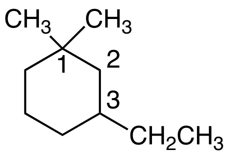
cyclohexane

Number the ring so that the lowest number is given to the substituent at the first point of difference between the two possible numbering schemes.



ethylcyclopentane

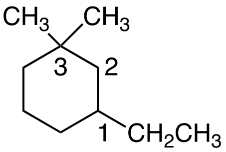
A



CORRECT

3-ethyl-1,1-dimethycyclohexane

B

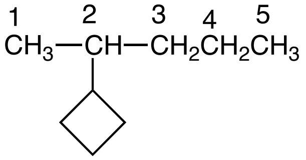


INCORRECT

1-ethyl-3,3-dimethylcyclohexane

Numbering scheme **A** is correct because the lowest number at the first point of difference is 1,1,3 and not 1,3,3- as in numbering scheme **B**.

When the ring itself has fewer carbons than the alkyl that is attached, the ring is considered as a substituent.



2-cyclobutylpentane

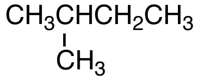
Physical Properties of Alkanes

There is a regular increase in the boiling point as the number of carbons increases. The boiling points are lowered for 2-methyl branched alkanes. This is due to a decrease in the weak intermolecular attractive forces. A branched alkane has a smaller surface area than a linear molecule. Therefore there is less surface area for the induced dipole-induced dipole interactions. (See below)

$CH_3CH_2CH_2CH_2CH_3$

pentane

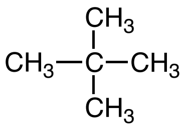
b.p. 36 °C



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$$

2-methylbutane

b.p. 28 °C



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

2,2-dimethylpropane

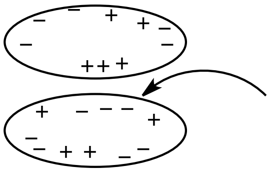
b.p. 9 °C

In general there are three types of attractive forces between molecules:

(1) dipole-dipole interactions, including hydrogen-bonding.
(2) dipole-induced dipole interactions
(3) induced dipole-induced dipole interactions

The intermolecular attractive forces in alkanes are due to the induced dipole-induced dipole interactions called van der Waal's forces. These are very weak. Alkanes are essentially non-polar so the only attractive forces are these weak van der Waal's forces. In small alkanes (four carbons or less) the overall effect is weak and the compounds are gases at room temperature. As the molecules become larger the cumulative effect of the forces increase and we see the increase in boiling points as the number of carbons increases until finally large hydrocarbons can be solids at room temperature.

The induced dipoles are caused by the moment of the electrons in the C-H bonds. At any given instant, as the electron moves in its wave pattern in the molecular orbital, it may create a slight excess of (-) charge in one localized region. This tiny, transient excess of (-) charge will in turn induce an excess of (+) charge in a neighboring molecule.



A temporary excess of negative charge induces a corresponding excess of (+) charge in a neighboring molecule.

Reactions of Alkanes

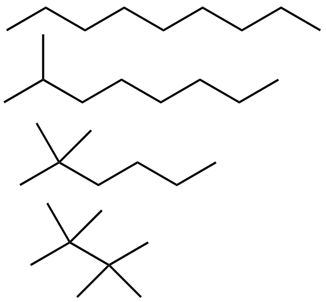
Alkanes are relatively unreactive. One important reaction that they do undergo is combustion.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \qquad \Delta H = -890\ KJ/mol$$

The heat of combustion, ΔH, is defined as the heat of the products at standard pressure minus the heat of the reactants. ΔH is the enthalpy or heat given off.

$$\Delta H = \Delta H°_{products} - \Delta H°_{reactants}$$

The heat of combustion is a measure of the stability and potential energy of the molecule. The smaller the heat of combustion, the more stable the molecule.



ΔH = –5471 KJ/mol

ΔH = –5466 KJ/mol

ΔH = –5458KJ/mol

ΔH = –5452KJ/mol lowest in energy, most stable

In general the heat of combustion decreases with increased branching. The attractive intramolecular forces increase more than the repulsive forces as the molecule becomes more compact.

