1. OIL CHEMISTRY

1.1. Introduction

Petroleum is not a uniform material. In fact, its composition can vary not only with the location and age of the oil field but also with the depth of the individual well. Indeed, two adjacent wells may produce petroleum with markedly different characteristics.

On a molecular basis, petroleum is a complex mixture of hydrocarbons plus organic compounds of sulfur, oxygen, and nitrogen, as well as compounds containing metallic constituents, particularly vanadium nickel, iron, and copper. The hydrocarbon content may be as high as 97%, for example in the lighter paraffinic petroleum, or as low as 50% or less as illustrated by the heavier asphaltic crude oils. Nevertheless, crude oils with as little as 50% hydrocarbon components are still assumed to retain most of the essential characteristics of the hydrocarbons since the nonhydrocarbon portion of the crude may actually consist of molecules containing one or perhaps two atoms of elements other than carbon and hydrogen.[1]

For a variety of reasons, it is often necessary to define petroleum in terms of their physical composition. Furthermore, the physical composition of the heavier feedstocks varies markedly with the method of isolation or separation, thereby leading to further complications in the choice of suitable processing schemes for these feedstocks. Thus if a petroleum or heavy oil can be defined (on a relative basis) in terms of three or four general fractions-asphaltenes, resins, and oils (saturates plus aromatics)-heavier oils can also be defined in terms of these fractions but usually with substantial variations in the relative proportions of these fractions (Fig. 1.1).
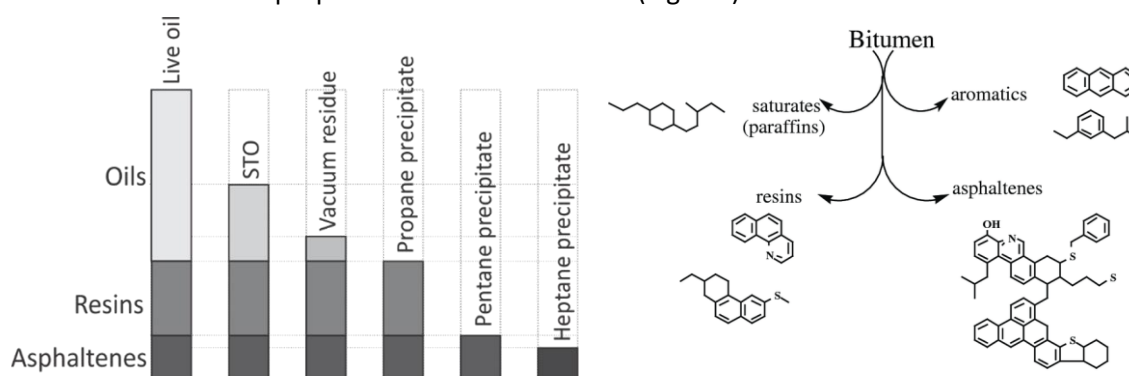

Fig. 1.1. Simplified relationship between a parent petroleum, the atmospheric and vacuum residua, and the various solvent fractions; a heavy oil may be approximated to the composition of atmospheric or vacuum residue.

1.2. Elemental composition

From the available data, it appears that the proportions of the elements in petroleum vary only slightly over fairly narrow limits (Tbl. 1.1, 1.2, and 1.3).

This is observed even though the wide variation in physical properties from the lighter and more mobile crude oils at one extreme, to the heavier asphaltic crude oils at the other extreme. [2]

Thus, it is not possible to classify petroleum on the basis of carbon content as coal is classified; carbon contents of coal can vary from as low as 75% in the lignites to 95% in the anthracites. Of course, other subdivisions are possible within the various carbon ranges of the coals, but petroleum, which seem to have so little in common except being fluids of subterranean origin, are restricted to a much narrower range of elemental composition.

Tbl. 1.1 Ultimate Analysis of Crude Oils					
Origin	Composition (wt%)				
	Carbon, C	Hydrogen, H	Nitrogen. N	Oxygen, O	Sulfur, S
Asia					
Borneo	86.5	12.4			
India	83.8	12.7			
Java	87.1	12.0			
	87.1	12.7			
UAR	82.8	10.8	0.8	0.8	4.8
	83.5	11.1	0.6	1.5	3.3
	83.9	11.8	0.6	1.3	2.4
	84.5	11.8	0.5	0.8	2.4
	84.6	11.8	0.5	0.5	2.6
	85.1	12.4	0.4	1.0	2.1
Europe					
France	86.5	12.5			
	86.1	13.8			
Poland	86.5	13.0	0.2		0.3
Rumania	87.2	11.3	1.1		0.4
	86.6	12.1	0.7		0.6
	86.4	0.2	3.1		0.3
	85.7	12.9	1.2		0.2
	85.8	13.1	0.6		0.5
	86.3	12.5	1.0		0.2
	85.1	13.7	1.1		0.1
	86.6	13.0	0.3		0.1
	86.0	13.3	0.6		0.1
USSR	83.6	16.1	0.1	0.2	
	85.5	13.4	0.1	0.6	0.4
	84.4	14.5	0.2	0.7	0.2
	85.1	13 .0	0.2	0.1	1.6
	86.6	12.7	0.1	0.4	0.2
	84.3	11.9	0.2	0.1	3.5
	86.7	12.5	0.1	0.3	0.4
	85.3	11.6			
	87.1	12.3			
	86.1	12.8	0.9		0.2
	86.3	13.6			
	86.3	12.9	0.6		0.2
	86.9	13.1			
	86.5	12.0	1.5		
North America					
Canada	86.9	12.9			
	86.9	12.9			
	83.4	10.4	0.5	1.2	4.5
	83.2	10.4	0.4	0.9	5.1
	83.1	10.6	0.4	1.1	4.8

Location					
	83.1	10.3	0.3	1.4	4.9
	82.8	11.8	0.3	1.7	3.4
Mexico	83 .0	11.0	1.7		4.3
	83 .8	11.3	1.1		3.8
United States	86.6	11.8			
	83.5	13.3			
	85.5	14.2			
	83.6	12.9	3.6		
	85.6	12.4			0.4
	85 .0	12.0			0.8
	86.4	11.7	1.1		0.6
	85.7	11.0	2.6		0.7
	87.9	12.1			
South America					
Argentina	87.0	10.8	0.9		1.3
	86.5	12.0	1.2		0.3
	86.7	2.1	1.0		0.2
Colombia	85.6	11.9	0.5		
Venezuela	82.5	10.4	0.6	0.8	5.7

The elemental analysis of oil sands bitumen has also been widely reported [3, 4, 5], but the data suffer from the disadvantage that identification of the source is too general (i.e., Athabasca bitumen) and is often not site specific. In addition, the analysis is quoted for separated bitumen, which may have been obtained by any one of several procedures and may therefore not be representative of the total bitumen on the sand. However, recent efforts have focused on a program to produce sound, reproducible data from samples for which the origin is carefully identified.[6] It is to be hoped that this program continues as it will provide a valuable data base for tar sand and bitumen characterization.

