2. Hydrocarbons

2.1 Composition of Petroleum

Naturally occurring petroleum is composed of organic chemicals: approximately 11 to 13% hydrogen and 84 to 87% carbon. Traces of oxygen, sulfur, nitrogen and helium may be present as impurities. Many different series of hydrocarbon have been found in crude petroleum. The most commonly encountered are the so-called paraffins, the olefins, the polymethylenes, the acetylenes, turpenes and benzenes. In general, the chemical mixture is a gas at normal temperatures and pressure if the molecules in the mixture are small. When the mixture contains predominantly larger molecules, it is a liquid at normal temperatures and pressures.

Natural Gas

Natural gas is composed predominantly of the lower-molecular weight hydrocarbons of the paraffin series. Table 2-1 give the component of typical natural gases.

	Natural gas
Hydrocarbon	
Methane	70-98%
Ethane	1-10%
Propane	trace-5%
Butanes	trace-2%
Pentanes	trace-1%
Hexanes	trace-0.5%
Heptanes +	trace-0.5%
Nonhydrocarbon	
Nitrogen	trace-15%
Carbon dioxide	trace-5%
Hydrogen sulfide	trace-3%
Helium	up to 5%, usually trace or none

	Gas from a well which also produces crude oil
Hydrocarbon	
Methane	45-92%
Ethane	4-21%
Propane	1-15%
Butanes	0.5-7%
Pentanes	trace-3%
Hexanes	trace-2%
Heptanes+	none-1.5%
Nonhydrocarbon	
Nitrogen	trace-10%
Carbon dioxide	trace-4%

Hydrogen sulfide	none-trace-6%
Helium	none

Crude Oil

A typical crude oil contains thousands of different chemical compounds. It is normally separated into crude fractions according to the range of boiling points of the compounds included in each fraction. Table 2-1 gives a list of typical fractions.

Typical crude oil fractions

Crude fraction	Boiling point, °F (Melting point)	Approx. chemical composition	Uses
Hydrocarbon gas	to 100	C1-C2	Fuel gas
		C3-C6	Bottled fuel gas, solvent
Gasoline	100-350	C5-C10	Motor fuel, solvent
Kerosene	350-450	C11-C12	Jet fuel, cracking stock
Light gas oil	450-580	C13-C17	Diesel fuel, furnace fuel
Heavy gas oil	580-750	C18-C25	Lubricating oil, bunker foil
Lubricants and waxes	750-950 (100)	C26-C38	Lubricating oil, paraffin wax, petroleum jelly
Residuum	950+ (200+)	C38+	Tars, roofing compounds, paving asphalts, coke, wood preservatives

Crude oils are classified chemical according to the structures of the larger molecules in the mixture. Classification methods use combinations of the words paraffinic, napthenic, aromatic and asphaltic. Liquids obtained from different petroleum reservoirs have widely different characteristics. Some are black, heavy and thick, like tar, while others are brown or nearly clear with low viscosity and low specific gravity.

2.2 Structure and classification of hydrocarbons

As stated above, petroleum consists primarily of hydrocarbons, containing hydrogen, H, and carbon, C. Carbon is quite the special element. The carbon-to-carbon bonds are very strong, and long chains of carbon atoms, one bonded to another, are possible. Carbon is unique in that the C-C bond remains strong even if the carbon atom is bonded with other elements. Carbon compounds are stable and relatively unreactive chemically (e.g. slow reaction with oxygen at room temperature). This is no true of the compounds of other chain-forming atoms.

The carbon-to-carbon and carbon-to-hydrogen bonds in hydrocarbons are so-called covalent bonds. Such bonds result when atoms share electrons. A well-known example is the formation of the hydrogen molecule. Each hydrogen atom has a single electron; thus, by sharing a pair of electrons, two hydrogen atoms can complete the first shell of electrons (which has two electrons).

Describe how the outer shell of a C atom is filled.

What is the other type of bond, and what is the difference?

