Throughout this book the *mol* will be used in many cases as a mass term in those processes where no chemical changes occur. It is particularly useful for gas calculations. At a given pressure and temperature equal volumes of different gas contain the same number of molecules. At 0°C [32°F] and 101.325 kPa [14.7 psia] a mol of any gas contains about 6×10^{23} molecules and occupies a volume of 22.4 liters.

The mol is thus a useful conversion factor from volume to mass, for the number of mols per unit volume is independent of gas composition.

Valence

Valence is a measure of the ability of atoms to form molecules by filling the electron shells of the atoms involved. The valence number is plus or minus, denoting the number of excess or shortage of electrons needed to fill its outer shell.

The question of atomic bonding is a complex subject involving many factors, as discussed in standard chemistry references. The concept is mentioned only to point out that the number of *bonds* or *linkages* used in the structural formulas that follow in the next section reflect the valence of the atoms in these compounds.

Mixture

A mixture is a combination of elements and compounds which may be separated by physical means. The properties of the mixture are a reflection of the properties of the constituents.

Natural gas and crude oil are mixtures. They are analyzed by separating the mixture into its component parts and identifying each by its properties.

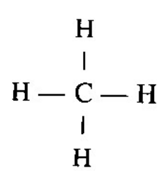
BASIC HYDROCARBON NOMENCLATURE

By definition, a hydrocarbon is any compound composed solely of carbon and hydrogen atoms. These atoms can combine in a number of ways to satisfy valence requirements. For convenience, these are separated into "families" or homologous series, each of which is given a name.

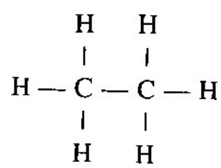
The carbon atoms can link together to form "chains" or "rings." Crude oil and natural gas mixtures consist primarily of "straight chain" hydrocarbon molecules, the bulk of which are paraffins.

Paraffin Series Formula: C_nH_{2n+2}

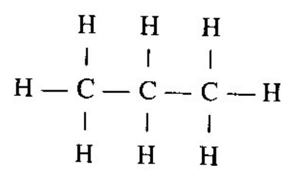
Hydrocarbons in this series are *saturated* compounds – all four carbon bonds are connected either to another carbon atom or a hydrogen atom, with one such atom for each bond.



Methane



Ethane



Propane

Notice that all names end in *-ane*, the ending used for the paraffin series. In each case, the number of hydrogen atoms is two times the number of carbon atoms plus two more for the ends of the chain.

The paraffin hydrocarbons are the most stable of the lot because all valence bonds are fully satisfied as indicated by the single line linkage. Most reactions involve the replacement of hydrogen atoms with other atoms; the carbon linkage remains stable.

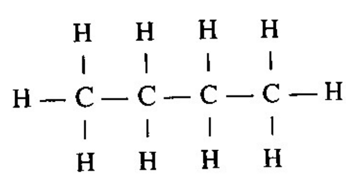
Each successive molecule in the paraffin series is created by adding a carbon and two hydrogens to the previous molecule. The incremental change in relative molecular weight is thus fourteen. Long chains containing scores of carbon atoms in series may be formed. However, the only ones normally identified by name contain ten or less carbons.

Name	Formula	Mol. Wt.	Name	Formula	Mol. Wt.
Methane	CH_4	16	Hexane	C_6H_{14}	86
Ethane	C_2H_6	30	Heptane	C_7H_{16}	100
Propane	C_3H_8	44	Octane	C_8H_{18}	114
Butane	C_4H_{10}	58	Nonane	C_9H_{20}	128
Pentane	C_5H_{12}	72	Decane	$C_{10}H_{22}$	142

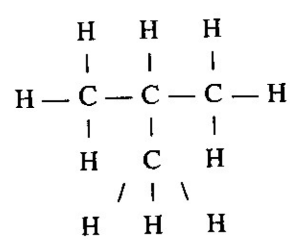
In referring to a given paraffin hydrocarbon, the abbreviation C_3 for propane, C_4 for butane, etc. may be used. Statements like "propanes plus fraction (C_3+)" refer to a mixture composed of propane and larger atoms.