Tbl. 1.2 Elemental Compositions of Tar Sand Bitumens

Location	Elements, wt%					Properties			Metals, ppm	
	C	H	N	O	S	H/C	MW	°API	Ni	V
Athabasca (Wabasca McMurry)	83.1	10.6	0.4	1.1	4.8	1.531	590	7.5	100	250
Asphalt Ridge	85.3	11.7	1.02	1.1	0.59	1.646	668	14.4	120	25
P.R.Springs	84.4	11.1	1.00	2.2	0.75	1.578	820	10.3	98	25
Tar Sand Triangle	84	10.0	0.46	1.1	4.4	1.443	578	11.1	53	108
San Miguel			0.4		9.5				24	85
Arroyo Grande	81.9	10.2	1.2	3.2	3.5	1.495	820			
Sunnyside	86.3	11.7	0.9	0.6	0.5	1.627	680			
Santa Rosa	84.6	10.2	0.5	1.7	2.4	1.447	600			
Bemolanga	87.1	11.2	0.7	1.2	0.5	1.543				

Tbl. 1.3. Elemental Analysis of Various Bitumen Samples

Location	Elements, wt%					Metals, ppm			
	C	H	N	O [a]	S	V 210	Ni	Fe	Cu
Abasand	83.1	10.3	0.3	1.3	5.0				
	83.3	10.4	0.4	0.8	5.1				
Mildred-Ruth Lakes	83.0	10.2	0.5	2.5	3.8				
	83.4	10.4	0.5	4.5	1.2				
	83.2	10.4	0.4	0.9	4.1				
	83.1	10.6	0.4	1.1	4.8	250	100		5
Horse River	83.3	10.4	0.5	1.3	4.5	290	82	75	2
	83.3	10.4	0.4	0.8	5.1				
Bitumount	83.3	10.5	0.4	0.9	4.9				
	83.3	10.4	0.4	1.2	4.7				
Ells River	83.3	10.4	0.4	1.3	4.6				
	83.3	10.4	0.4	1.3	4.6				
Clear Water River	83.6	10.3	0.4	0.2	5.5				
Ft McMrry (75mi.s120.i.w)	83.4	10.4	0.6	0.9	4.7				
	82.9	10.3	0.5	0.9	5.4				
GCOS lease	83.9	10.5	0.4	1.0	4.2				

[a] By difference.

Of the data that are available the elemental composition of oil sand bitumen is generally constant and, like the data for other petroleums (Tbl. 1.2), falls into a narrow range (Tbl. 1.4)

Tbl. 1.4 Elemental composition of oil sand bitumen

Element	Weight%
Carbon	83.4 ± 0.5%
Hydrogen	10.4 ± 0 .2%
Nitrogen	0.4 ± 0.2%
Oxygen	1.0 ± 0.2%
Sulfur	5.0 ± 0.5%

The major exception to these narrow limits is the oxygen content of bitumen, which can vary from as little as 0.2% to as high as 4.5%. This is not surprising, since when oxygen is estimated by difference the analysis is subject to the accumulation of all the errors in the other elemental data. On the other hand, bitumen is susceptible to aerial oxygen and the oxygen content is very dependent upon the sample history. In addition, the ultimate composition of the Alberta bitumen does not appear to be influenced by the proportion of bitumen in the oil sand or by the particle size of the oil sand minerals.

Bitumens from U.S. tar sands have an ultimate composition like that of the Athabasca or Cold Lake bitumen (Tbl. 1.3). When the many localized or regional variations in maturation conditions are assessed it is perhaps surprising that the ultimate compositions are so similar.

The hydrogen-carbon (H/C) ratio of a bitumen affects its viscosity (and hence the required supplementary heat energy for a thermal extraction process). It also affects the bitumen's distillation

curve or thermodynamic characteristics, its gravity, and its pour point. H/C ratios as low as 1.3 have been observed for U.S. tar sand bitumen. However, a ratio of 1.5 is more typical. The higher H/C ratio of a bitumen, the higher the value as refinery feedstock due to relatively lesser upgrading and refining requirements. Elements related to the hydrogen-carbon ratio are distillation curve, bitumen gravity, pour point, and bitumen viscosity.

Even though sulfur is a valuable commodity, its inclusion in bitumen as organic or elemental sulfur or in produced gas as compounds of oxygen and hydrogen is an expensive nuisance. It must be removed from the bitumen at some point in the upgrading and refining process. Sulfur contents of U.S. tar sand bitumen can exceed 10% by weight. Elements related to sulfur content are nitrogen and hydrogen contents, hydrogen-carbon ratio, distillation curve, and viscosity.

Nitrogen contents of tar sand bitumen as high as 1.3 Wt% have been observed. Nitrogen complicates the refining process by poisoning the catalysts employed. Elements related to nitrogen content are sulfur and hydrogen content, H/C ratio, bitumen viscosity, and distillation curve.

1.3. Chemical composition of Crude Oils

The chemical composition of many feedstocks is, despite the large volume of work performed in this area, largely speculative. Indeed, the "simpler" petroleum are extremely complex mixtures of organic compounds. In fact, the composition of petroleum can vary with the location and age of the field in addition to any variations that occur with the depth of the individual well. Two adjacent wells are more than likely to produce petroleum with very different characteristics.

On a molecular basis, petroleum contains hydrocarbons as well as the organic compounds of sulfur, nitrogen, and oxygen; metallic constituents may also be present, but only to a minor extent. The hydrocarbon content of petroleum may be as high as 97% (for example in the lighter paraffinic crude oils), but it is nevertheless the nonhydrocarbon (i.e., sulfur, oxygen, and nitrogen) constituents that play a large part in determining the nature and, hence, the processability of the crude oil [7, 8, 9, 10, 11, 12].

Nevertheless, the high proportion of carbon and hydrogen in petroleum indicates that hydrocarbons are the major constituents and may actually account for more than 75% of the constituents of many petroleums. The inclusion of organic compounds of sulfur, nitrogen, and oxygen serves only to present crude oils as even more complex mixtures, and the appearance of appreciable amounts of these nonhydrocarbon compounds causes some concern in the refining of crude oils. Even though the concentration of nonhydrocarbon constituents (i.e., those organic compounds containing one or more sulfur, oxygen, or nitrogen atoms) in certain fractions may be quite small, they tend to concentrate in the higher boiling fractions of petroleum. Indeed , their influence on the processability of the petroleum is important irrespective of their molecular size and the fraction in which they occur.

Thus, the presence of traces of nonhydrocarbon compounds can impart objectionable characteristics to finished products, leading to discoloration and/or lack of stability during storage. On the other hand , catalyst poisoning and corrosion are the most noticeable effects during refining sequences when these compounds are present. It is therefore not surprising that considerable attention must be given to the nonhydrocarbon constituents of petroleum as the trend in the refining industry, of late, has been to process the heavier crude oil as well as residua that contain substantial proportions of these nonhydrocarbon materials.

In approaches to the chemical constitution of petroleum the most direct and simple method is by the use of the atomic C/H (or H/C) ratio as a chemical criterion (Tbl. 1.5). This ratio classifies various hydrocarbon groups and furnishes basic information:

Tbl. 1.5. C/H (and H/C) ratios for different crude oil components.