With few exceptions, carbon compounds are formed with four covalent bonds to each carbon atom, regardless of whether the combination is between two or more carbon atoms or between carbon and some other element. The carbon atom is capable of forming four single bonds (single: sharing one electron). Double and triple bonds are also possible.

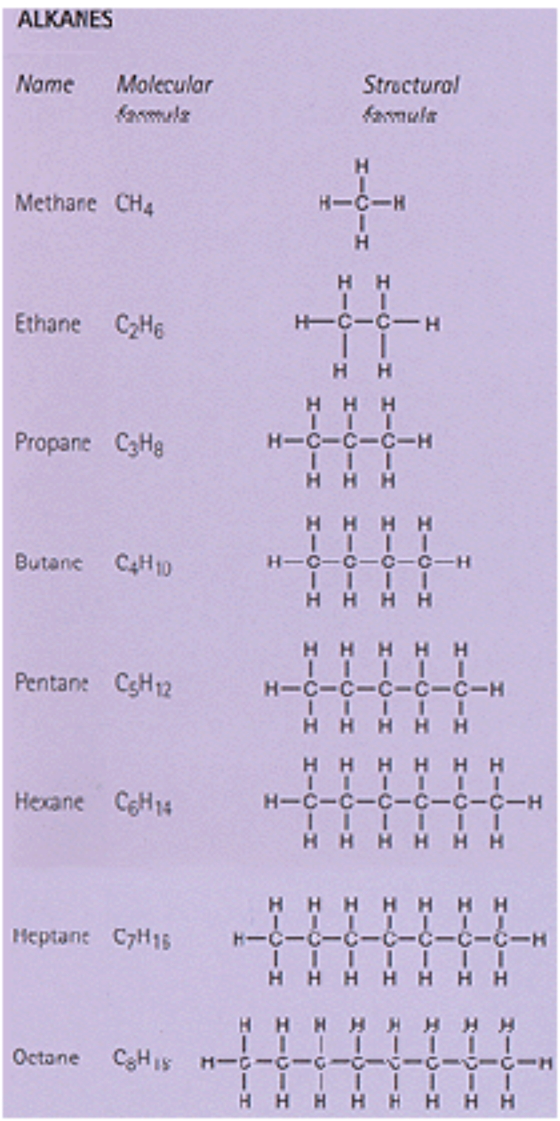


Fig 2-1 Alkanes C1-C8

Normally, the carbon atom forms its four single bonds so that the four attached atoms lie at corners of a regular tetrahedron (angles of 109.5 degrees). Carbon chains can be open or closed (cyclic).

On the basis of structure, hydrocarbons are divided into two main classes: aliphatic and aromatic. Aliphatics are further divided into alkanes, alkenes, alkynes and their cyclic analogs.

The number of organic materials is very wide, on the order of 10^6.

Alkanes

The alkane family is saturated hydrocarbons or paraffins. They have a general formula C_nH_{2n+2}. Names for the various alkanes follow a similar patter: prefix + -ane suffix. The prefix indicates how many carbon atoms are present.

Under standard conditions, methane, ethane, propane and butane are gases, the C_5H_{12} through the $C_{17}H_{36}$ alkanes are liquids and from $C_{18}H_{38}$ and larger alkanes are solid. Natural gases are described as dry or wet gases depending on the amount of condensable hydrocarbons present. Pentane and heavier are considered condensable.

Note that in the above figure the carbon atoms are depicted as forming a continuous chain. As the number of carbon atoms increases, several different configurations may be formed of the same alkane through branching. The different configurations are referred to as isomers. As an example, consider the isomers of pentane:

PICTURES

In this example, non-standardized names are used: The prefix iso- is used for isomers with two methyl groups (CH_3) attached to carbon atoms at the end of an otherwise straight chain. The prefix neo- indicates three methyl groups on a carbon atom at the end of a chain. Straight chain alkanes are often written with the prefix n- (as in n-hexane).

Draw the various representations of C_6H_{14}. Do you expect the boiling points of the isomers to be different? How would they vary?