Paraffin Isomers. When the paraffin series molecule contains four or more carbon atoms there are different ways these can be connected without affecting the formula. Compounds which have the same chemical formula but a different atomic structure are called isomers. They possess different physical and chemical properties.

There are only two isomers of butane. In the structural diagram shown for i-butane we could draw the carbon atom below instead of above the carbon chain. But, this would be just a "mirror image" of the molecule as drawn. It is the same molecule with the same properties. The adjective "normal" is used to designate a molecule wherein all of the carbon atoms are in a straight line. An "isomer" has the same formula but a different arrangement of the carbon atoms. In an analysis, these are often abbreviated as "n" and "i" respectively.



Normal butane
(n-butane)



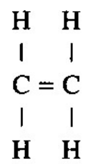
Isobutane
(i-butane)

Olefin or Ethylene Series (Alkenes) Formula: C_nH_{2n}

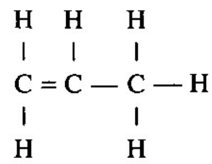
The olefin group of compounds is a simple straight chain series in which all the names end in *-ene*. Ethylene (ethene) C_2H_4 is the simplest molecule in the series.

Hydrocarbons in this series combine easily with other atoms like chlorine and bromine, without the replacement of a hydrogen atom. Since they are so reactive, they are called *unsaturated hydrocarbons*.

Unlike the paraffins, the maximum bonding capacity of the carbon atom is not fully satisfied by hydrogen or carbon atoms. Two adjacent carbon atoms form a "temporary" bond (in the absence of other available atoms) to meet bonding requirements fixed by valence. It is a necessary but unstable alliance. The structural formula for the olefins uses a double line to indicate the double carbon-carbon linkage, the most reactive point in the molecule.

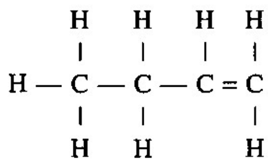
 , $H_2C = CH_2$

Ethylene (Ethene)

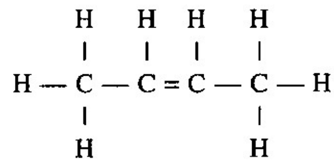
 , $H_2C = CHCH_3$

Propylene (Propene)

With four or more carbon atoms, isomers also may result from the position of the double bond as well as the arrangement of the carbon atoms.

 , $CH_3CH_2CH = CH_2$

1-Butene

 , $CH_3CH = CHCH_3$

2-Butene

These molecules possess many different properties. They may furthermore react at the double bond or be split into two molecules at the double bond to form compounds with different characteristics.

The amount of olefins in natural gas usually is fairly small. Certain crude oils contain them in measurable amounts.

Acetylenic or Alkyne Series Formula: C_nH_{2n-2}

This series is of basic importance only in certain refining and petrochemical applications. Acetylene is the most important member of this series. It has the formula C_2H_2. The structural formula for acetylene is

$$H - C \equiv C - H$$

There is a triple bond between the carbon atoms. This satisfies the valence requirements but the carbon linkage is very weak.

Acetylene is even more reactive than the olefins. Carbon likes the sharing of three valence linkages even less than sharing two. Acetylene not only is unsaturated, it is almost unstable chemically. In the liquid state it is explosive if subjected to a sudden shock.

Diolefins Formula: C_nH_{2n-2}

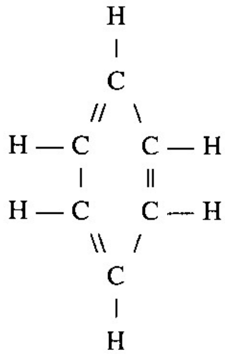
The *diolefins* have the same formula as acetylene. The members of this series contain two double linkages. They normally are named by replacing the *-ane* for paraffins by *-diene.*

Diolefins are primarily of concern in petrochemical plants. Butadiene is possibly the most interesting and useful since it is a primary ingredient in synthetic rubber compounds. It has the formula:

$$CH_2 = CH - CH = CH_2$$

All of these unsaturated compounds are reactive. They may be hydrogenated. Liquid cooking oils (unsaturated) may be hydrogenated to form solid fats.