Type	C/H	H/C
Simple aromatics (e.g. benzene)	1.0	1.0
Condensed aromatics (e.g. naphthalene)	1.25	0.8
Polycondensed aromatics	> 1.40	< 0.75
General aliphatic hydrocarbons	~0.5	~2.0
Paraffins	~0.5	~2.0

However, it is essential that, for the C/H (H/C) ratios to have any meaning, the fractions must be separated by exact and precise methods that give, say, a very narrow boiling range or whatever other property is used to separate the material. Unless these fractions are narrow-range materials, C/H (H/C) determinations, or for that matter any other determinations, have little if any meaning.

1.3.1 Hydrocarbons in Crude oils

The study of the individual hydrocarbon constituents in petroleum began in the 1850s when alkyl benzenes were reported in a petroleum from Burma. Later, methyl-cyclopentane was isolated from a Caucasian petroleum, followed by the isolation of paraffin hydrocarbons from various petroleum fractions. Distillation techniques were also employed in some of this early work, and the separation of cyclohexane by crystallization of a distillate fraction into which it had been concentrated is an example of what could be accomplished at that early date. Nevertheless, the isolation of pure compounds from petroleum is an exceedingly difficult task, and the overwhelming complexity of petroleum fractions, especially of the higher fractions, in addition to the presence of compounds of sulfur, oxygen, and nitrogen, is the main cause for the difficulties encountered. It is therefore not surprising that until 1930 investigations on this subject gave mainly qualitative information and also contributed much to the knowledge concerning high-molecular weight hydrocarbons of the type present in the higher boiling fractions , such as lubricating stocks.

It is rather difficult on the basis of the data obtained from synthesized hydrocarbons to determine the identity or even the similarity of the synthetic hydrocarbons to those that constitute many of the higher boiling fractions of petroleum. Nevertheless, it has been well established that the hydrocarbon components of petroleum are composed of paraffinic, naphthenic, and aromatic groups. Olefinic groups are not usually found in crude oils, and acetylenic hydrocarbons are very rare indeed. It is therefore convenient to divide the hydrocarbon components of petroleum into the following three classes, Fig. 1.2.

The amount of paraffins in crude oils varies with the type of oil, but within any one crude oil, the proportion of paraffinic hydrocarbons usually decreases with increasing molecular weight (Fig. 1.3).

In the gasoline range, for instance, paraffin contents as high as 80% have been noted, whereas in the lubricating oil range a 30% paraffin content is exceptionally high. In fact, many oils yield lubricating fractions that are totally devoid of paraffins.
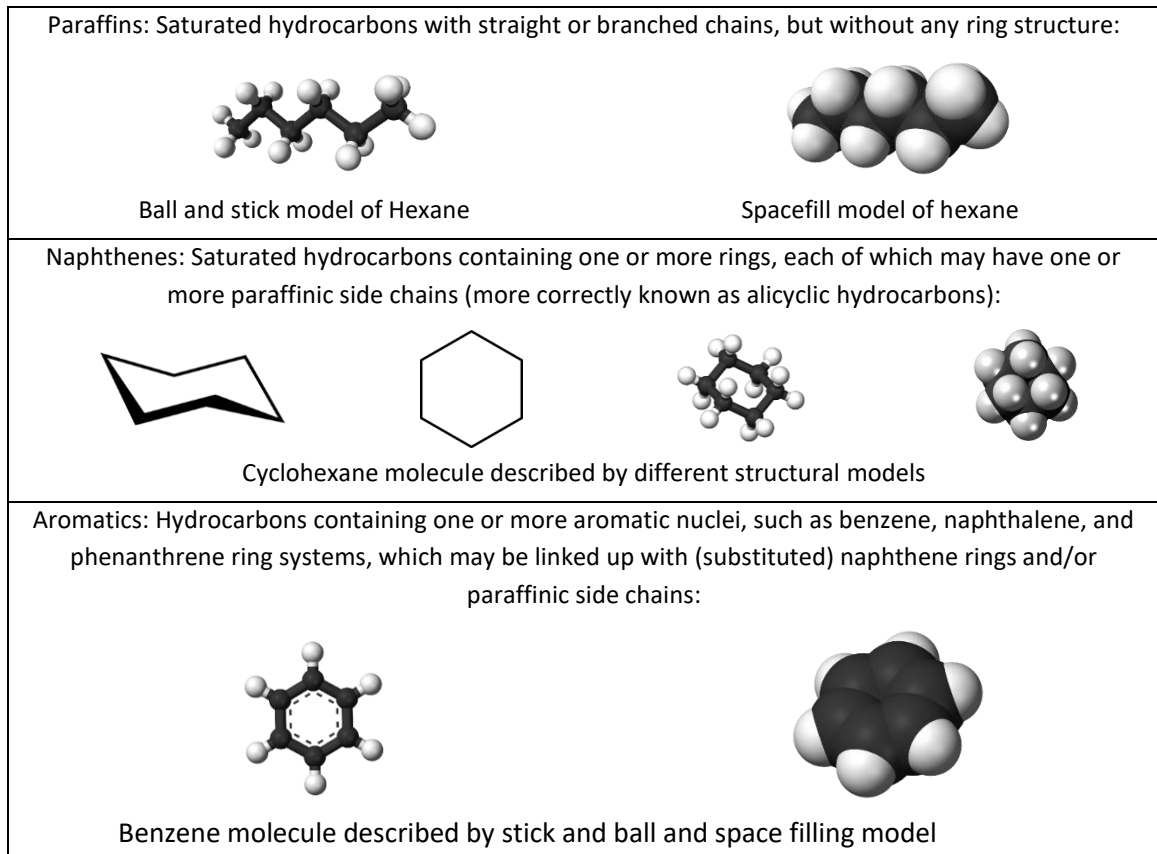
Paraffins: Saturated hydrocarbons with straight or branched chains, but without any ring structure:

Ball and stick model of Hexane | Spacefill model of hexane

Naphthenes: Saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (more correctly known as alicyclic hydrocarbons):

Cyclohexane molecule described by different structural models

Aromatics: Hydrocarbons containing one or more aromatic nuclei, such as benzene, naphthalene, and phenanthrene ring systems, which may be linked up with (substituted) naphthene rings and/or paraffinic side chains:

Benzene molecule described by stick and ball and space filling model

Fig. 1.2. Hydrocarbon (HC) components of petroleum
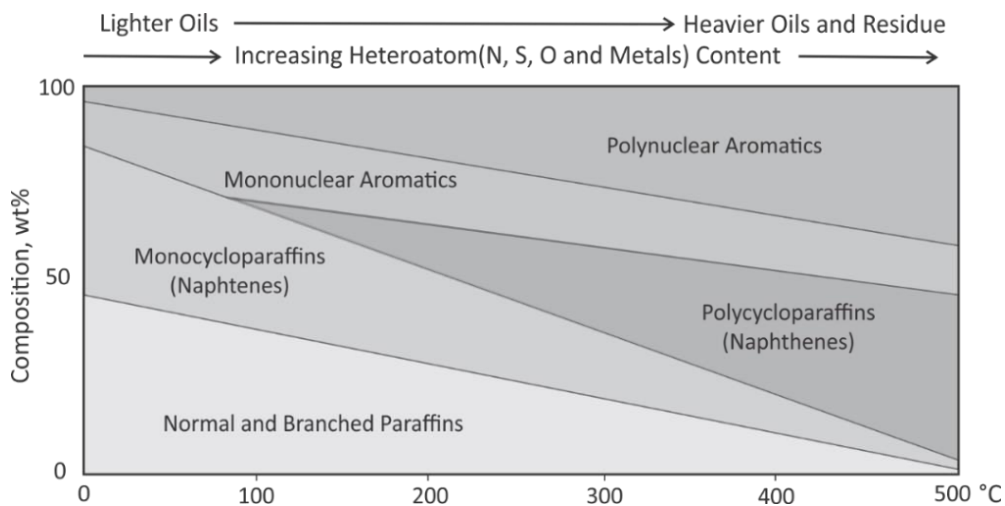
Fig. 1.3. The distribution of the various compound types throughout the boiling range of petroleum.

The relationship between the various hydrocarbon constituents of crude oils is one of hydrogen addition or hydrogen loss (Fig. 1.4), and there is no reason to deny the occurrence of these interconversion schemes during the formation, maturation, and in situ alteration of petroleum. Indeed, a scheme of this type lends even more credence to the complexity of petroleum within the hydrocarbon series alone.

Tbl. 1.6. Distribution of Hydrocarbon types in Ponca Petroleum

Type of compound	Number of compounds in the given boiling range			
	Below 25 °C	25-180°C	Above 180 °C	Total
Normal paraffin	4	6	2	12
Isoparaffin	1	29		30
Cyclopentane		13		13
Cyclohexane		8		8
Benzene		15	5	20
Naphthalene			3	3
Tetrahydronaphthalene			3	3
Benzene-cyclopentane			1	1
Bicycloparaffin		1		1
Total	5	72	14	91
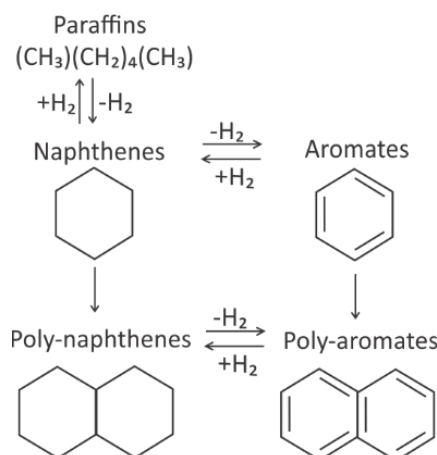
Fig. 1.4 Interrelationship of the various hydrocarbon compounds.

The abundance of the different members of the same homologous series varies considerably in absolute and relative values. However, in any particular crude oil or crude oil fraction, there may be a small number of constituents forming the greater part of the fraction, and these have been referred to as the " predominant constituents" [13, 14]. This generality may also apply to other constituents and is very dependent upon the nature of the source material as well as the relative amounts of the individual source materials prevailing during maturation conditions.

1.3.1.1. Paraffins

To understand the nomenclature, composition, properties, and uses of petroleum, a basic knowledge of organic chemistry is necessary. Organic chemistry deals with the behavior and composition of compounds of carbon, the simplest of which contain only carbon and hydrogen (hydrocarbons). The different types that are of some importance in the petroleum industry are briefly described here.

Carbon has a covalence of 4, and the smallest hydrocarbon molecule, methane, may be represented by the formula CH_4, Fig. 1.5.
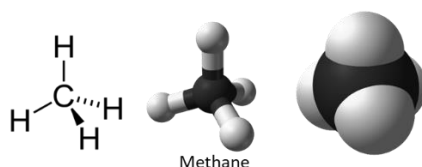
Fig. 1.5. Molecular structures of Methane

This is a structural formula and indicates that the hydrogen atoms are arranged symmetrically around the carbon, but it does not show that the hydrogens are at the corners of a tetrahedron. Nevertheless, despite dimensional limitations, such formulae are very useful in depicting molecular structure. When molecules contain two or more carbon atoms, the carbons form the skeleton. Saturated hydrocarbons, that is, those compounds in which each valency of the carbon is occupied by another atom, are commonly called alkanes or paraffins. The molecular formula for any alkane is C_nH_{2n+2}, where n is the number of carbon atoms per hydrocarbon molecule. The names of all but the first four compounds are obtained by adding ane to the Greek prefix indicating the number of carbon atoms. Heptadecane (mp 22°C, 72°F), the 17-carbon atom member, is the first alkane that is solid at room temperature; paraffin wax is a mixture of hydrocarbons containing from 18 to 35 carbon atoms per molecule.

The alkanes, or saturated hydrocarbons, are more chemically inert than the other hydrocarbons, but they do form derivatives in which hydrogen may be replaced by other atoms or groups. If only one hydrogen has been replaced, the resulting radical is named by changing the -ane of the hydrocarbon to the suffix -yl: for example, CH_3-methyl, C_2H_5- ethyl, C_4H_9-butyl, and C_8H_{17} octyl.

There is only one structure for methane, ethane, or propane, but there are two different butanes. One of these is the normal or straight-chain compound, and the other has a branched structure; the common name for this compound is isobutene. Molecules having the same composition but differing in structure are called isomers. The structure of the molecule determines many of the properties of the substance, such as the boiling point; for example, considering the pentanes, normal pentane boils at 36.4°C (98°F), isopentane at 30.0°C (86°F), and a third isomer, neopentane, boils at 9.0°C (48°F), (Fig. 1.6)

n-butane   **i-butane (isobutane)**

n-pentane   **i-pentane**   **neopentane**
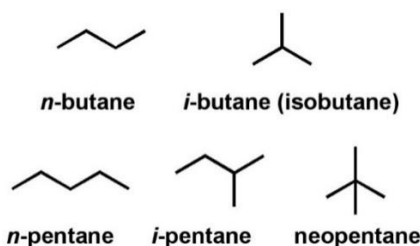
Fig.1.6. isomer structures of C4 (butane) and C5 (pentane)

There are 5 hexane (C_6H_{14}) isomers, 9 heptane (C_7H_{16}) isomers, 18 octane (C_8H_{18}) isomers, and for larger molecules the number of possible isomers increases phenomenally, Tbl. 1.7.

Consequently, it would be impractical to invent a name for every isomer and certainly impossible to remember them. Fortunately, by using a system adopted by the International Union of Pure and Applied Chemistry (IUPAC), substances represented by the most complex formula can be named correctly. The IUPAC system treats any branched molecule as a derivative of the hydrocarbon represented by the longest carbon chain in that compound.

Thus, normal pentane has no branches and its name is the same by the IUPAC method. However, isopentane has four carbons in its longest segment, and since this four carbon chain has a methyl group attached to the second carbon atom, the official name is 2-methylbutane. Neopentane is more

properly named 2 ,2-dimethylpropane since the longest chain consists of three carbon atoms with two methyl groups attached to the central carbon atom.