Since you would quickly run out of prefixes as you increase the number of carbon atoms, and thus the number of isomers, ($C_{19}H_{40}$ has 1013 isomers), the easier-to-generalize IUPAC system is generally used. This considers isomers to be formed by linking alkyl groups to parent chains of carbon atoms. An alkyl group is simply an alkane with one H missing.

What are ethyl and propyl groups?

The IUPAC rules are as follows:

1. Select the longest continuous chain of carbon atoms (the parent chain). Base the name of the alkane on the number of carbon atoms in this parent chain.
2. Number these carbon atoms such that the sum of the positions of the side-chains is minimal.
3. Where there are two identical chains in the same position, supply numbers for both.
4. If a side-chain is again comprised of a carbon chain + side-chains, the naming system is extended in a trivial manner. The longest chain of the side-chain is numbered starting with the carbon attached directly to the parent chain. Parentheses separate the numbering of the substituents from the main hydrocarbon chain.
5. When two or more side-chains are present, they are listed in alphabetical odder or in the order of increasing complexity.

Alkenes

Alkenes are unsaturated hydrocarbons and also referred to as the olefins. The general formula for alkenes is C_nH_{2n}. Alkenes have a double carbon bond. In a double carbon bond, two electrons from each of the two carbon atoms are shared. The alkene names use the same prefix as the alkanes. The suffix is –ene. Note that ethene is commonly known as ethylene and propene as propylene. The IUPAC rules are similar to those used for the alkanes. The position of the double bond is indicated by a number.

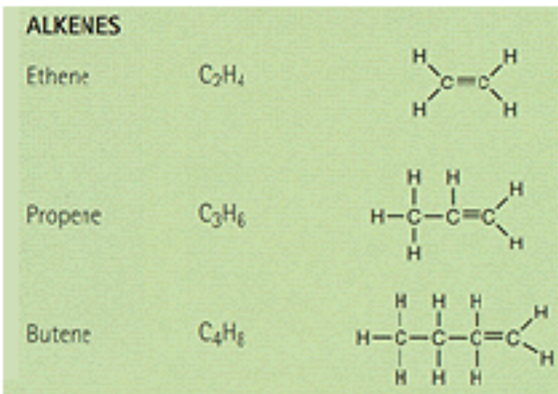


Fig 2-2 Alkenes

Because the carbon double bond does not permit the rotation of the carbon atoms, another type of isomerism is introduced: geometric isomerism. Let's look at 2-butene (CH_3-CH=CH-CH_3). The two methyl groups can be located on the same side of the basic structure or on the opposite sides. The two isomers formed this way are called stereoisomers (cis- and trans-). This results in cis-2-butene and trans-2-butene.

If there are two double bonds, the hydrocarbons are called alkadienes. If there are three we use alkatrienes and for four, alkatetraenes.

Alkynes

Alkynes have a carbon-carbon triple bond. The general formula is C_nH_{2n-2}. The nomenclature of the alkynes is the same as the alkenes, replacing –ene with –yne. The simplest compound is ethyne, also called acetylene.

Give the structure of 3,3,-dimethyl-1-butyne.

Cyclic hydrocarbons

Saturated hydrocarbon compounds that are arranged in rings instead of chains are called cycloalkanes. The cycloalkanes are also known as napthenes (name most commonly used in the petroleum industry) or cycloparaffins. The napthenes have the general structure C_nH_{2n} (same as alkenes, but physical and chemical properties are not all the same). The most common cycloalkanes are cyclopentane and cycloheptane. The naming system is again similar to what was used earlier. Substituents on the rings are named and positions are numbered to give the lowest possible combination of numbers.