These compounds also polymerize – the process wherein a very large molecule is built up from the self-addition reaction of small identical molecules (monomers). Ethylene and propylene polymerize to form polyethylene and polypropylene, the basic ingredients in plastic materials. Acetylene polymerizes to form benzene, a cyclic hydrocarbon.



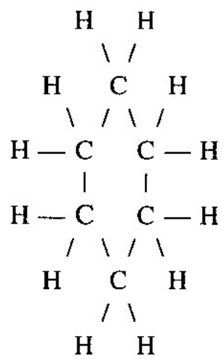
Benzene

Aromatic (Benzene) Series Formula: C_nH_{2n-6}

Aromatic is the word used to describe an unsaturated hydrocarbon molecule where the carbon atoms form a ring, a cyclic compound. *Benzene*, the parent compound of this series, has the structural formula of C_6H_6.

Since the aromatics are *unsaturated*, they react readily. They may be oxidized to form organic acids. They also promote foaming and other operational problems in the production and handling of crude oil and natural gas.

Most petroleum contains only a trace of aromatics. Some contain significant amounts. Any analysis of crude oil and natural gas should include aromatics. Even small amounts can influence physical behavior and affect design.



Cyclohexane

Naphthene Series Formula: C_nH_{2n}

The naphthene series has a ring structure but is saturated. Naphthenes may be found in most crude oils but are seldom shown in routine analyses. Being saturated molecules, they are not very reactive. Cyclohexane is a common member of this series. Its structural formula is C_6H_{12}.

Cyclohexane is similar to benzene except that it is saturated. On chromatographic analysis it occurs between n-hexane and n-heptane. Cyclopentane (C_5H_{10}) also occurs. On chromatographic analysis it occurs between n-pentane and n-hexane.

PARAFFIN HYDROCARBON COMPOUNDS

In the production, gathering, conditioning, and processing of natural gas and its associated liquids, the primary concern is the behavior of the paraffin series hydrocarbons with 10 or less carbon atoms (C_1–C_{10}). This concern includes nitrogen and water and contaminants in the gas, such as sulfur compounds.

Paraffin hydrocarbons are less reactive with other materials than many hydrocarbons, but it must be remembered that they have been in contact with the chemicals present in the reservoir rock for many millions of years. They are also conditioned by use of alcohols, glycols, and amines in which they are soluble and with which they react to some degree.

Radicals

A radical represents a group of atoms that act as a single unit in the formation of many common compounds.

Alkyl Radical. At least the simpler paraffins often react by replacing one hydrogen with some other radical or element. This alkyl radical has the formula:

$$C_nH_{2n+1} : \underset{\text{methyl}}{(CH_3)},\ \underset{\text{ethyl}}{(C_2H_5)},\ \underset{\text{propyl}}{(C_3H_7)}$$

The parenthesis indicates the radical group. The alkyl radical normally has a valence of +1.

In many cases the alkyl radical is indicated by the symbol "R." The formula for methanol is CH_3OH; for ethanol it is C_2H_5OH. Both may be written as ROH. When "R" is used, one cannot identify the specific alkyl radical. It is used only to show general reaction characteristics.

Hydroxyl Radical, (OH). This combination occurs in many common compounds. It combines with hydrogen to form water – H(OH) or H_2O; with metallic salts like sodium, calcium and magnesium to form hydroxides (bases, caustics); and with alkyl radicals to form alcohols, such as methanol, ethanol, etc.

(SO_4), (CO_3). If radicals like these combine with hydrogen, an acid is formed. When combined with metallic salts like sodium, calcium, and magnesium, a salt is formed (which occurs commonly in water systems). The scale formed in water systems is caused by precipitation of salts like these. The common names for some common radicals of this type are:

SO_4 – sulfate	CO_3 – carbonate
SO_3 – sulfite	HCO_3 – bicarbonate

Each of the radicals has a valence found from the valence of its elements. The hydroxyl radical (OH) has a valence of minus one and is sometimes written as $(OH)^{-1}$. It therefore combines in proportions fixed by this valence: H(OH), NaOH, $Mg(OH)_2$ – so that the sum of plus and minus valences equals zero.