Tbl. 1.7. Number of possible isomers with increasing carbon atoms for HC compounds.

Carbon atoms	Isomers
6	5
7	9
8	18
9	35
12	355
15	4 347
18	60 523

The hydrocarbon incorrectly called "isooctane" has a carbon skeleton represented by the formula and this particular hydrocarbon is used as a standard in grading gasolines. It has eight carbons and is one of the isomers of octane, but the longest chain in the molecule contains five carbon atoms, so according to the IUPAC system it is a derivative of pentane, which carries three methyl groups. The carbon atoms are numbered to give the lowest numbers to the most methyl groups, and hence the proper name of this compound is 2,2,4-trimethylpentane, Fig. 1.7.
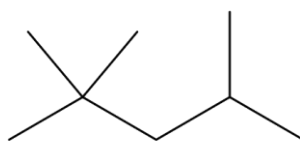
Fig. 1.7. Iso-octane (2,2,4-Trimethylpentane) structure

Normal paraffin hydrocarbons occur in varying proportions in most crude oils; in fact, paraffinic petroleums may contain 20-50% of normal paraffins in the gas oil fraction. A Pennsylvania gas oil (boiling range 150-350°C, 300-660°F) contained every normal paraffin possible that could be present in this fraction. Furthermore, all the normal paraffins up to n-dodecane (12 carbon atoms) have been isolated from Ponca crude oil (Tbl. 1.8), and the 55-180°C (l30-355°F) fraction contains about one-third normal paraffins. However, naphthenic or asphaltic crudes sometimes contain only very small amounts of normal paraffins, as illustrated by the isolation of less than I% of paraffins from Borneo crude oil.

Considerable quantities of isoparaffins have been noted to be present in the gasoline fraction of a variety of petroleums. The 2- and 3-methyl derivatives are the most abundant, and the 4-methyl derivative is present in small amounts, if at all, and it is generally accepted that the slightly branched paraffins predominate over the highly branched materials. It seems that the isoparaffins occur throughout the boiling range of petroleum fractions, but their proportion tends to decrease with increasing boiling point; it appears that if the isoparaffins are present in lubricating oils their amount is too small to have any significant influence on the physical properties of the lubricating oils.

Tbl. 1.8 Paraffins Isolated from Ponca and Santa Barbara Crude Oils

Compound	vol/vol%	
	Ponca	Santa Barbara
Hexanes		
n-Hexane	1.8	0.723
2-Methylpentane	0.4	0.347
3-Methylpentane	0.3	0.418
2,2-Dimethylbutane	0.04	0.043
2,3-Dimethylbutane	0.08	0.140
Heptanes		
n-Heptane	2.3	0.846
3-Methylhexane	0.5	0.188
3-Ethylpentane	0.05	
2-Methylhexane	0.7	
2,3-Dimethylpenlane	0.1	0.601
2,4-Dimethylpentane		0.049
Octanes		
n-Octane	1.9	0.923
2-Methylheptane		
2,2-Dimethylhexane	0.01	0.118
2,3-Dimethylhexane	0.06	0.163
2,4-Dimethylhexane	0.06	
2,5-Dimethylhexane	0.06	0.095
3 ,3-Dimethylhexane	0.03	
2-Methyl-3-ethylpentane	0.04	
2,2,3-Trimethylpentane	0.004	
2,3,3-Trimethylpentane	0.006	
2 ,3,4-Trimethylpentane	0.005	
Nonanes		
n-Nonane	1.8	0.58
2-Methyloctane	0.4	
3-Methyloctane	0.1	0.42
4-Methyloctane	0.1	
2,3-Dimethylheptane	0.05	
2,6-Dimethylheptane	0.05	0.25
Higher paraffins		
n-Decane	1.8	
n-Undecane	1.7	
n-Dodecane	1.7	

1.3.1.2. Cycloparaffins

There are also a series of saturated hydrocarbons with the general formula C_nH_{2n} that contain a "ring" structure, Fig. 1.8.

Cyclopentane
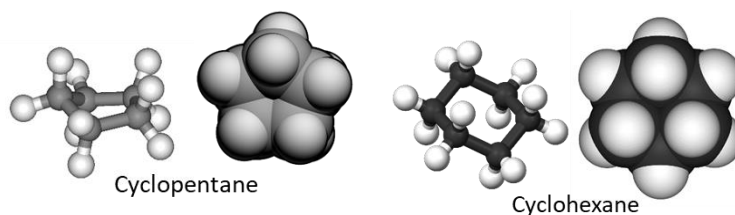
Cyclohexane

Fig. 1.8. Structures of cyclopentane and cyclohexane

These cyclic paraffins, or alicyclics, and their derivatives are found in petroleum, and in the oil industry these compounds are also called naphthenes.

Just as for paraffins, the proportion of naphthenic hydrocarbons varies with the type of crude, and in general, naphthenic compounds constitute a substantial amount of the whole crude. Isolation of naphthenes from crude oils has been successful in the gasoline range but is somewhat more difficult in the higher fractions; the number of isomers increases very rapidly because of (1) variation in the number of carbon atoms per ring, (2) the possibility of cis-trans isomerism of the substituents, that is, positions relative to one another above or below the plane of the ring, and (3) ring stereoisomerism (in addition to the divergency in the way in which different naphthene rings may be linked).

Although only a small number of representatives have been isolated so far, cyclohexane-, cyclopentane-, and decahydronaphthalene derivatives are largely represented in oil fractions. Petroleum also contains polycyclic naphthenes, such as terpenes, and such molecules, often designated bridge-ring hydrocarbons, occur even in the heavy gasoline fractions (boiling point 150 - 200°C, 300- 390°F). Naphthene rings may be built up of a varying number of carbon atoms, and among the synthesized hydrocarbons there are individuals with rings of the three-, four-, five-, six-, seven-, and eight-membered type. It is now generally believed that oil fractions contain chiefly five- and six-membered rings because (1) only naphthenes with five- and six-membered rings have been isolated from the lower boiling fractions, (2) thermodynamic studies show that naphthene rings with five and six carbon atoms are the most stable, and (3) the naphthenic acids contain chiefly cyclopentane as well as cyclohexane rings.

The cycloparaffins (naphthenes) are represented in all fractions in which the constituent molecules contain more than five carbon atoms. Several series of cycloparaffins, usually containing five- or six-membered rings or their combinations, occur as polycyclic structures. The content of cycloparaffins in petroleums varies up to 60% of the total hydrocarbons . However, the cycloparaffin content of different boiling range fractions of a crude oil may not vary considerably and generally remains within rather close limits. Nevertheless, the structure of these constituents may change from one petroleum to another, as well as in the same crude oil, as a function of the molecular weight or boiling range of the individual fractions.

The principal structural variation of naphthenes is the number of rings present in the molecule. The mono- and bicyclic naphthenes are generally the major types of cycloparaffins in the lower boiling fractions of petroleum, with boiling point or molecular weight increased by the presence of alkyl chains. The higher boiling point fractions, such as the lubricating oils, may contain two to six rings per molecule.