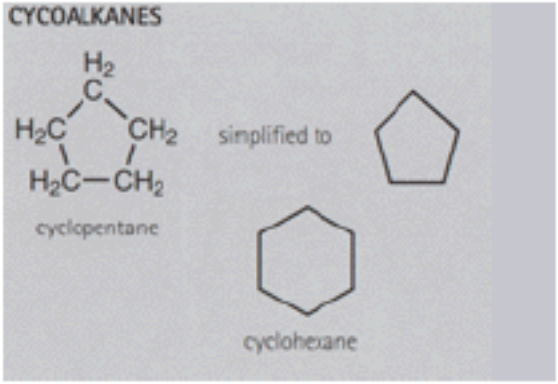


Fig 2-3 Cyclo-alkanes

What is 1,2-dumethulcyclopentane?

If a double bond is present in the ring, the hydrocarbon is referred to as a cycloalkane. When two double bonds are present it will be a cycloalkadiene. Cycloparaffins can have more than one ring, with rings sharing carbon atoms. These are referred to as condensed rings.

Aromatics

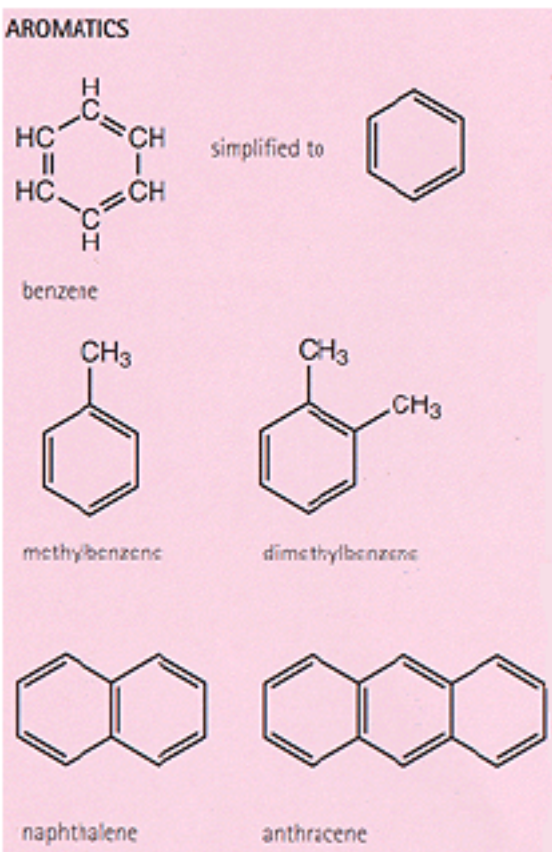


Fig 2-4 Aromatics

The aromatics include benzene and compounds that resemble benzene in behavior. AS shown above, benzene is a flat molecule with size carbon atoms arranged in a hexagonal ring. All bond angles are 120 degrees. Benzene this seems like a 1,3,5-hexatriene, but behaves very differently. 1,3,5-hexatriene is very reactive, benzene is not; it is very stable and cab be involved in many reactions in which the formed products retain the benzene ring. Thus the bonds in benzene are much more stable than normal double bonds. It is postulated that the bonds in benzene are all similar. In other words, that benzene has size one and a half bonds instead of three single bonds and three double bonds.

The name aromatic is used because many of the compounds containing benzene rings have very pleasant odors, although most are carcinogenic.

Nonhydrocarbon components

Nitrogen, carbon dioxide and hydrogen sulfide are common nonhydrocarbon constituents of petroleum. They are mainly part of the gas at the surface. Petroleum liquids can also have compounds in which sulfur or oxygen are connected to carbon or hydrogen. These elements usually occur in the large molecules with complex ring structures and are referred to as resins or asphaltines. As much as 50% of the total molecules in some heavy crude oils are resins and asphaltines.

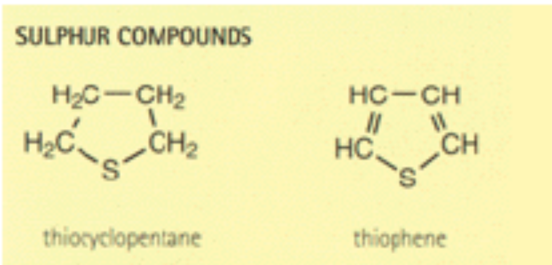


Fig 2-5 Compounds containing sulfur

As far as sulfur is concerned, the quantity of sulfur generally increases as the density of the crude increases. The amount of sulfur accepted in products is legally limited, so sulfur compounds must be removed or, often, destroyed.

