

Alkanes

Alkanes

Methane

Bonding

Geometry

Hybridization

Combustion

Ethane

Propane

Butane

Pentane

Higher of alkanes

Heats of combustion and formation

Cyclic Alkanes

Structure activity Relationships

Nomenclature of branched-chain alkanes

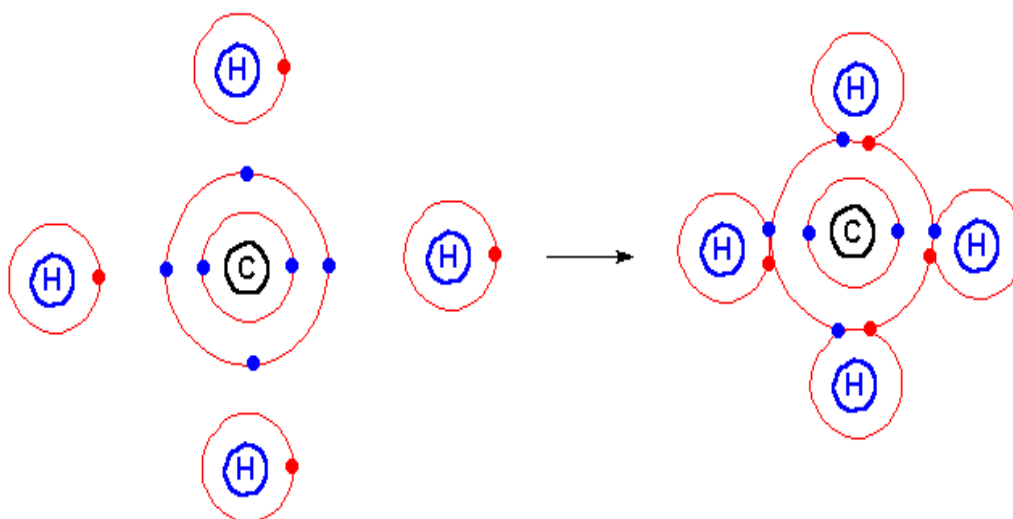
Chemical reactions of alkanes

Acyclic Alkanes

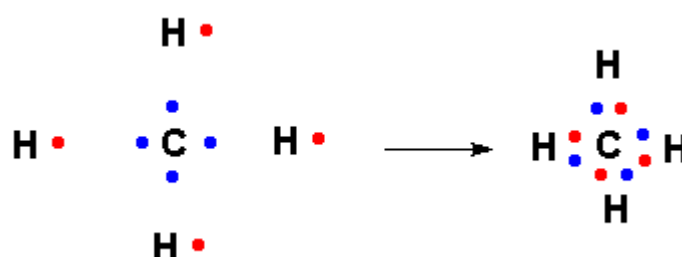
Methane

Bonding

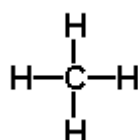
Methane, the simplest hydrocarbon, is composed of a single carbon atom and four hydrogen atoms. By the middle of the nineteenth century chemists recognized that carbon was tetravalent, forming four bonds to monovalent atoms such as hydrogen or chlorine. By the 1920's chemists began to interpret this tetravalent nature of carbon in terms of the electronic structure of the carbon atom. On the basis of electronic structure, each of the four electrons in the outer shell of the carbon atom pair with an electron from each of the four hydrogen atoms to complete an octet. Each hydrogen atom gains an electron to have a helium-like electronic configuration and the carbon has an electronic configuration like the noble gas neon.



To simplify this representation of the electronic arrangement of methane, the Lewis Dot representation is often used. In this representation the symbol of the element represents the nucleus and the inner shell electrons. The outer electrons are designated by dots.



Since a chemical bond consists of pairs of electrons, the Lewis dot representation can be simplified further into a line bond representation. Each pair of electrons is designated by a line. The line bond structure of methane shows how the four hydrogen atoms are attached to the central carbon atom but it does not show how these atoms are arranged in three-dimensional space. The formula of methane can be further simplified by writing a condensed formula (CH_4) which shows the composition of the molecule but does not indicate how the atoms are bonded.

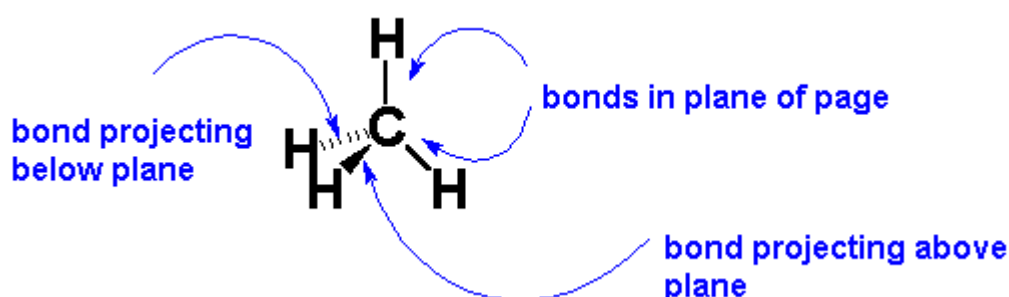
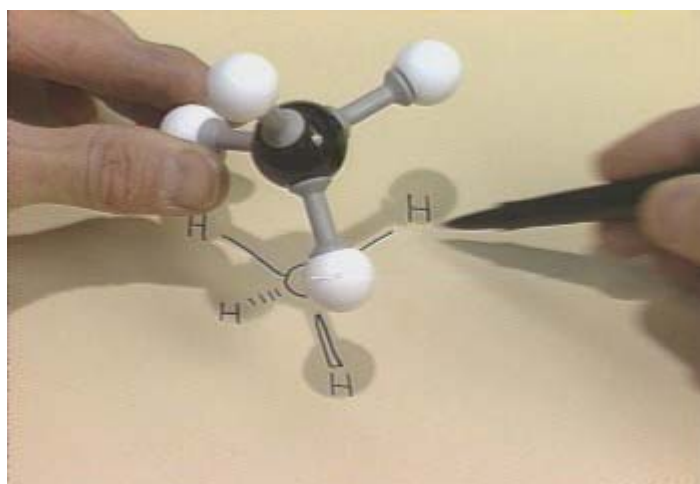


Geometry

A simple way of predicting the geometry of covalent molecules relies on the principle that nonbonded atoms in a molecule repel each other and arrange themselves as far apart as possible. For four atoms bonded to a central atom this arrangement is a tetrahedron with H-C-H bond angles of 109.5° . Ball and stick models show bond angles clearly. Space filling models indicate the electron density

of atoms in the molecule

How do you write a three-dimensional structure on a sheet of paper or on a computer screen? The convention adopted by chemists uses projection diagrams that are the equivalent of the shadow cast by the three-dimensional object. In this projection diagram bonds in the plane of the page are represented by solid lines, bonds projecting above the page are shown by using wedged lines, and bonds below the plane by broken or hatched lines.



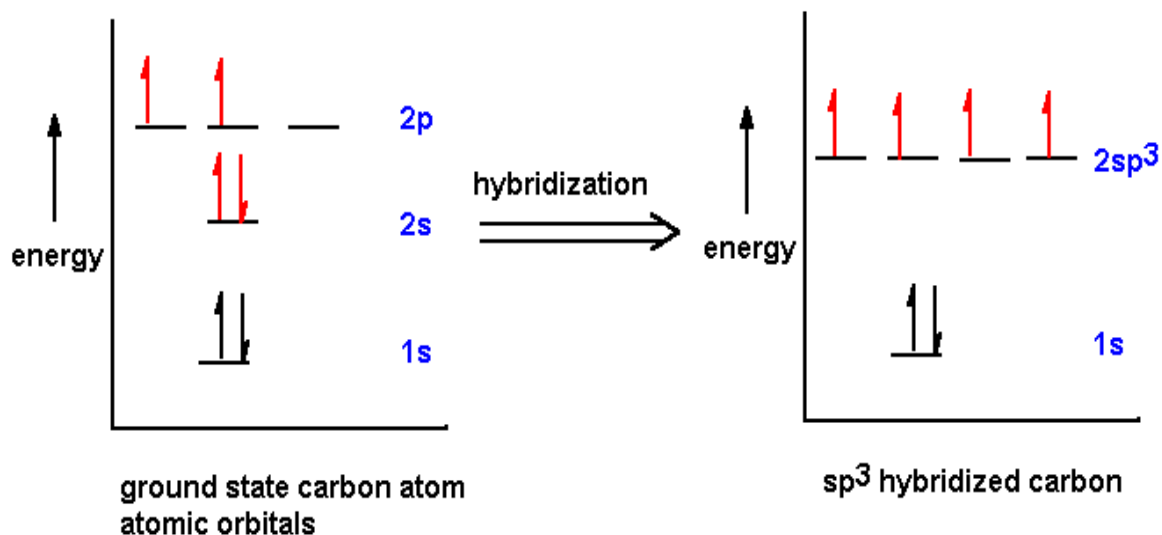
To describe any molecule we need to know the angles, lengths, and strength of all of its bonds. For methane these parameters are shown in the following table.