Another series exists with the general formula C_nH_{2n}; the members of this series, called olefins (or alkenes), are said to be unsaturated because they contain less than the amount of hydrogen necessary to saturate all the valences of the carbon atoms. If the compound is simple , it can be named by adding -ene to the stem derived from the corresponding paraffins; or in the older but still common practice these compounds are named by adding ene to the alkyl radical; To name the more complex members of this series, the location of the unsaturated (double) bond is indicated by citing the number of the carbon atom preceding it. The carbons are numbered from the end nearest the double bond. The "surname" of the compound is the longest carbon chain that includes the unsaturated linkage. Thus, the hydrocarbon is numbered from right to left. The number 3 carbon holds a substituent methyl group, and the correct name is 3-methyl- 1-butene. The compound is called 3-isobutyl-1 -heptene, Fig. 1.9.

Fig. 1.9. Structures of common alkenes (olefins),
3-methyl- 1-butene (left) and 2-Methyl-2-butene (right)

The presence of olefins in crude has been under dispute for many years because there are investigators who claim that olefins are actually present; in fact these claims usually refer to distilled fractions, and it is very difficult to entirely avoid cracking during the distillation process. Nevertheless, evidence for the presence of considerable proportions of olefins in Pennsylvanian crude oils has been obtained; spectroscopic and chemical methods showed that the crude oils, as well as all distillate fractions, contained up to 3% wt/wt olefins. Hence, although the opinion that petroleum does not contain olefins requires some revision, it is perhaps reasonable to assume that the Pennsylvania crude oils may hold an exceptional position and that olefins are present in crudes in only a few special cases.

Hydrocarbons having two double bonds are called dienes. In naming derivatives, or isomers, of dienes, the parent name is obtained by taking the longest chain containing both double bonds and the carbon atoms are numbered from the end closest to one of the double bonds. For example, is 4-methyl 2 propyl- 1,3-pentadiene, Fig. 1.10.
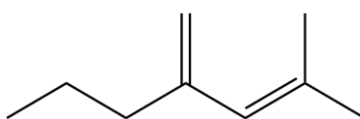
Fig. 1.10. Structure of a diene, 4-methyl-2-propyl-1,3-pentadiene

Another class of unsaturated hydrocarbons (the acetylenes) also exists and is centered around the occurrence of a carbon-carbon triple bond (-C ≡ C-) within the molecule.

Acetylenes follow a naming system similar to that for the olefins but using the suffix **yne** instead of **ene**. Nevertheless, acetylenes, like the olefins and dienes, are rarely if at all found in natural petroleum because of the reactivity of the unsaturated bond. However, acetylenes, olefins, and dienes are important building blocks in the petrochemical industry, which relies heavily upon the generation of these compounds during the refining of petroleum, Fig. 1.11.
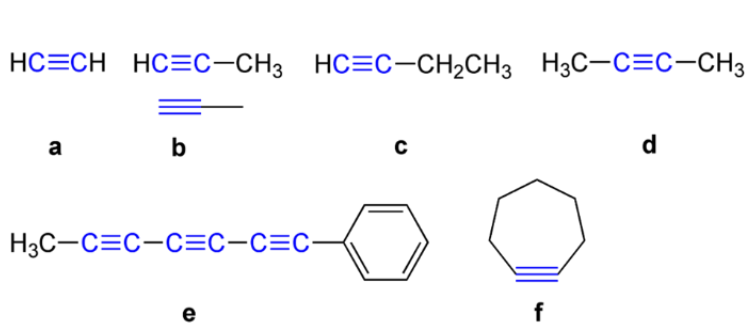
Fig. 1.11. Illustrative alkynes (triple bonds highlighted **blue**):

a; acetylene

b; two depictions of propyne

c; 1-butyne,

d; 2-butyne,

e; naturally-occurring 1-phenylhepta-1,3,5-triyne

f; the strained cycloheptyne

1.3.1.4. Aromatics

Finally, a very important class of compounds that occur in petroleum are those based on benzene. The benzene ring is represented by a six-carbon ring or hexagon in which the carbons are joined by alternate single and double bonds. The remaining single valence of each carbon holds one hydrogen atom at each corner of the hexagon. The benzene ring is a very symmetrical structure and is much less reactive than would be expected from the presence of three unsaturated linkages, Fig. 1.12.
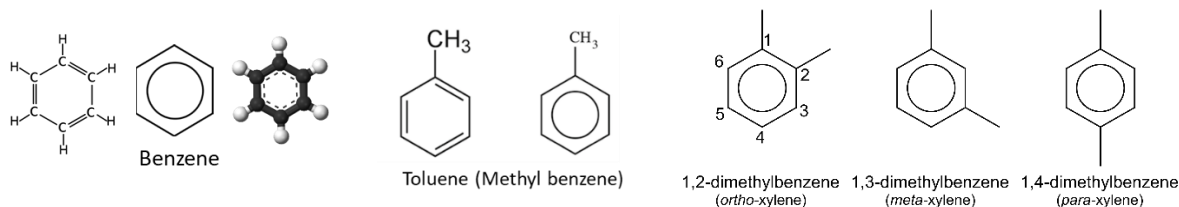
Fig. 1.12. Structure of typical aromatic componed with one benzene ring.

If one or more of the hydrogens of the benzene are replaced by other atoms or groups, the structure is indicated by a hexagon with the formula for the substituent group shown in its particular position. Methylbenzene (toluene) and can only have one structure. Xylene, however, exists in three different isomeric forms and each has different physical properties.

Aromatic compounds with two or more fused rings are also known. The simplest member of this series is naphthalene, which may be thought of as consisting of two fused benzene rings. Fig. 1.13.
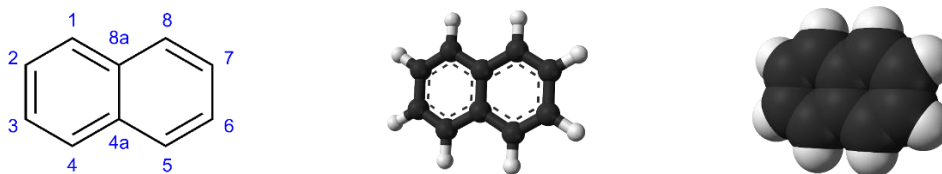
Fig. 1.13. Naphthalene molecule structure

In naming derivatives of naphthalene, the carbons are numbered as described , and positions 1 and 2 are often referred to as α and β.

Derivatives of multi-ring condensed aromatic compounds, such as anthracene, and phenanthrene also occur in petroleum, but derivatives of the non-condensed multiring compounds, such as biphenyl, and terphenyl, are found only rarely, if at all, in petroleum, Fig. 1.14.

Anthracene   Phenanthrene   p-Terphenyl
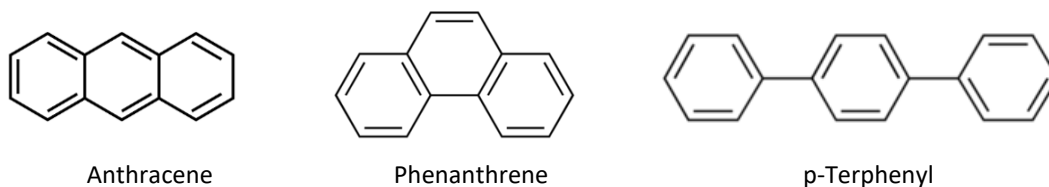
Fig. 1.14. Molecule structures of multiring condensed aromatic compounds.