Alcohols

The common alcohols are formed from the addition of a single hydroxyl radical to an alkyl radical. The name of the alcohol ends in "ol," or the name of the alkyl radical is followed by the word "alcohol."

$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & OH \\ & & | & & \\ & & H & & \end{array} \quad , \quad CH_3OH$$

Methan<u>ol</u> or methyl alcohol

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & OH \\ & & | & & | & & \\ & & H & & H & & \end{array} \quad , \quad C_2H_5OH$$

Ethan<u>ol</u> or ethyl alcohol

Both C_2H_5OH and CH_3OH could be written as ROH in denoting the general reaction of an alcohol.

Mercaptans

Compounds with the general formula RSH are known as mercaptans. They may be regarded as sulfur alcohols since the formula is the same if you replace the oxygen atom in the (OH) radical by a sulfur atom.

Formulas for typical mercaptans are:

CH_3SH – methyl mercaptan	C_2H_5SH – ethyl mercaptan

Other Carbon-Sulfur Compounds

There are several other carbon-sulfur compounds present in sour petroleum fluids. Some are:

Carbonyl sulfide – COS	Carbon disulfide – CS_2

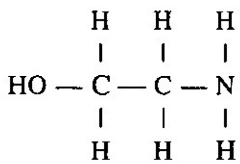
Thiophene – an unsaturated compound having the formula: HC = CH – S – HC = CH

Sulfur is a very reactive element that combines chemically with many other elements and compounds. Its compounds react with carbon steel to form sulfides and oxides of iron. Many compounds polymerize and form the "sludge" so common in sour petroleum systems. This sludge is often very corrosive and should be removed by filtration.

Organic Nitrogen Compounds - Amines

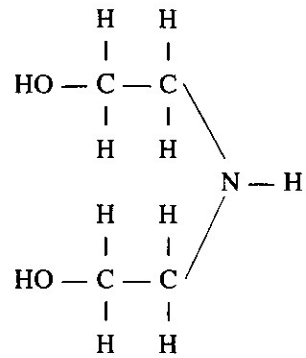
There are a number of common organic compounds formed by the reaction of organic materials with ammonia (NH_3). In this basic reaction one or more hydrogen atoms are replaced by an organic radical. The word "amine" is used commonly to denote this type of compound. There are a large number of amines used in the chemical industry.

The alkanolamines are commonly used for treating sour gases and liquids, particularly monoethanolamine and diethanolamine. As the names indicate, the alkanolamines may be considered a combination of an alcohol and ammonia.



, $HOCH_2CH_2NH_2$

Monoethanolamine (MEA)



, $(HOCH_2CH_2)_2NH$

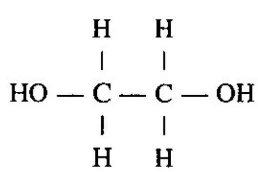
Diethanolamine (DEA)

Notice that the only difference in the above compounds is how many hydrogen atoms of ammonia are replaced by the radical (C_2H_4OH), ethanol minus one hydrogen atom.

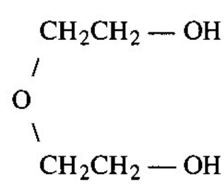
Glycols

The glycols are a family of chemicals, sometimes called diols. They may be regarded as complex alcohols since they contain alkyl and hydroxyl radicals. The glycols used for dehydration are based on the ethyl radical.

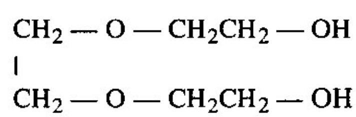
As with most compounds containing hydroxyl groups, the glycols react readily with other compounds and elements. In DEG and TEG the oxygen atom also is very reactive.



Ethylene Glycol (EG)



Diethylene Glycol (DEG)



Triethylene Glycol (TEG)

ACIDS, BASES AND SALTS

We are always talking about acids and bases in the handling of petroleum-water mixtures, processing, and other such functions of the petroleum industry.