Properties of Methane	
H-C-H bond angle	109.5°
C-H bond length	1.1 Å
C-H bond strength	104 Kcal/mol

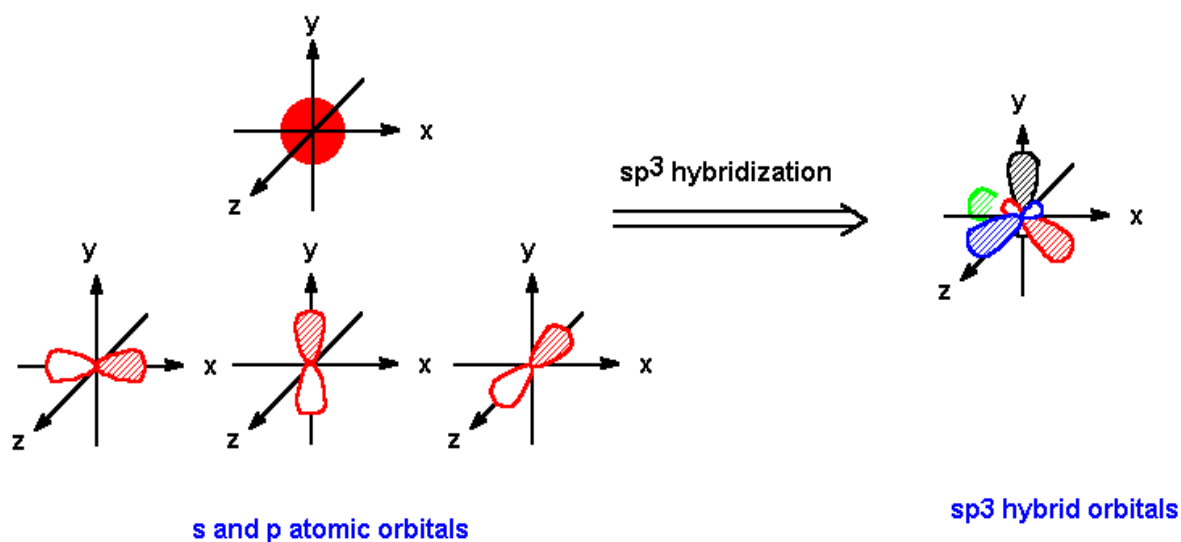
Hybridization

How can we resolve the tetrahedral geometry of methane with the geometry of the 2s and 2p atomic orbitals of carbon? The most visual approach is through the Valence Bond theory developed by Linus Pauling. A carbon atom in its lowest energy state has the electron configuration shown below. This leaves only two unpaired electrons available for bonding. In the valence bond approach, an electron is promoted from the ground state of carbon into an excited state in which all the

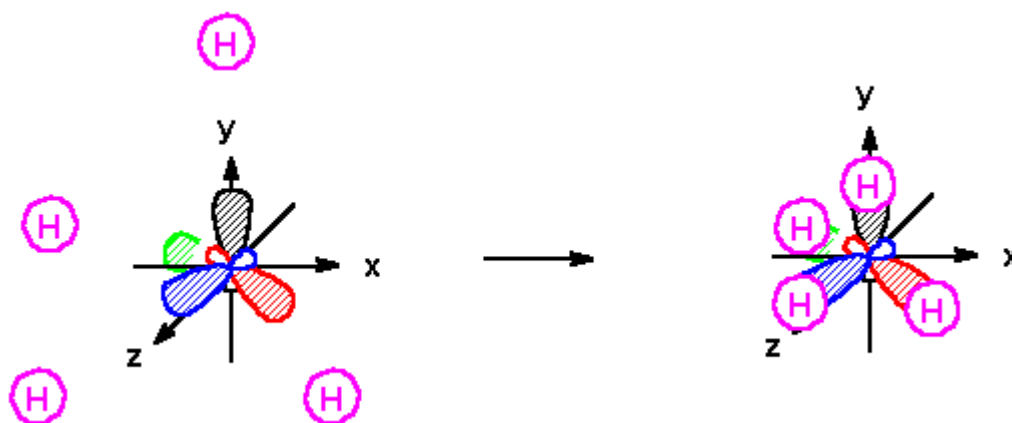
electrons are unpaired. The orbitals are then hybridized to produce four equivalent sp^3 orbitals with tetrahedral geometry. It is important to realize that this is a mathematical model and does not necessarily reflect what is really happening at the atomic level. It does give us molecular orbitals that are geometrically equivalent to the balls and sticks in our molecular models.



Hybridization of ground state carbon atomic orbitals to produce an sp^3 hybridized carbon atom. Note that the hybrid sp^3 orbitals are lower in energy than the 2p atomic orbitals.



Hybridization of one s and three p atomic orbitals to produce four sp^3 hybrid orbitals

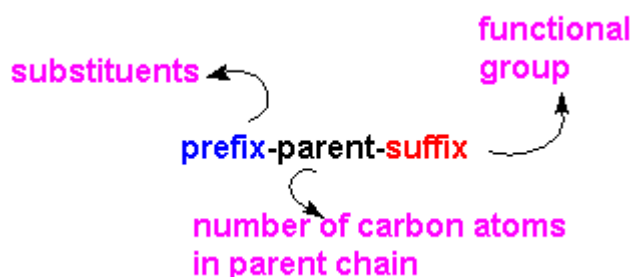


with 109.5° angles.

Hybridization model of methane showing overlap of four hydrogen atoms with an sp^3 hybridized carbon atom.

Organic Nomenclature

These rules were developed by the [International Union of Pure and Applied Chemistry \(IUPAC\)](#). A complete list of the IUPAC rules is available at the [ACD Labs](#) site.



IUPAC names are written in the form:

IUPAC Rules for Branched-Chain Alkanes

I. Identify the parent hydrocarbon

Find the longest continuous chain of carbon atoms. The name of the straight-chain alkane with that number of carbon atoms is the parent name. Alkanes have the family name (suffix) **-ane**. The structure may be drawn so that the longest chain is not in a straight line.

If two different chains have the same number of carbon atoms, the parent hydrocarbon is the one with the larger number of branches.

II. Number the parent chain

Number the parent chain starting from the end nearer the first branch.

III. Assign each substituent a name and a number

The number of each substituent is the number of the carbon atom of the parent chain to which it is attached.

The names of each substituent are determined by taking the name of the parent alkane with the same number of carbon atoms and replacing the **-ane** ending with **-yl**. Complex substituents have common names such as n-propyl for the straight chain propyl group attached at C-1 and isopropyl for the propyl group attached at the secondary carbon C-2. IUPAC names for complex substituents are similar to those for alkanes. Isopropyl is 1-methylethyl.

Each substituent must have a name and a number, even if two or more substituents are identical.

IV. Form a single word name for the alkane

Combine the numbers and names of all substituents with the parent name to form one word. Use hyphens to separate numbers from names. Use commas to separate numbers. If two or more substituents are attached to the parent chain, write them in alphabetical order. If two or more substituents are identical, use prefixes di-, tri-, tetra-, penta-, etc. Each substituent must have a number, even if the numbers must be repeated. Do not use prefixes for alphabetizing.

The names of complex alkyl groups are enclosed in parentheses.

IUPAC Rules for Cycloalkanes

For simple rings or small alkyl substituents

I. Name the ring

Give the ring the name of the alkane with the same number of carbon atoms as the ring adding the prefix **cyclo**.

II. Name any substituents

If only one substituent is present, name the substituent and append it as a prefix to the name of the cycloalkane. For a single substituent, only one isomer is possible and no number is needed.

If two or more substituents are present, starting with one substituent as position 1, number around the ring in the direction that gives the next substituent the lower number. Give each substituent a name and a number.

List substituents in alphabetical order.

Designate the stereochemistry of geometric isomers with prefixes *cis-* and *trans-*.

For alkyl substituents with more carbon atoms than the ring

I. Name the alkyl group as a branched alkane

II. Name and number the ring as a substituent.

Number the alkane and name the ring as a substituent **cycloalkyl** group.

If substituents are present on the ring, the point of attachment to the alkyl chain is position 1. Name and number any ring substituents and place the name of the ring and substituents in parentheses.

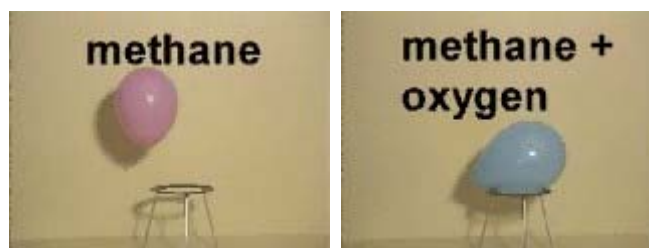
Combustion of Methane: A Look at Chemical Reactions

Methane is familiar to us as natural gas. Combustion of methane is an exothermic reaction that we use to heat our homes and cook our food. The burners in gas stoves and furnaces are modifications of the laboratory burner developed by Robert Bunsen.

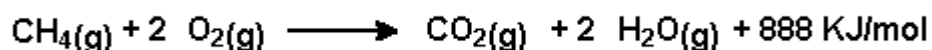


Bunsen Burner

Let's examine the combustion of methane. A balloon containing methane floats showing that methane is gas less dense than air. A second balloon containing approximately equal volumes of methane and oxygen is more dense than air. Each balloon is ignited in the dark. Which reaction is more dramatic?