All crudes contain aromatic compounds in proportions varying from 10 to 50% or even higher. By far the majority of these aromatics contain paraffinic chains, naphthene rings, and aromatic rings side by side.

There is a general increase in the proportion of aromatic hydrocarbons with increasing molecular weight, but aromatic hydrocarbons without the accompanying naphthene rings or alkyl-substituted derivatives seem to be present in appreciable amounts only in the lower petroleum fractions; it is not surprising that spectrographic identification of such compounds has been concerned with these low-boiling aromatics.

All known aromatics are present in gasoline fractions, but the benzene content is usually low compared to the benzene homologs, such as toluene and the xylenes. Tbl. 1.9 is a list of aromatics that have been isolated from various low-boiling petroleum fractions, and it is particularly noticeable that, with a few exceptions (e.g., 1-methyl-3-ethylbenzene and 1 -methyl-4-ethylbenzene in the Winkler gasoline), the various hydrocarbons are present in similar proportions in the different crudes. In addition to the 1- and 2-methylnaphthalenes, other simple alkylnaphthalenes have also been isolated from crudes, such as 0.12% by weight of dimethylnaphthalenes, mainly the 1,6-isomer with minor amounts of the 1,3- and 1 ,7-compounds obtained from a Borneo crude.

Aromatics without naphthene rings appear to be relatively rare in the heavier fractions of petroleum (e.g., lubricating oils). Indeed, a lubricating oil (constituting 10% of the crude oil) was divided into four main portions: a wax portion, an asphaltic portion, a waterwhite portion, and an extract portion. The latter two fractions were exhaustively separated into fractions consisting of compounds of substantially similar size and type so that each fraction represented 1/40,000 part of the original crude, and the results show that substantial amounts of the water-white fraction and the extract fraction are mixed naphthenic-aromatic hydrocarbons with one or two aromatic rings and one to three naphthene rings. The rings are usually condensed together; thus components with two aromatic rings are presumed to be naphthalene derivatives and those with three aromatic rings may be either phenanthrene or anthracene derivatives.

In summation, it is worthy of note that all compounds that have aromatic rings, in addition to the presence of alkyl chains and naphthenic rings within the same molecule, are classified as aromatic compounds. Many separation procedures that have been applied to petroleum result in the isolation of a compound as an "aromatic" even if there is only one such ring (i.e., six carbon atoms) that is substituted by many more than six nonaromatic carbon atoms.

Although not specifically mentioned here, the polycyclic aromatic hydrocarbons pyrene, methylchrysene, methyl-, and dimethylperylenes, and benzoftuorenes have been identified in crude oils. However, the polycyclic aromatics are usually found in somewhat lower amounts (fractions of a percent) in petroleum and appear to be predominantly the methyl homologs. Higher members of these polyaromatic series with side chains longer than two or three carbon atoms are quite rare: remember that their higher boiling points would make separation more difficult. Chrysene and benzoftuorene homologs seem to predominate over those of pyrene.

It should also be emphasized that in the higher boiling point petroleum fractions, many polycyclic structures occur in naphthenoaromatic systems. The naphthenoaromatic hydrocarbons, together with

the naphthenic hydrocarbon series, form the major content of higher boiling point petroleum fractions. Usually the different naphthenoaromatic components are classified according to the number of aromatic rings in their molecules. The first to be distinguished is the series with an equal number of aromatic and naphthenic rings. The first members of the bicyclic series C9-C11 are the simplest, such as the I-methyl-, 2-methyl-, and 4-methylindanes and 2-methyl- and 6-methyltetralins. Tetralin and methyl- dimethyl-, methylethyl-, and tetramethyltetralins have been found in several crude oils, particularly in the heavier, naphthenic, crude oils.

Tbl. 1.9. Aromatics Isolated from Various Crude Oils

Compound	Santa Barbara	East Texas	Bradford	Greendale	Winkler	Midway	Conroe	Ponca
Benzene	0.221	0.07	0.06	0.21	0.04	0.07	0.41	0.2
Toluene	0.778	0.58	0.51	0.59	0.09	0.43	2.46	0.5
Ethyl benzene	0.209	0.22	0.09	0.12	0.08	0.22	0.31	0.2
a-Xylene	0.29	0.30	0.21	0.17	0.03	0.31	0.68	0.3
m-Xylene	0.68	0.64	0.61	0.40	0.08	0.36	2.03	0.5
p-Xylene	0.68	0.17	0.17	0.09	0.12	0.15	0.59	0.1
N-propylbenzene	0.26	0.08	0.05	0.03	0.02	0.04	0.12	0.09
Isopropylbenzene	0.06	0.04	0.03	0.03	0.03	0.03	0.09	0.07
1-Methyl-2-ethylbenzene	-	0.07	0.03	0.04	0.01	0.03	O.09	0.09
1-Methyl-3-ethylbenzene	-	0.16	0.13	0.08	0.01	0.04	0.40	0.17
1-Methyl-4-ethylbenzene	-	0.07	0.05	0.03	0.05	0.03	0.13	0.06
l ,2,3~ Trimethylbenzene	-							0.1
1,2,4-Trimethylbenzene	-	0.34	0.33	0.15	0.13	0.13	0.69	0.51
1,3,5-Trimethylbenzene	0.18	0.09	0.17	0.05	0.05	0.05	0.36	0.12
tert-Butylbenzene	-	0.01	0.002	0.003	0.002	0.00	0.01	0.01
1,2,3,4-Tetramethylbenzene	-							0.2
Tetrahydronaphthalene	-							0.03
Naphthalene	-							0.06
1-Methyl naphthalene	-							0.1
2-Methylnaphthalene	-							0.2
5-Methyltetrahydronaphthalene	-							0.08
6-Methyltetrahydronaphthalene	-							0.09

It is interesting that the distribution of the chains between aromatic and naphthenic rings within the same molecules follows a particular pattern that may also be evident in the single ring constituents. The short chains (methyl and ethyl) appear to be characteristic substituents of the aromatic portion of the molecule, whereas a limited number (one or two) of longer chains may be attached to the cycloparaffin rings. The total number of chains, which is in general four to six, as well as their length, increases according to the molecular weight of the naphthenoaromatic compounds.

In summary, a variety of hydrocarbon compounds occur throughout petroleum (Tbl. 1.10, and 1.11). Although the amount of any particular hydrocarbon varies from one petroleum to another, the family from which that hydrocarbon arises is well represented.