Except for water and hydroxides (compounds containing the OH radical), all inorganic compounds of hydrogen are acids. They consist of hydrogen combined with an acid radical (anion).

Acid Radical (anion)	Symbol	Acid	Formula
Chloride	Cl^{-1}	Hydrochloric	HCl
Carbonate	CO_3^{-2}	Carbonic	H_2CO_3
Sulfate	SO_4^{-2}	Sulfuric	H_2SO_4
Nitrate	NO_3^{-1}	Nitric	HNO_3
Phosphate	PO_4^{-3}	Phosphoric	H_3PO_4

Notice that hydrogen (valence of +1) combines with the acid radical in a proportion such that the net valence of the compound formed is zero. This is the rule to be followed in all compound formation. Since the valence of the sulfate radical is -2, it takes two hydrogens.

The combination of a metal cation such as sodium with the hydroxyl anion (OH) produces a base. Sodium hydroxide (NaOH) is commonly called caustic.

pH. The acidity or alkalinity of a material is measured on a scale similar to that of a thermometer. This pH scale is the logarithm of the reciprocal of the hydrogen ion concentration. It runs between 0 and 14. A pH of 7 is neutral. Acids have a pH less than 7; bases (alkaline solutions) have a pH greater than 7.

Since pH is a logarithmic function, a solution possessing a pH of 5.0 is 100 times more acidic than one with a pH of 7.0.

ANALYSIS OF MIXTURES

A routine analysis of a hydrocarbon mixture is shown in Table 1.1. Notice that only paraffin hydrocarbons are shown. This is not entirely correct, although the paraffins may be the predominant series present. Notice also that all molecules heptane and larger are lumped together as a heptanes plus fraction.

The hydrocarbon portion of an analysis like this usually is obtained from a chromatograph. The printed output from this technique is a series of "peaks" rising from a base line. The area under the peak for any component is proportional to the amount present. The instrument is calibrated using standard samples of known analysis so that peak area can be converted to the amount present.

Figure 1.1 is an example of a chromatogram (chart) from a chromatographic analysis. When the ordinary peak height is so low it is difficult to measure, it is attenuated (multiplied). The attenuation factor is used to convert the peak height shown to analysis.

The chromatograph used to obtain Figure 1.1 was capable of showing hydrocarbons other than paraffins. Notice that all of these occur in the hexane-heptane range of molecules. Many chromatographs, particularly those used for routine gas analyses, are unable to detect all of these components. The nonparaffins combine with a single peak which is reported (erroneously) as being a paraffin material.

Many system operating problems are the direct or indirect result of inadequate analysis. This may result from failure to:

TABLE 1.1
Fluid Analysis

Component	Mol %
Nitrogen	0.34
Carbon Dioxide	0.91
Sulfur (as H_2S)	0.50
Methane (C_1)	21.36
Ethane (C_2)	36.78
Propane (C_3)	10.21
i-Butane (iC_4)	6.38
n-Butane (nC_4)	9.84
i-Pentane (iC_5)	2.63
n-Pentane (nC_5)	4.01
Hexanes (C_6)	3.90
Heptanes Plus (C_7+)	3.14
Total	100.00
Mol wt. C_7+ = 118	
Rel. Density C_7+ = 0.71	

1. Analyze for CO_2 and sulfur compounds
2. Identify the presence of aromatics and other nonparaffin hydrocarbons
3. Adequately characterize the heaviest fraction