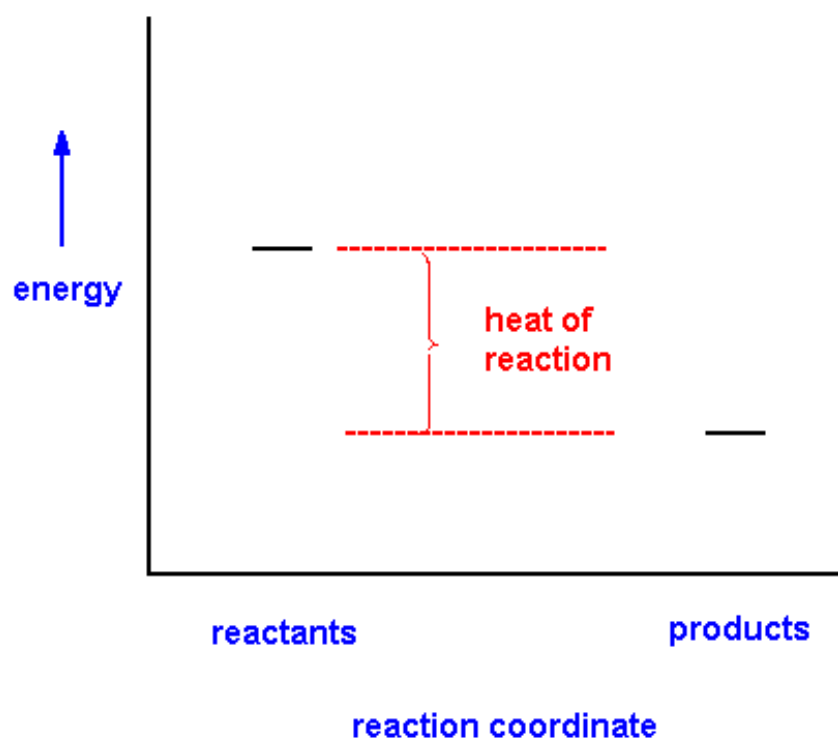


One way to describe this reaction is to write a balanced equation. The methane and oxygen balloon explodes with greater violence due to a more stoichiometric mixture of reactants.



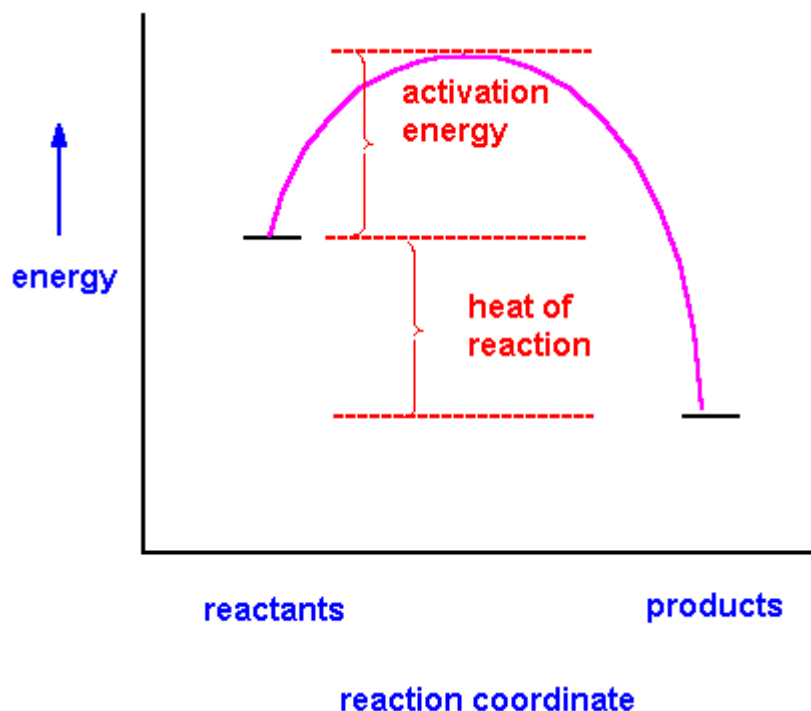
Since the combustion of methane is exothermic, the products are lower in energy (more stable) than the reactants by 888 KJ/mol. We will find later that heats of combustion data are useful ways of comparing the stability of molecules.

Another way chemists consider the energy changes (thermodynamics) in the reaction is by constructing an energy level diagram. The relative energies of reactants and products are displayed on the Y axis and the progress of the reaction (reaction coordinate) is given on the X axis. For the combustion of methane, the reaction is exothermic so the products are lower in energy than the reactants.



Although the energy course of the reaction is downhill, the reaction does not occur spontaneously. That is, methane and oxygen in the balloon are stable at room temperature and a reaction only occurs when additional energy is supplied. The course of the reaction does not go directly from reactants to products, but proceeds through a pathway that requires energy. The energy required for the reaction to

proceed is called the activation energy.



What do molecules need to react?

For a chemical reaction to occur between molecules not only must the activation energy be supplied, but reactants must collide with each other. The frequency of collisions is one factor that determines the rate at which a reaction occurs (reaction kinetics).

A collision between reactants may not be sufficient. For a reaction to occur chemical bonds must be broken and reformed. This rearrangement of bonds requires a minimum energy.

Not only must reactants collide with sufficient energy to reform the bonds but the collisions must have the proper orientation. In summary, the rate of a reaction depends on the following factors:

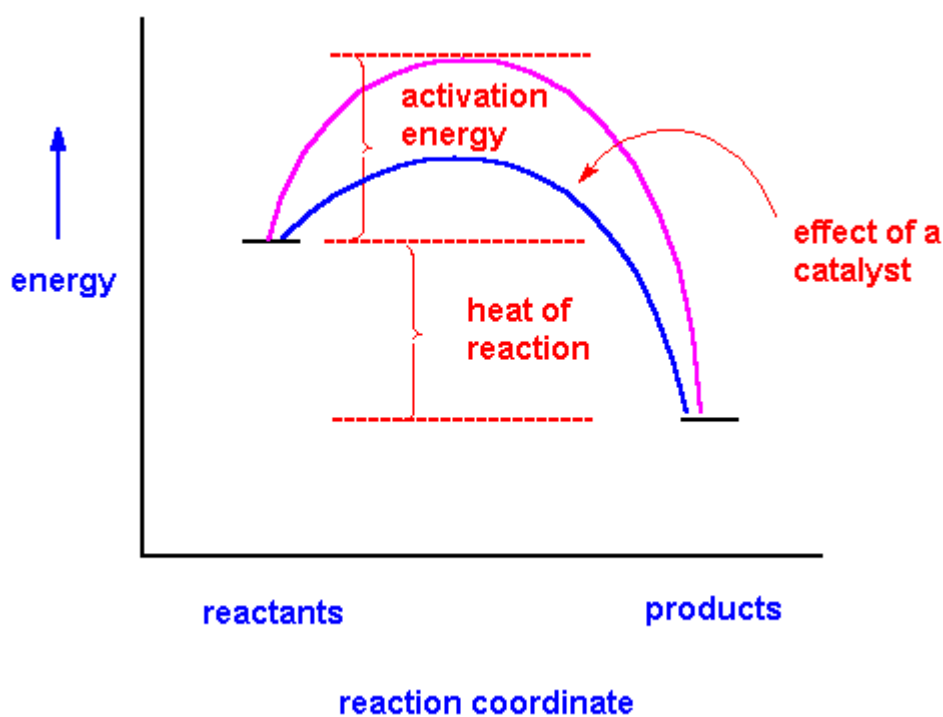
- frequency of collision
- energy of collision
- orientation of collision

In the laboratory it is usually easy to control the frequency of collision by increasing the concentration of reactants, using efficient stirring, grinding solids into powdered states, and so on. We can usually supply the minimum energy by heating the reactants or irradiating the sample with visible or ultraviolet light. The orientation factor is more difficult to deal with in the test tube. However, enzymes in your body and in all living organisms carry out chemical reactions very efficiently at room temperature by manipulating reactant molecules into the proper orientation. Chemists are beginning to mimic enzymes, and this area of research is of considerable interest for both theoretical and practical reasons.



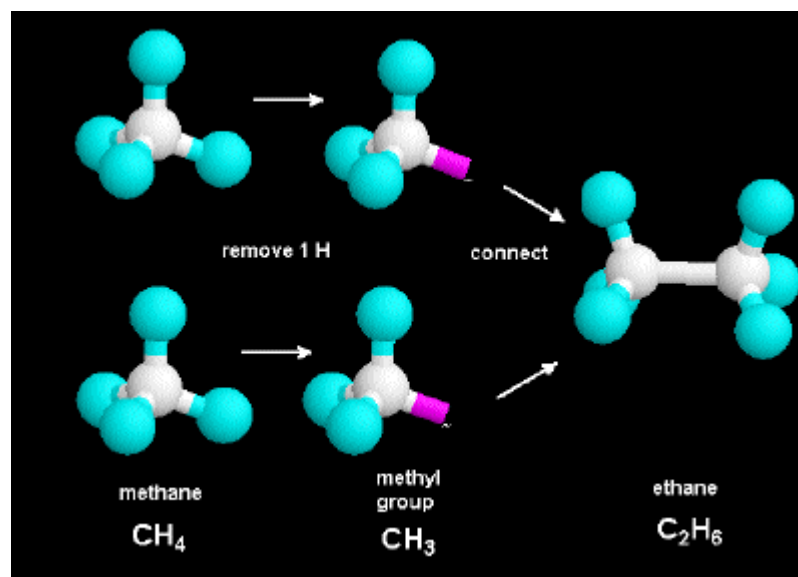
The rates of chemical reactions can be increased with the aid of catalysts. The effect of a catalyst on a chemical reaction can be shown in the following demonstration of the oxidation of tartaric acid with hydrogen peroxide.