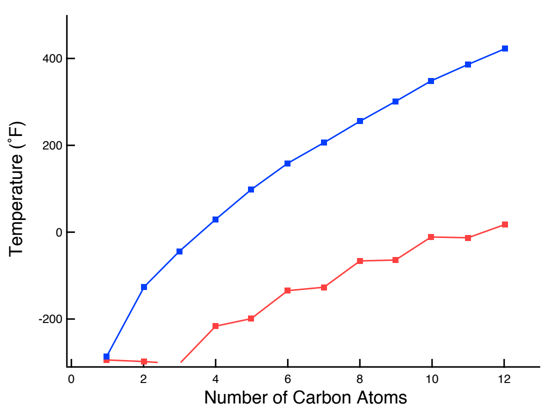
Properties of hydrocarbon fluids

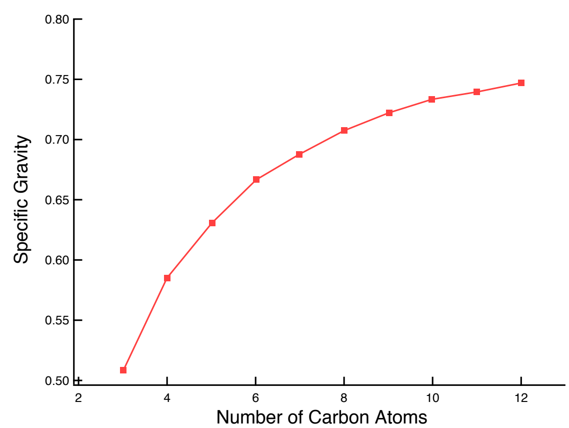
The physical properties of a substance can be classed as intensive or extensive. Intensive properties do not depend on the quantity of material; extensive properties do. Examples of intensive properties are color, odor, boiling point, viscosity, pressure and temperature.

What are examples of extensive properties?

Let's investigate some physical properties for the various types of hydrocarbons. The following graph shows the dependency of boiling and melting point and specific gravity for straight chain alkanes. Specific gravity is defined as:

$$S = \frac{\rho_{liquid}}{\rho_{water}}$$





The boiling points and melting points are fairly low. This is because the molecules are highly symmetrical and there fore the intermolecular forces are small. The intermolecular forces are greater between larger molecules.

Why do you think that the increases in melting points are not as regular as the increases in boiling points?

For isomers, an increase in branching causes a decrease in intermolecular attraction, which results in a lower boiling point. The melting points of the isomers differ as well because the branching changes the way the molecules fit into the crystal lattice of the solid. Chemically, alkanes are unreactive. The name paraffin means "not enough affinity". The strong single C-H and C-C bonds are vulnerable only to very strong reactants at normal temperatures. If the temperatures are high and oxygen is present, complete combustion to carbon dioxide and water occurs (i.e. the principle use of natural gas is combustion).

The properties of alkenes are similar to those of the alkanes. The double bonds are les stable than the single bonds and are therefore more likely to be attached by the other chemicals. Thus, alkenes are more reactive than alkanes. The alkynes are chemically very much alike to the alkenes, meaning they are more reactive than the alkanes. Note that although it seems to make sense to expect the triple bond is more reactive than the double bond, it is not always the case.

Cycloalkanes also have reasonably regular changes in boiling points, melting points and specific gravities. However, cycloalkanes can differ a fair amount in reactivity, depending on their bond angles. Cyclopentane and cyclohexane (which occur naturally in petroleum) are as stable as the corresponding straight chain alkanes. Cyclobutane and cyclopropane have bond angles that are smaller than the normal 109.5 degrees and therefore the angle strain is great, resulting in very reactive compounds. The larger rings are reasonably stable, but not very common.