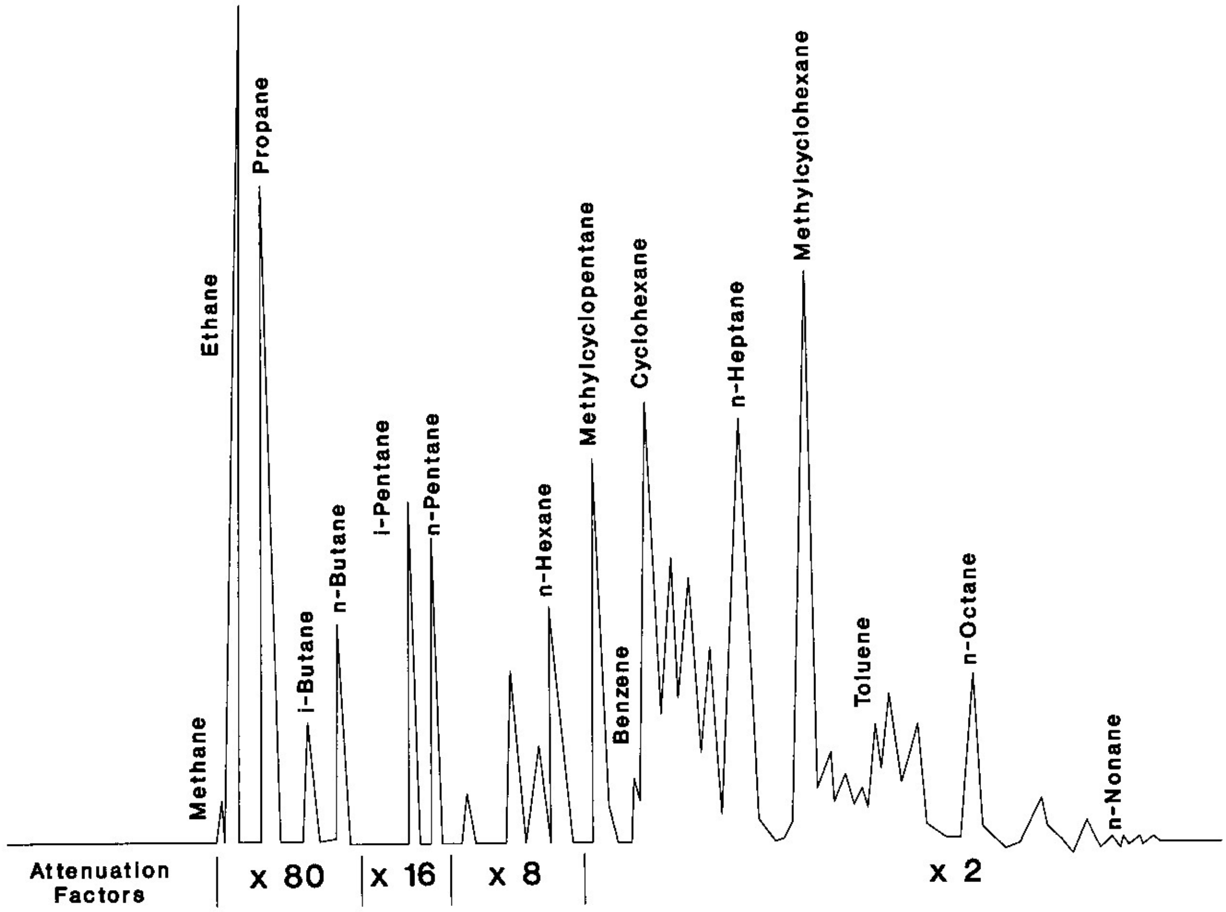


Figure 1.1 Chromatogram of Condensed Liquid

All of these will be discussed in more detail in subsequent chapters. There are, however, some general guidelines.

1. Always analyze for CO_2 and H_2S. Sulfur contents as low as 3-10 parts per million may prove troublesome. If the sulfur content (reported as H_2S) is higher than this, a special analysis for carbonyl sulfide (COS), carbon disulfide (CS_2) and mercaptans is intelligent.
2. Some crude oil may contain up to 10-12% aromatics. Failure to be aware of this affects mechanical design problems and reduces validity of equilibrium calculations.
3. If the gas is from a separator, characterizing the heaviest fraction through C_{7+} may be adequate; if it is wellbore gas it may not be adequate. Crude oil may need to be characterized through C_{20+} to achieve reliable equilibrium predictions.

The prompt and proper analysis of representative samples is a critical factor. Any calculation is an exercise in futility unless the analyses used are reliable. Inadequate sampling and analysis is a major cause of problem systems.

A sampling program should be planned carefully. Appendix A, at the end of this volume, summarizes good sampling procedures.