A catalyst performs its task by providing a lower energy pathway between reactants and products. The enzymes in your body and other living organisms are exquisite catalysts. The catalytic converter in your car removes nitrogen oxides and unburned hydrocarbons from the exhaust.

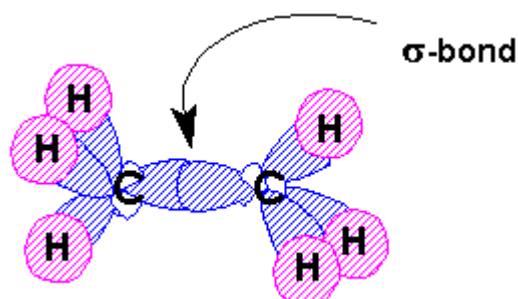
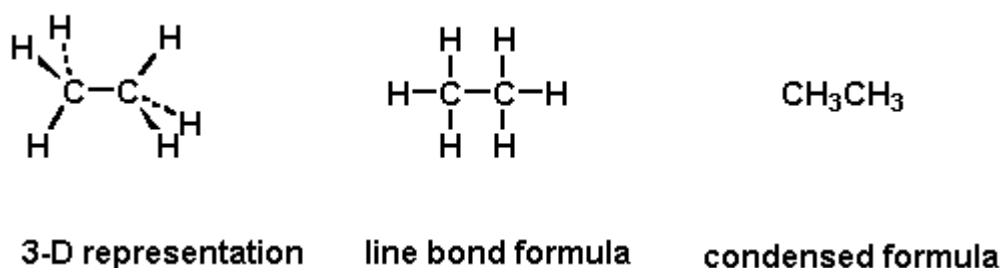


Ethane

Methane (CH_4) is the first of a series of hydrocarbons that make up the alkane family. Alkanes are hydrocarbons that contain only hydrogen and saturated carbon atoms, those bonded to four atoms. The second member of the series is ethane (C_2H_6). We can construct a model of ethane by removing a hydrogen atom from each of two methane molecules. The resulting CH_3 - fragment is called a methyl group. Connecting the two carbon atoms together by a single bond gives ethane.



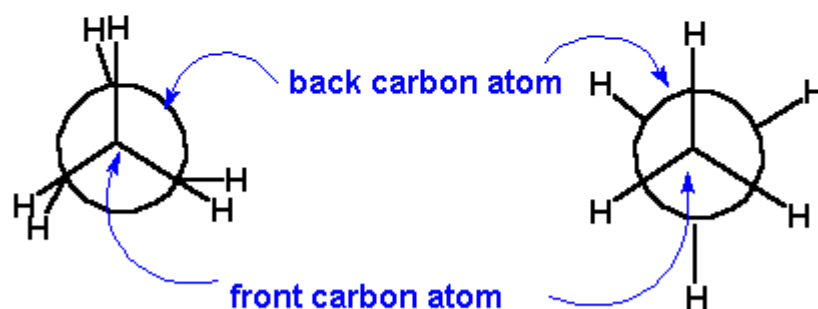
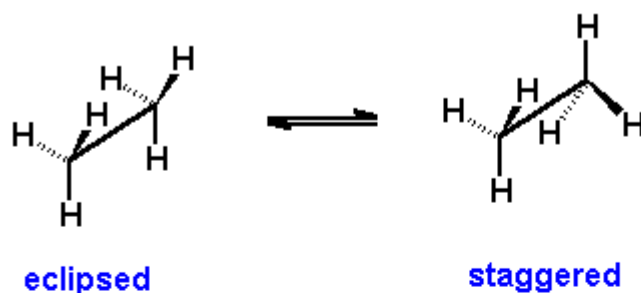
The bonding of the atoms in ethane can be represented by a line bond formula or by the **orbital representation**. The single bond formed by the overlay of two sp^3 orbitals is called a sigma (σ) bond. Sigma bonds are aligned linearly between the two bonding nuclei.



Atoms connected by sigma bonds are free to rotate. At room temperature thermal energy is sufficient for the two carbon atoms to rotate freely. When the hydrogen atoms are aligned with each other they are closest together. This arrangement is called the eclipsed conformation. The eclipsed conformation is high in energy because of repulsion of the electrons in the C-H bonds on adjacent carbon atoms. If ethane is twisted about the single bond from the eclipsed conformation, the hydrogen atoms on the adjacent carbon atoms move farther apart. When the molecule is twisted by 60° the hydrogen atoms are farthest apart. This is called the staggered conformation.

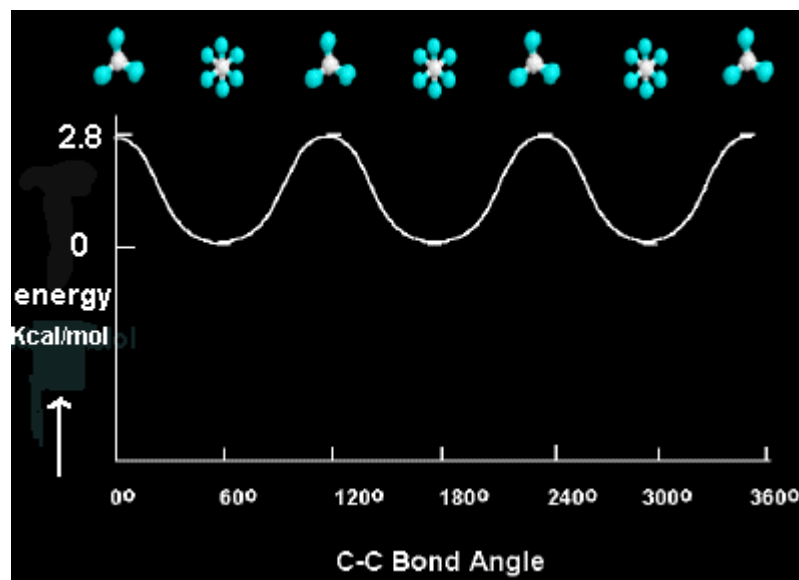


These conformations are represented in two dimensions by means of projection diagrams. A side-on projection of ethane gives the following representations of the staggered and eclipsed conformations. An alternate view of the conformations of ethane is given by the Newman projection diagrams.



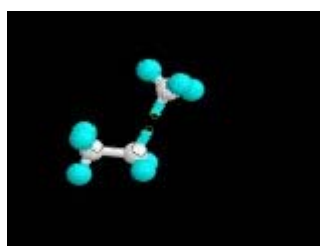
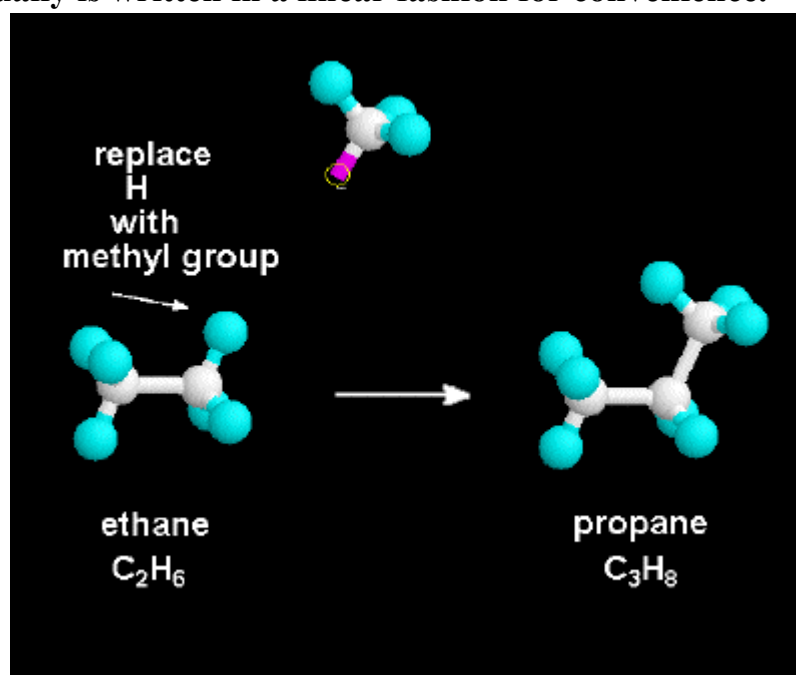
Newman Projections

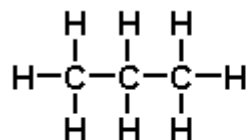
Since the hydrogen atoms are surrounded by an electron cloud with a negative charge, atoms repel each other. The farther apart the atoms are, the lower the energy of the system. For ethane, the staggered conformation is lower in energy than the eclipsed conformation by 2.8 Kcal/mole.



Propane

The next member of the alkane series is propane, C_3H_8 . We can build a propane model by removing one of the six hydrogens from our ethane model to produce a C_2H_5 - or ethyl group. Since all six hydrogen atoms of ethane are equivalent, it doesn't matter which one we remove. Connecting the ethyl group with a methyl group gives propane. Notice that propane is a bent molecule even though the line bond structure usually is written in a linear fashion for convenience.