The hybrid bonds of the benzene rings have the same stability as the C-C single bonds found in the alkanes. The usual relationship between physical properties and molecular size can be observed. The aromatic compounds can enter into many reactions that do not affect the ring structure.

The most important physical properties from a classification standpoint are the density (specific gravity_ and the viscosity of the liquid petroleum. The specific gravity of crude oils ranges from about 0.75 to 1.01 (so crude oils are generally lighter than water). In the petroleum industry, the API (American Petroleum Institute) gravity is often defined as

$$°API = \frac{141.5}{S} - 131.5$$

where S is the specific gravity. Water has an °API of 10, A lighter oil has a higher °API (and a higher price). Oils range from 57 to 8 °API.

For gas, the gas gravity is defined as

$$\gamma_g = \frac{\rho_{gas}}{\rho_{air}} = \frac{M}{28.97}$$

where M is the molecular weight.

Viscosity, μ, measures the resistance to flow of a fluid. Viscosity is really a coefficient that relates the applied stress to the resulting shear rate. For example, if a fluid flows in the x-direction in a 2D domain with a speed *u = u(y),* then

$$\mu = {}^{\tau}\Big/\frac{du}{dy}$$

or shear stress (τ) over the velocity gradient. The viscosity of water at 1 atm and 20 °C is 10^{-3} Pa*s, or 1 centipoise (cP). The viscosity of crude oil varies between 0.3 cP and 10^3 cP

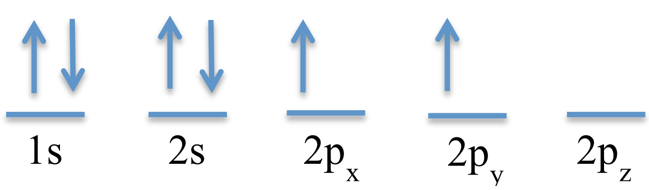
Orbital Hybridization

Orbital hybridization is the concept of mixing atomic orbitals into hybrid orbitals that share electrons suitable for valence bond theory. Orbital hybridization is a useful concept because the lowest energy is obtained if each of the 4 bonds off of a carbon atom is identical.

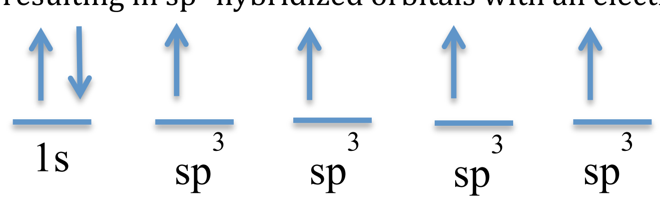
Using classic atomic orbitals, the carbon orbitals can be defined as:

$1s^2 2s^2 2p^2$ or $1s^2 2s^2 2p_x^1 2p_y^1$

Or



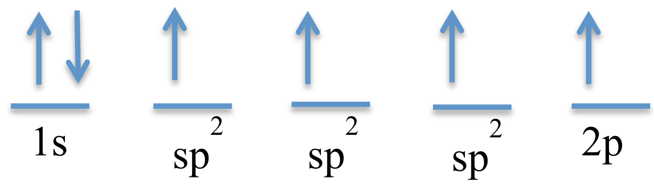
Hybridization will promote one electron from the 2s orbital to the empty 2p orbital, resulting in sp^3 hybridized orbitals with an electron in an excited state.



Each sp^3 orbital is known as a σ bond. In the case of CH_4, 4 σ bonds are formed.

What hybridized bonds are formed in ethane, C_2H_6?

Hybridization of alkene and alkyne orbitals are slightly differ. Since alkene requires a C-C double bond, the orbital hybridization requires the 2s to interact with only two of the three 2p orbitals:



This forms sp^2 orbitals, which form σ bonds, while the 2p orbitals on each carbon interact to form a π bond. Ethene formation then requires 1 π bond and 6 σ bonds.

Alkyne, with a C-C triple bond, forms two π bonds on the 2p orbitals, and two sp hybridized orbitals.

What does the electron spin configuration diagram look like for ethyne (aka acetylene)?