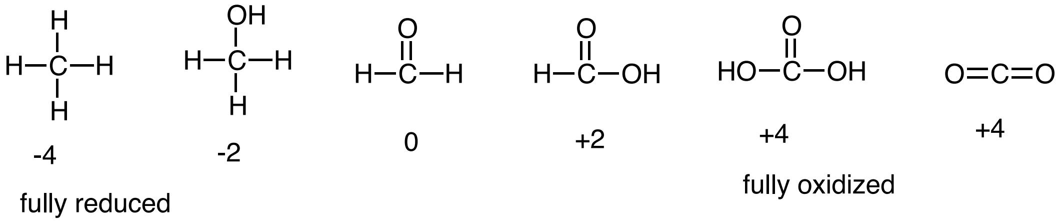
Oxidation/Reduction

Calculation of oxidation state for carbon:

For CH_4, assume that H has an oxidation state of +1; therefore carbon is -4.

For CO_2, oxygen has an oxidation state of -2; therefore carbon is +2.

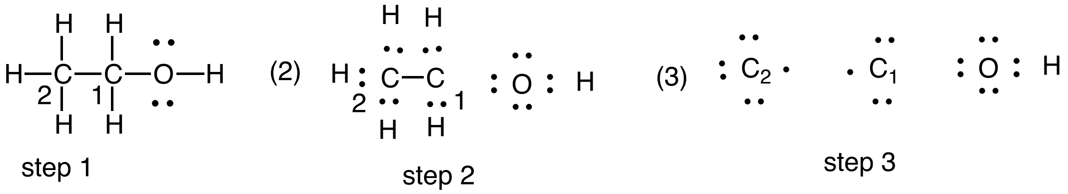
Look at the following carbon oxidation states.



In general, when carbon is oxidized there is an increase in the number of bonds between C and O and there is a decrease in the number of hydrogens attached to the carbon.

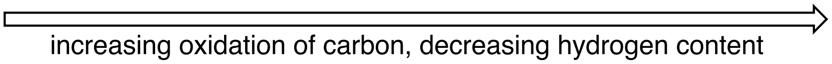
In general when carbon is reduced, there is an increase in the number of C-H bonds and a decrease in the number of C-O bonds.

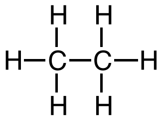
To calculate the oxidation number of carbon:
(1) Write a Lewis structure with the electron pair. (2) Assign the electrons in a covalent bond to the more electronegative partner. (3) For the bond between two atoms that are the same, give one electron to each atom. (4) Count the electrons assigned to each atom and subtract this from the number of valence electrons in the neutral atom (carbon has 4 valence electrons). For ethanol:



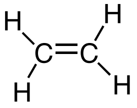
C_1 has 5 electrons – 4 valence electrons = -1 oxidation state.
C_2 has 7 electrons – 4 valence electrons = -3 oxidation state.
Oxygen has oxidation state -2 and hydrogen has oxidation state +1.

A carbon is oxidized if a hydrogen atom is replaced by a more electronegative atom. For the hydrocarbons:

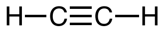




ethane, fully reduced
(contains 14 electrons)



ethene, partially oxidized
contains 12 electrons



ethyne, more oxidized
contains 10 electrons

For CH_3Cl and CH_3OH both carbons have the same oxidation state of -2. The reaction of chlorine with methane, to be discussed in CH. 4, involves an oxidation of the carbon.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

And, a carbon is reduced if a hydrogen atom is replaced by a less electronegative atom. Here the carbon goes from oxidation state -2 to oxidation states -4, the same as in CH_4.

$$CH_3Cl + 2Li \longrightarrow CH_3Li + LiCl$$

Bonding in Ammonia and Water

We can use the same valence bond theory to describe the bonding in ammonia, NH_3, and water, H_2O, which we have used for the hydrocarbons. It is useful to view the central atom in both these molecules as sp^3 hybridized and therefore tetrahedral in shape.

In ammonia, we have an sp^3 hybridized nitrogen and three hydrogen atoms and one lone pair. The lone pair occupies one of the four equivalent sp^3 orbitals and the three hydrogens occupy the other three sp^3 orbitals. There is a slight deviation from the ideal 109.5° tetrahedral angles. The H-N-H angles is 107° because the lone pair takes up a bit more space since the two electrons are not bonded to another atom.

In water, we have an sp^3 hybridized oxygen and two hydrogens occupying sp^3 orbitals and two lone pair in similar orbitals. In water the H-O-H angle is 105°, smaller than the tetrahedral 109.5° due to the larger space occupied by the lone pair.