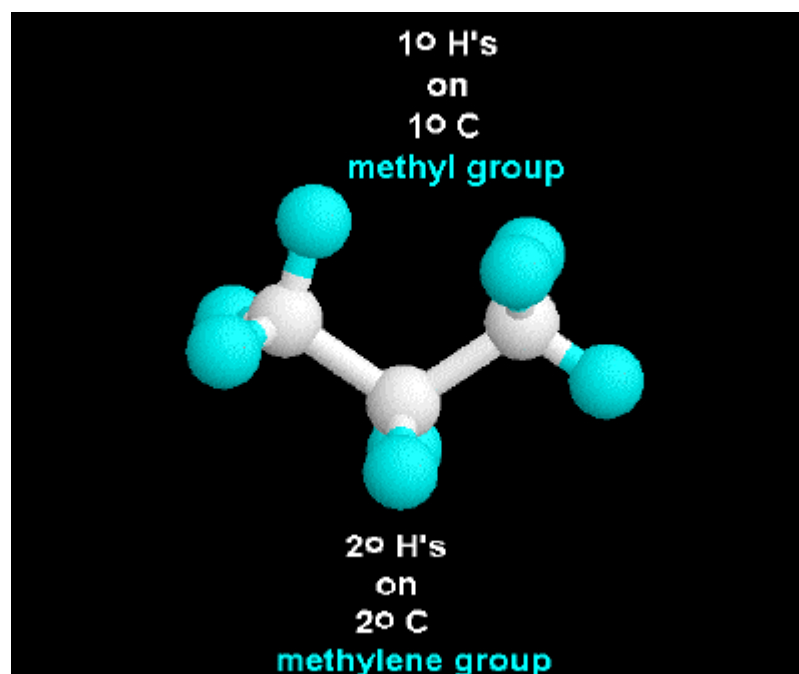


line bond representation

condensed formula

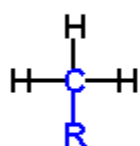
Representations of the propane molecule.

Propane has two distinct kinds of carbon atoms. The two carbon atoms on the end are bonded to only one carbon atom and are called primary carbons (1°). The central carbon atom is bonded to two other carbon atoms and is designated as a secondary (2°) carbon.

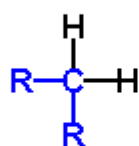


Carbon atoms are classified as primary, secondary, tertiary, or quaternary based on the number of non-hydrogen groups attached to the sp^3 carbon. The hydrogen atoms attached to these carbon atoms are given the same designation.

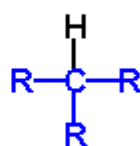
Classification of Carbon Atoms



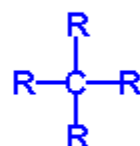
primary
 1°



secondary
 2°



tertiary
 3°



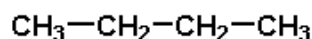
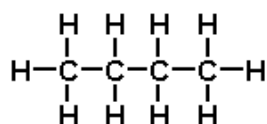
quaternary
 4°

Butane

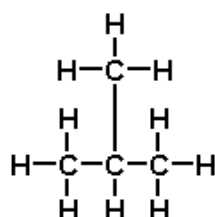
If we continue to build members of the alkane family, we can remove any one of the six equivalent hydrogen atoms from the primary carbon atoms of propane and attach a methyl group. This gives a linear molecule with the formula C_4H_{10} . This compound is known as butane (also n-butane for normal butane). However, if we remove one of the two hydrogen atoms from the secondary carbon and replace it with a methyl group, we get a different structure with the same composition (C_4H_{10}). This branched compound is known as isobutane or 2-methylpropane.

Compounds like n-butane and isobutane that have the same elemental composition but different arrangement of atoms are called *constitutional isomers*.

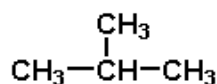
Butane



Isobutane



line-bond formula



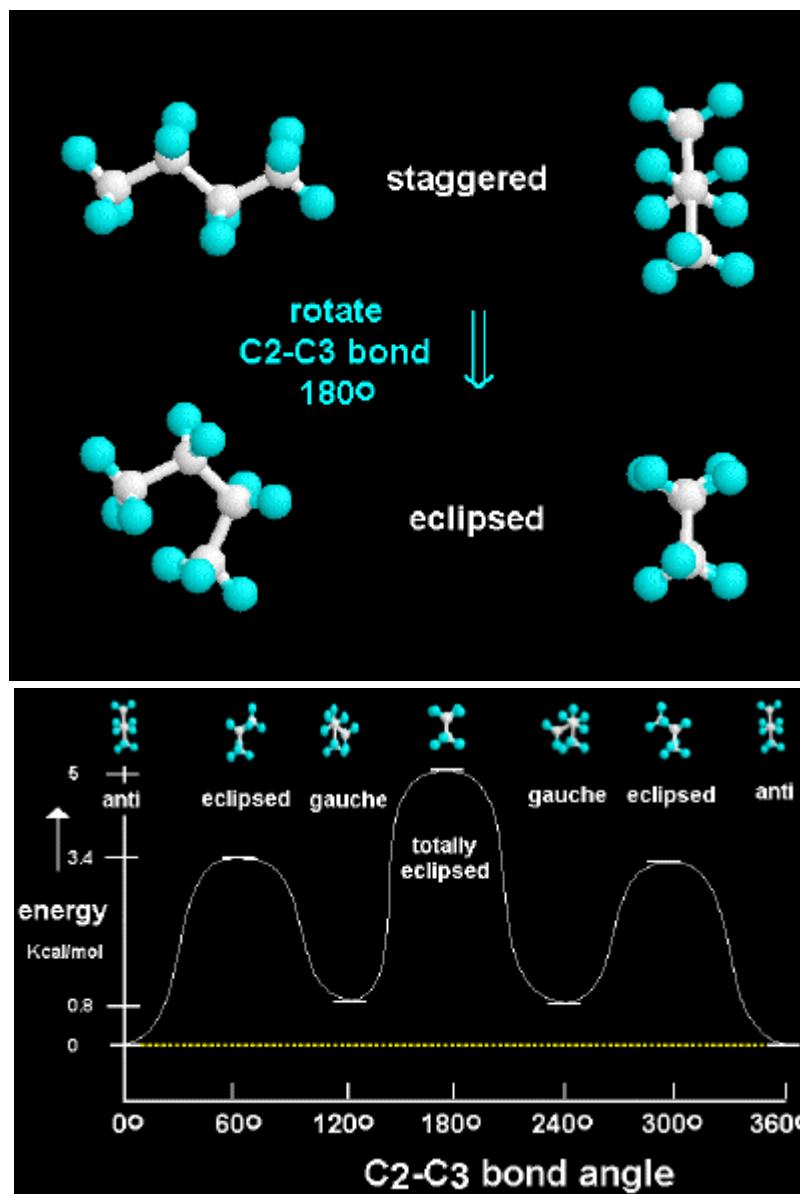
condensed formula



zig-zag formula

Free rotation occurs around the carbon-carbon bonds in butane just as in ethane. Rotation about the C_1-C_2 and C_3-C_4 bonds gives similar C-H repulsions to those in methane. However, if we consider rotations about the C_2-C_3 bond, we now have to consider interactions of methyl groups. Since methyl groups are much larger than hydrogen atoms, these interactions can be important in determining the energy of the molecule.

The lowest energy conformation occurs when the methyl groups are 180° apart in the *anti*-conformation. Rotation about the C_2-C_3 bond by 60° produces eclipsing of the methyl group and hydrogen atom resulting in a higher energy conformation. Further rotation into the *gauche* conformation brings the methyl groups closer together but in a staggered conformation. Final rotation by 60° causes eclipsing of the two large methyl groups and results in the highest energy conformation.



Pentane

The next member of the alkane series is pentane. There are three isomers of pentane all with the formula C_5H_{12} . We can classify each carbon atom of these three pentane isomers as primary (1°), secondary (2°), tertiary (3°), or quaternary (4°). The hydrogen atoms connected to each type of carbon atom also can be classified using this designation. We will see later that this classification is very useful in categorizing organic reactions.

Isomers of C_5H_{12}
and Classification
of Carbon Atoms



	<p>C = primary (1°)</p> <p>C = secondary (2°)</p> <p>C = tertiary (3°)</p> <p>C = quaternary (4°)</p>		
Structure	pentane (n-pentane)	2-methylbutane (isopentane)	2 d (1
line-bond			
Carbon classification			
Condensed	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—CH}_3$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—CH—CH}_2\text{—CH}_3 \end{array}$	
zig-zag			

Higher Alkanes

We can continue adding carbon atoms to build up further members of the alkane series. Notice that each member increases the formula unit by CH_2 . A series made

up of an orderly increase in a formula unit is a homologous series. The general formula for any alkane with n carbon atoms is $C_nH_{(2n+2)}$. The names and isomer number of the first 10 members of the alkane family are shown in the table. Observe how the number of isomers increases with increasing number of carbon atoms. A general formula has been developed that allows one to calculate the number of isomers of a given alkane. On this basis you can determine that dodecane $C_{20}H_{42}$ has 366,319 isomers.

Example: Draw all of the isomers of hexane (C_6H_{12}).

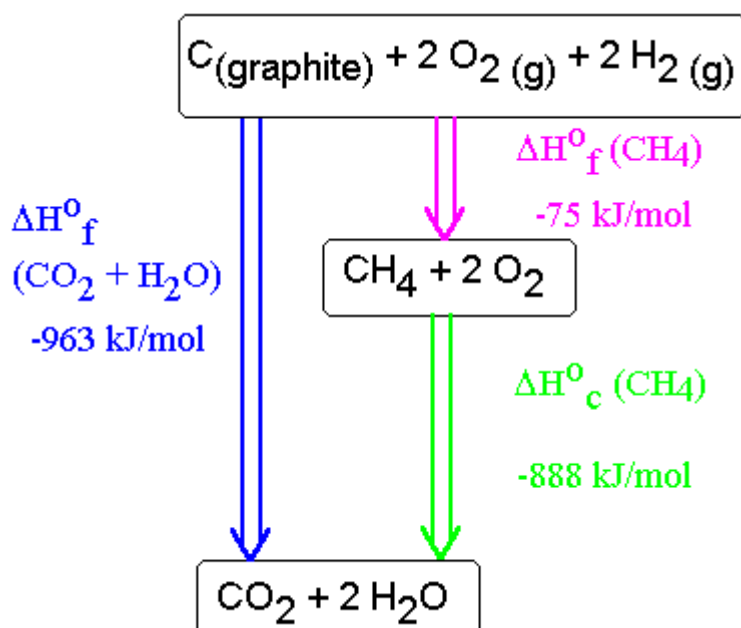
Isomers of Alkanes			
Number of C Atoms	Formula	Name	Number of Isomers
1	CH_4	methane	1
2	C_2H_6	ethane	1
3	C_3H_8	propane	1
4	C_4H_{10}	butane	2
5	C_5H_{12}	pentane	3
6	C_6H_{14}	hexane	5
7	C_7H_{16}	heptane	9
8	C_8H_{18}	octane	18
9	C_9H_{20}	nonane	35
10	$C_{10}H_{22}$	decane	75
n	$C_nH_{(2n+2)}$		

Heat of Combustion and Formation

The heat of combustion of methane is the energy released when methane reacts completely with oxygen. Heats of combustion are most easily measured in the laboratory in a calorimeter. One application of heats of combustion data is to determine the relative stability of a series of compounds. The more stable a particular compound is, the lower its heat of combustion. The laws of thermodynamics tell us that the heat of reaction depends only on the initial and final state, not the path that is used to get there. This allows us to calculate the heat of formation, the energy required to prepare a compound from its elements, from the heat of combustion of the compound and the heat of combustion of the same number of carbon and hydrogen atoms.

The heat of combustion of graphite (C) and two hydrogen molecules represents the

sum of the heat of combustion of (ΔH°_c) methane and its heat of formation (ΔH°_f). The delta (Δ) symbol refers to the energy difference between initial and final states, the change in energy during a reaction. H is the symbol for the type of energy known as enthalpy, usually defined as the heat of reaction.



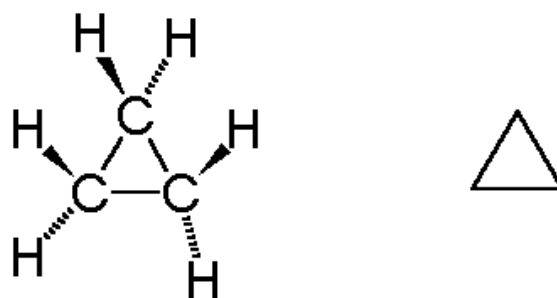
Cyclic Alkanes

Simple ring systems

Cyclopropane

The carbon chain in alkanes may connect with themselves to form rings. These hydrocarbons are the cycloalkanes. The simplest cycloalkane with three carbon atoms joined in a ring is cyclopropane. Cyclopropane has a high energy relative to propane because the three sp^3 carbon atoms are distorted from their normal 109.5° bond angles to 60° .

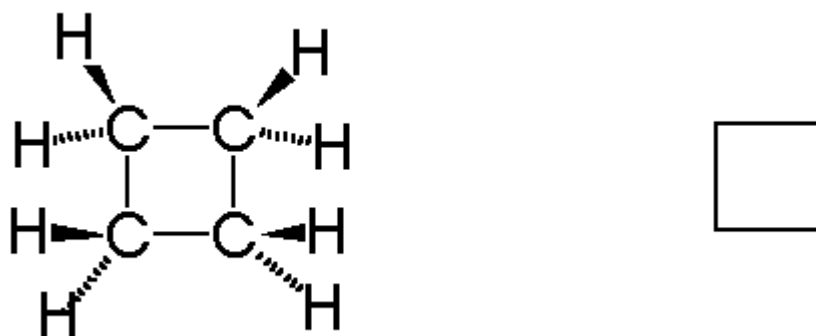
Cyclopropane can be represented as a line-bond structure showing all the carbon and hydrogen atoms or as a triangle. In this geometric representation, each corner of the figure represents a carbon atom and the hydrogens needed to form the four bonds to each carbon are omitted for clarity.



Very few naturally occurring molecules contain three membered rings due to the severe ring strain. An important exception is the natural insecticide [pyrethrin I](#).

Cyclobutane

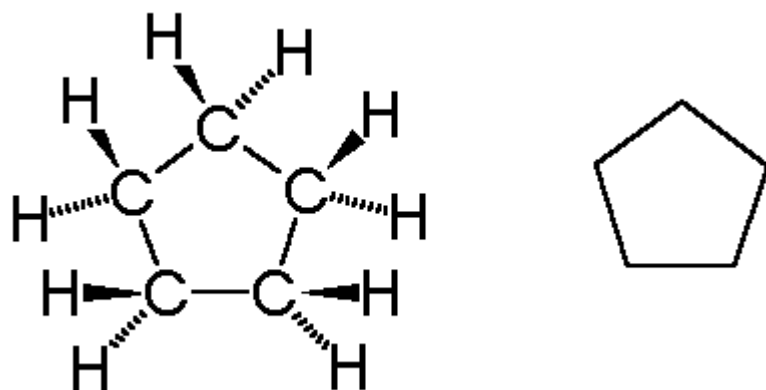
Cyclobutane, the four carbon ring, is also highly strained because the sp^3 carbon atoms are forced from their normal 109.5° bond angles. Planar cyclobutane would have 90° bond angles, however, by twisting out of the plane it can assume a lower energy conformation. Two and three dimensional representations of cyclobutane are shown below.



Compounds containing the highly strained four-membered ring are rarely found in nature. One example is the insect pheromone [grandisol](#), a sex attractant for boll weevils. The bicyclic compound α -pinene, a major constituent of turpentine, reacts readily with iodine in a highly exothermic reaction driven by relief of ring strain. During the reaction, the four-membered ring rearranges to a more stable, less strained, five-membered ring.

Cyclopentane

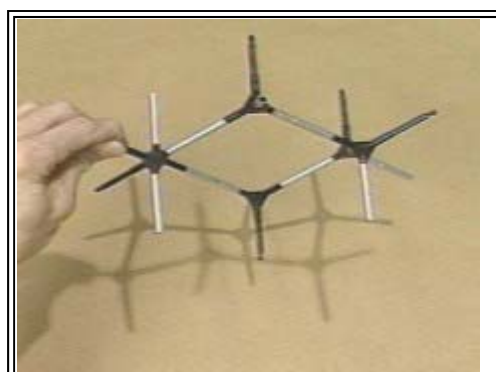
In the five membered cyclopentane ring, the bond angles are much less strained than in three and four membered rings. The cyclopentane molecule is puckered and looks somewhat like an envelope.



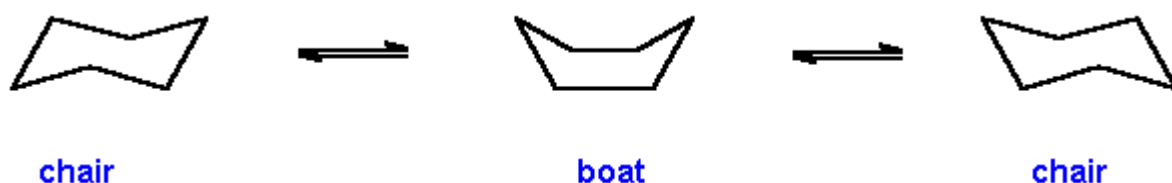
Five membered rings are found in many natural products. The chemical that makes catnip attractive to cats, [nepetalactone](#), is an example of a naturally occurring cyclopentane derivative.

Cyclohexane

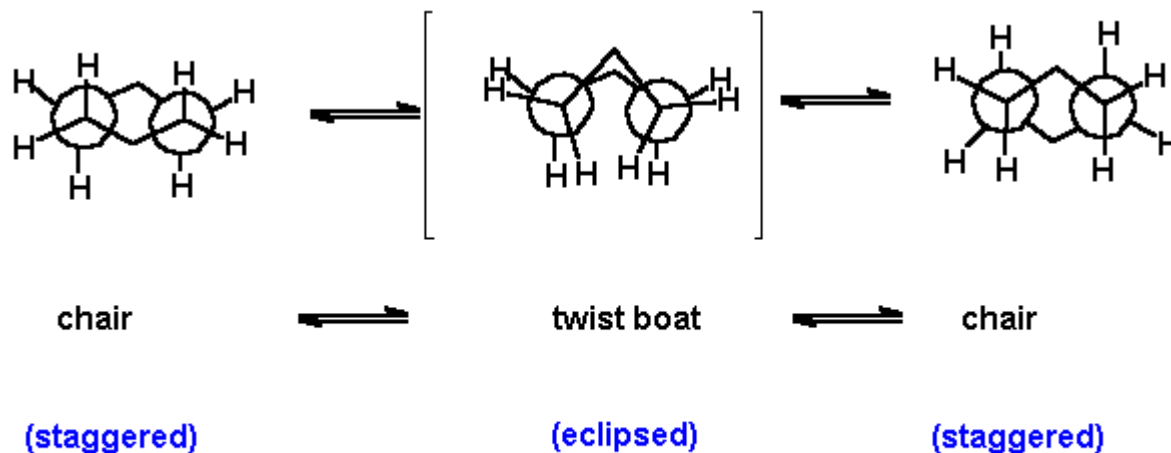
Cyclohexane (C_6H_{12}) is the smallest hydrocarbon that has tetrahedral 109.5° bond angles. This molecule is not planar but exists as a three dimensional molecule. The lowest energy arrangement of the atoms in cyclohexane is the chair conformation which is shaped like a patio chair. In this conformation, if you look straight along any bond, the carbon atoms that make up the rest of the ring are in staggered gauche-butane arrangements. A higher energy conformation occurs when adjacent bonds are eclipsed. This conformation is called a boat. These conformations are shown in the following diagrams which show the carbon skeleton (hydrogens are omitted for clarity). These two chair conformations are equal in energy and the barrier to rotation is small enough that this interconversion occurs readily at room temperature.



This model shows the gauche-butane interactions of chair cyclohexane. The shadow projection shows why it is called a chair.



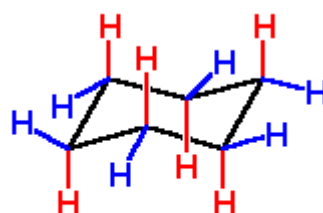
Chair and boat conformations of cyclohexane. Hydrogen atoms omitted for clarity.



[higher energy]

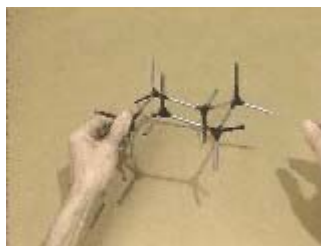
Newman projection of chair cyclohexane.

The cyclohexane ring has two different kinds of hydrogen atoms. In the chair conformation the six hydrogens pointing perpendicular to the ring are designated **axial** and the six hydrogens near the plane of the ring are called **equatorial**.



axial and **equatorial** bonds

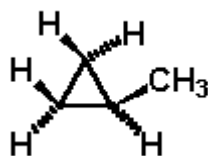
Cyclohexane can flip from one chair conformation to another by rotation about C-C single bonds. In this interconversion, the axial hydrogens become equatorial and equatorial hydrogens assume axial positions.



Click on the image for a video of the interconversions of the two chair conformations of cyclohexane.

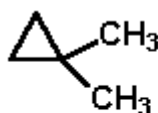
Substituted Cycloalkanes

If we replace any of the six hydrogen atoms of cyclopropane with a methyl group, we obtain methylcyclopropane (click here for the rules for [naming cycloalkanes](#)).

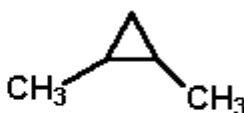


Methylcyclopropane

With dimethylcyclopropane, we can place the second methyl group on the same carbon atom as the first and obtain 1,1-dimethylcyclopropane, or we can place it on one of the adjacent carbon atoms and obtain 1,2-dimethylcyclopropane. These are [constitutional isomers](#).

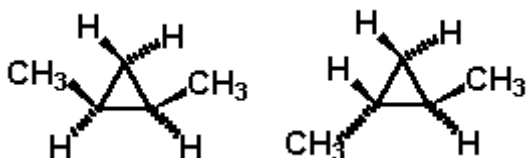


1,1-dimethylcyclopropane



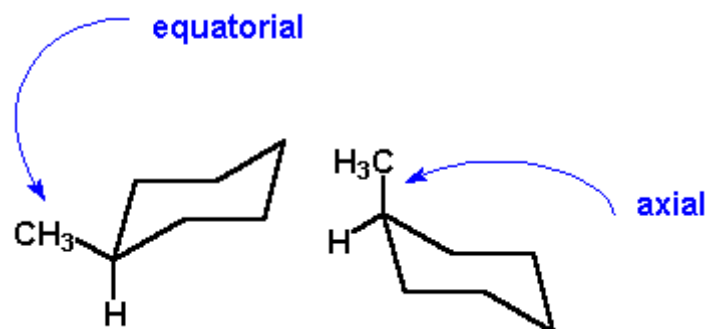
1,2-dimethylcyclopropane

The situation with 1,2-dimethylcyclopropane becomes even more complex because of the three-dimensional shape of the cyclopropane ring and the restriction the ring makes to free rotation about C-C bonds. The two methyl groups can be placed on the same side of the ring (*cis*- isomer) or on opposite sides (*trans*- isomer). These two isomers are sometimes called [geometric isomers](#).



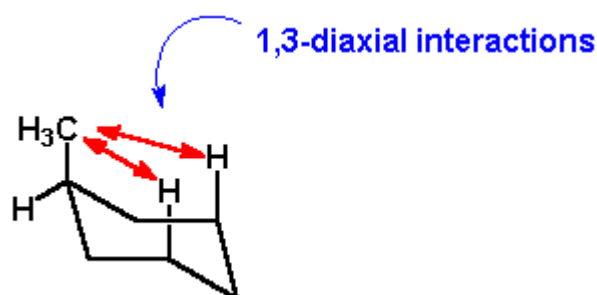
Substituted cyclohexanes pose more challenges because of the existence of axial and equatorial bonds in the more stable chair conformation. Methylcyclohexane can

exist in either the equatorial or axial conformation.



Methylcyclohexane in equatorial and axial conformations. The other hydrogen atoms are omitted for clarity.

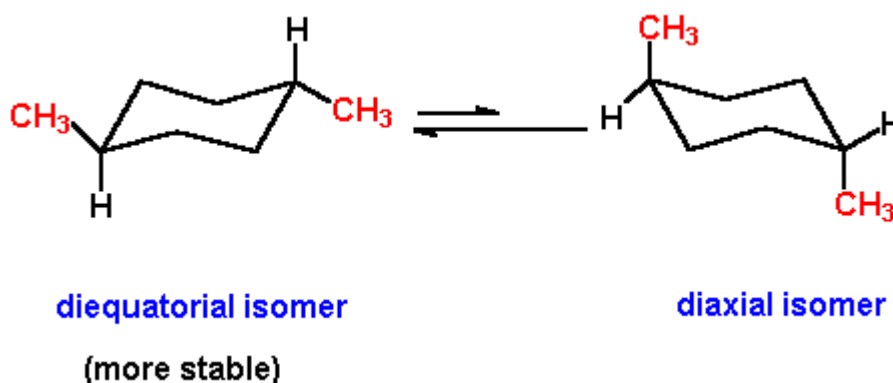
These two conformations are not equivalent in energy. The equatorial conformation is more stable than the axial by 7.5 kJ mol^{-1} . This energy difference corresponds to an equilibrium mixture composed of 95% equatorial methylcyclohexane at room temperature. The stability of the equatorial isomer relative to the axial is attributed to steric strain due to interaction of the axial methyl with the axial hydrogens on C-3 and C-5. Examine the Chime representations of the two isomers to visualize this repulsion. It is helpful to display the models with the [van der Waals radii](#) to illustrate the importance of electronic crowding and repulsion in the axial isomer.



With the dimethylcyclohexanes the situation becomes even more complex. Consider 1,4-dimethylcyclohexane. With two substituents on different carbon atoms of a ring, we again have the possibility for *cis*- and *trans*- isomers. If we place one methyl group in the equatorial position at C1 the *cis*- arrangement requires the methyl group at C4 to be in an axial position. When this isomer converts to the other chair form, the *cis*- arrangement of the groups does not change. Furthermore, because each conformation has one axial and one equatorial methyl group, the energy of the two conformations is the same.



In the case of the *trans*- isomer, if we place the methyl groups at C1 in the more stable equatorial position, the methyl group at C4 must occupy an equatorial position also. When the ring flips into the other chair conformation, the two methyl groups remain *trans*- but now occupy axial positions. These two conformations are no longer equivalent in energy. The diequatorial isomer is more stable than the diaxial form by twice the steric strain energy of methylcyclohexane ($2 \times 7.5 \text{ kJ mol}^{-1} = 15.0 \text{ kJ mol}^{-1}$). This corresponds to an equilibrium mixture composed of about 99.5% of the diequatorial isomer at room temperature.

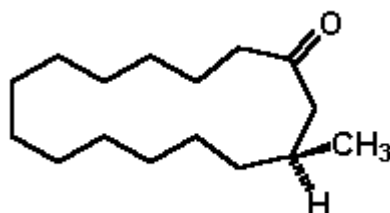


Example	Draw both chair conformations of the following disubstituted cyclohexanes. Predict which conformation, if any, is the more stable.
1	<i>cis</i>-1,2-dimethylcyclohexane
2	<i>trans</i>-1,2-dimethylcyclohexane
3	<i>cis</i>-1,3-dimethylcyclohexane
4	<i>trans</i>-1,3-dimethylcyclohexane

Medium and Large Ring Systems

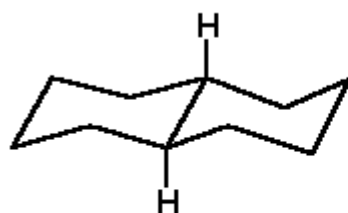
Cyclic organic compounds found in natural sources usually have 5 or 6 member rings. However many compounds may be found with larger rings. We have seen that cyclohexane does not have bond strain like the smaller three and four membered rings. Rings made up of seven and eight carbon atoms, called medium rings, possess steric strain due to van der Waals interaction with nonbonded atoms. The floppy nature of these medium rings can be shown by examining models of their conformations.

Large ring systems are also possible. Muscone, a natural product found in the scent gland of the musk deer, is used in musk perfumes and fragrances. This molecule possesses a 15 membered ring. Today commercial muscone is usually manufactured by chemical synthesis, not extracted from its natural source.

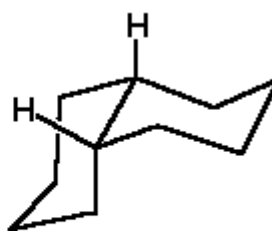


Polycyclic Ring Systems

Many organic compounds are made up of several simple rings joined together. For example, decalin (bicyclo[4.4.0]decane) has two cyclohexane rings fused together. Two geometric isomers, *cis*-decalin and *trans*-decalin are possible.

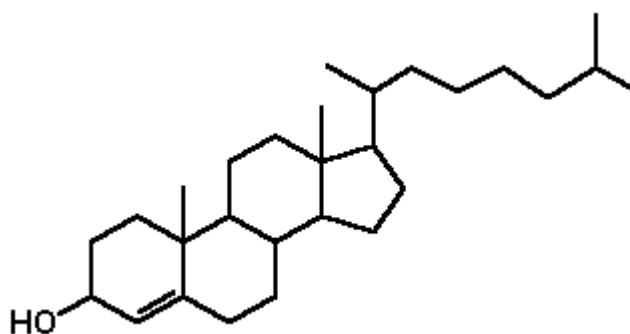


trans-decalin



cis-decalin


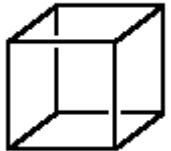

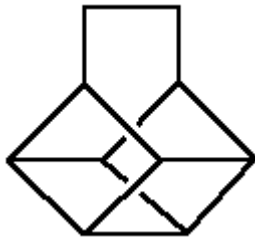
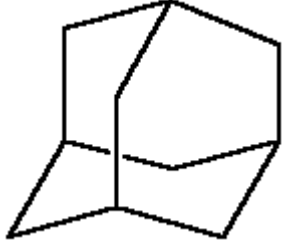

Steroids are important natural products and include cholesterol and the hormones testosterone, estrogen, and progesterone. These steroids are tetracyclic compounds made up of three six-membered rings and one five-membered ring. The structure of cholesterol is shown below. Notice the chair conformation of the six-membered rings in the Chime representation.



Fused Ring Systems

Chemists respond to the beauty and challenge of synthesizing hydrocarbon

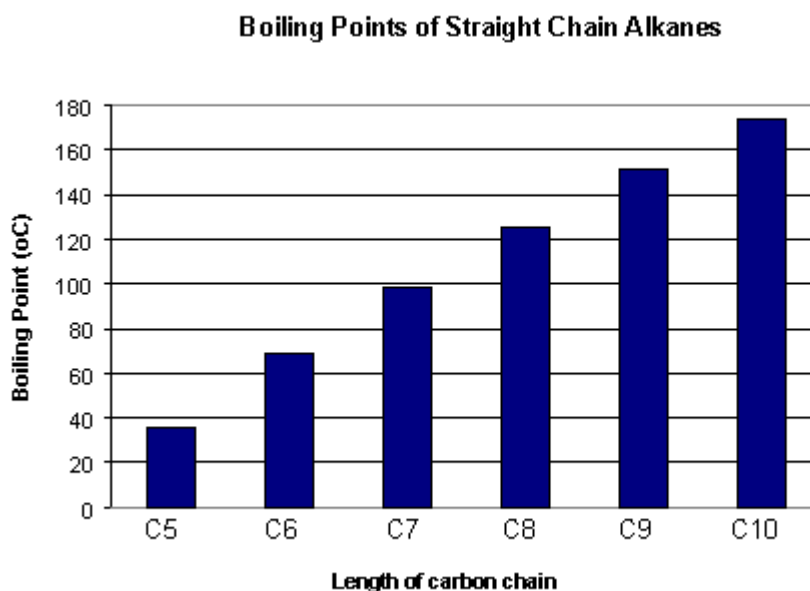
compounds with several rings fused together to make more complex structures. One goal of synthetic chemistry is the preparation of the Platonic rectangular solids, prismane and cubane are simple examples of these structures. If two cyclopentane rings are joined together, the resulting structure looks somewhat like a child's drawing of a house and was named housane. Similarly, the polycyclic compound basketane looks like a basket. Adamantane is a 10 carbon polycyclic structure and has an atomic arrangement like the carbon atoms in diamond. Adamantane's very high melting (314°C) reveals the close packing of the molecules in the solid. Dodecahedrane is a twelve sided regular figure. Its symmetry gives the compound a very high melting point ($> 450^{\circ}\text{C}$).

Polycyclic Hydrocarbons	
Name	Structure
prismane	
cubane	
housane	
basketane	
adamantane	
dodecahedrane	

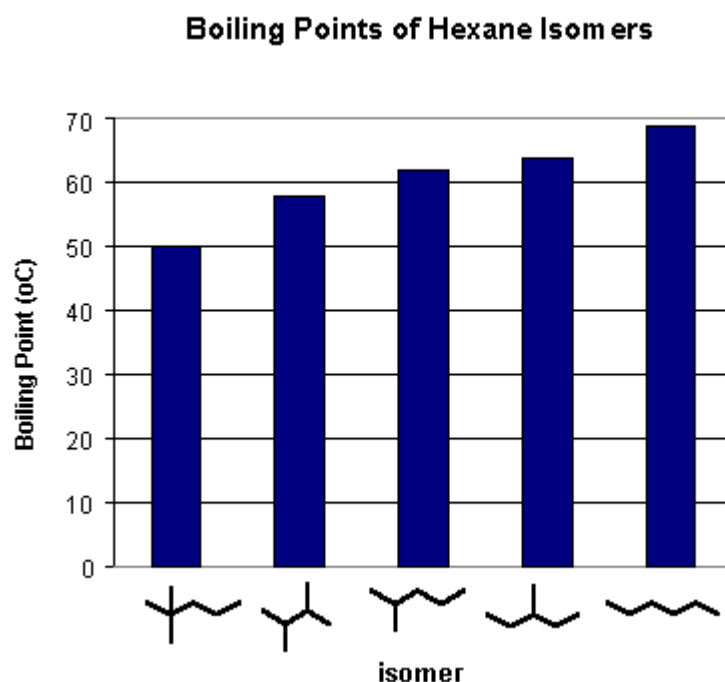
Structure Activity Relationships

One of the fundamental principles of organic chemistry is that the structure of a molecule determines its chemical and physical properties. This principle is easily demonstrated by comparing the boiling points of a homologous series of alkanes from pentane to decane.

The effect of structure on the b



Boiling point can be observed by looking at the boiling points of the five hexane isomers (C_6H_{14}).



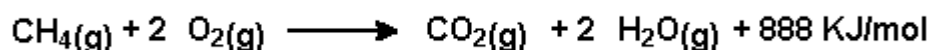
An important practical application of the relationship of structure and function is in the octane rating of gasoline. Branched hydrocarbons burn more efficiently in internal combustion engines without knocking and have a higher octane rating.

Chemical Reactions of Alkanes

For alkanes to undergo a chemical reaction either C-C or C-H bonds must be broken. Since both of these bonds are very strong, alkanes are ordinarily very stable with high bond strengths. They combine with oxygen only at high temperature in combustion reactions unless a catalyst is present. Developing catalysts that can oxidize methane and other alkanes to alcohols is an important goal of industrial chemistry because these alcohols are important items of commerce. Alkanes also react with the halogens chlorine and bromine only when high energy is supplied to the reaction. The following reaction map summarizes the reactions of alkanes.

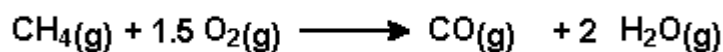
Combustion:

The combustion of alkanes is important in the production of energy and in industrial chemistry. Complete combustion of alkanes gives carbon dioxide and water plus heat, and it is this heat that we use to run our cars, heat our homes and cook our food.

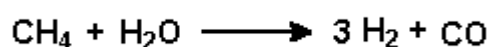


If the combustion of alkanes is carried out under a limited amount of oxygen,

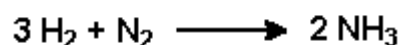
incomplete combustion occurs with the production of carbon monoxide and water. Since carbon monoxide binds to the hemoglobin in our blood about 200 times more tightly than oxygen, incomplete combustion in improperly adjusted furnaces can lead to death.



A very important industrial reaction involves the decomposition of methane with steam to give hydrogen and carbon monoxide. The hydrogen gas produced in this reaction can be combined with nitrogen in the Haber process to produce ammonia for fertilizer. Over 95% of the ammonia fertilizer made in the United States is made from hydrogen derived from natural gas which consists mostly of methane.



The hydrogen is then combined with nitrogen from the atmosphere at high temperature and pressure with catalysts to produce ammonia.



Halogenation

Alkanes also react with halogens with activation energy provided by light or heat. Under these conditions, a substitution reaction occurs in which a halogen atom replaces hydrogen in a C-H bond. For example, methane reacts with chlorine in a light initiated reaction to produce chloromethane (methyl chloride) and HCl. This reaction is a free radical substitution reaction and will be discussed in a [later section](#).