Tbl. 1.10 Individual Hydrocarbons and their families that have been isolated from Petroleum

Hydrocarbons	Series	C atoms per molecule
Normal paraffins	C_nH_{2n+2}	C1-C35
Branched paraffins	C_nH_{2n+2}	C4- C10
Branched paraffins	C_nH_{2n+2}	C11-C15
Branched paraffins	C_nH_{2n+2}	C16-C20
Branched paraffins	C_nH_{2n+2}	C21- C23
Cycloparaffins (monocyclic)	C_nH_{2n}	
Cycloparaffins (cyclopentanes)	C_nH_{2n}	C5-C10
Cycloparaffins (cyclohexanes)	C_nH_{2n}	C6- C10
Cycloparaffins (cycloheptanes)	C_nH_{2n}	C7
Cycloparaffins (bicyclic)	C_nH_{2n-2}	C8-C11
Cycloparaffins (tricyclic)	C_nH_{2n-4}	C10- C12
Aromatics monocyclic	C_nH_{2n-6}	C6-C12
Aromatics bicyclic (naphthalenes)	C_nH_{2n-12}	C10-C16
Aromatics bicyclic (diphenyls)	C_nH_{2n-14}	C12-C14
Aromatics tricyclic	C_nH_{2n-18}	C14 – C18
	C_nH_{2n-20}	
Aromatics tetracyclic	C_nH_{2n-24}	C16-C18
Naphthenoaromatics		
Indane group	C_nH_{2n-8}	C9- C13
Tetraline group	C_nH_{2n-8}	C10-C14

Tbl. 1.11. Predominant Hydrocarbon Constituents of Petroleum

No	Series of hydrocarbons	Carbon no.
1	Pentane	C5
2	Hexane	C6
3	Heptane	C7
4	Octane-decane	C8 - C10
5	Undecane-Pentadecane	C11 – C15
6	Hexadecane and higher	C16 and higher
Isoparaffins		
1	2-Methylpentane	C6
2	3-Methylpentane	C6
3	2-Methylhexane	C7
4	3-Methylhexane	C7
5	2-Methylheptane	C8
6	3-Methylheptane	C9
7	2-Methyloctane	C9
8	3-Methyloctane	C9
9	2-Methylnonane	C10
10	3-Methylnonane	C10
11	4-Methylnonane	C10
12	Pristane (isoprenoid)	C19
Cycloparaffins		
1	Methylcyclopentane	C6
2	Cyclohexane	C6
3	Methylcyclohexane	C7
4	l-trans-2-Dimethylcyclopentane	C7
5	l-cis-3-Dimethylcyclopentane	C7
6	1-cis-3-Dimethylcyclohexane	C7
7	l-cis-2-Dimethylcyclohexane	C8
8	I, 1,3-Trimethylcyclohexane	C9
Aromatics		
1	Benzene	C6
2	Toluene	C7
3	Ethylbenzene	C8
4	m-Xylene	C8
5	l -Methyl-3-ethylbenzene	C9
6	1,2 ,4-Trimethylbenzene	C9
7	1,2,3-Trimethylbenzene	C9
8	1,2,3,4-Tetramethylbenzene	C10
9	2-Methy I naphthalene	C11"
10	2,6-Dimethylnaphthalene	C12
11	Trimethylnaphthalene	C13

1.3.2. Nonhydrocarbon Components

The previous sections present some indication of the types and nomenclature of the organic hydrocarbons that occur in various petroleum. Thus, it is not surprising that the "simplest" petroleum which contain only hydrocarbons, are in fact extremely complex mixtures. The phenomenal increase in the number of possible isomers for the higher hydrocarbons makes it very difficult, if not impossible in most cases, to isolate individual members of any one series having more than, say, 12 carbon atoms. Inclusion of organic compounds of nitrogen, oxygen, and sulfur serves only to present crude oil as an even more complex mixture than was originally conceived. Nevertheless, considerable progress has been made in the isolation and/or identification of the lower molecular weight hydrocarbons, as well as accurate estimations of the overall proportions of the hydrocarbon types present in various petroleums. Indeed, it has been established that, as the boiling point of the petroleum fraction increases, not only the number of the constituents but the molecular complexity of the constituents also increases (Fig. 1.3).
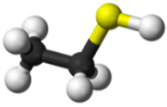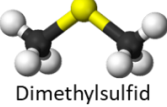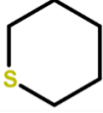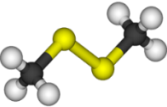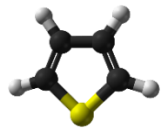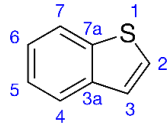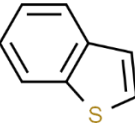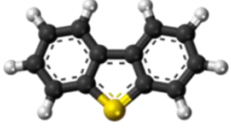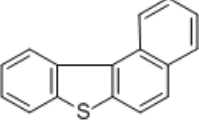
Crude oils contain appreciable amounts of organic nonhydrocarbon constituents, mainly sulfur-, nitrogen-, and oxygen-containing compounds and, in smaller amounts, organometallic compounds in solution and inorganic salts in colloidal suspension. These constituents appear throughout the entire boiling range of the crude oil but tend to concentrate mainly in the heavier fractions and in the nonvolatile residues.

Although their concentration in certain fractions may be quite small, their influence is important. For example, the decomposition of inorganic salts suspended in the crude can cause serious breakdowns in refinery operations; the thermal decomposition of deposited inorganic chlorides with evolution of free hydrochloric acid can give rise to serious corrosion problems in the distillation equipment. The presence of organic acid components, such as mercaptans and acids, can also promote metallic corrosion. In catalytic operations, passivation and/or poisoning of the catalyst can be caused by deposition of traces of metals (vanadium and nickel) or by chemisorption of nitrogen-containing compounds on the catalyst, thus necessitating the frequent regeneration of the catalyst or its expensive replacement.

The presence of traces of nonhydrocarbons may impart objectionable characteristics in finished products, such as discoloration, lack of stability on storage, or a reduction in the effectiveness of organic lead antiknock additives. It is thus obvious that a more extensive knowledge of these compounds and of their characteristics could result in improved refining methods and even in finished products of better quality. The nonhydrocarbon compounds, particularly the porphyrins and related compounds, are also of fundamental interest in the elucidation of the origin and nature of crude oils. Furthermore, a knowledge of their surface-active characteristics is of help in understanding problems related to the migration of oil from the source rocks to the actual reservoirs.

1.3.2.1. Sulfur Compounds

Sulfur compounds are among the most important heteroatomic constituents of petroleum. Although there are many varieties of sulfur compounds (Fig. 1.15), the prevailing conditions during the fondation, maturation, and even in situ alteration may dictate that only preferred types exist in any particular crude oil. Nevertheless, sulfur compounds of one type or another are present in all crude oils. In general, the higher the density of the crude oil (lower the API gravity), the higher the sulfur content (Fig. 1.16). The total sulfur in the crude can vary from, perhaps, 0.04% for a light paraffin oil to about 5.0% for heavy crude oils. The sulfur content of crude oils produced from broad geographic regions varies with time, depending on the composition of newly discovered fields, particularly those in different geological environments.

R—S—H	Ethanethiol	Thiols (Mercaptans)
H_3C—S—CH_3	Dimethylsulfid	Sulfides
	Thiocyclohexane	Cyclic Sulfides
H_3C—S—S—CH_3	Dimethyl disulfide	Disulfides
		Thiophene
		Benzothiophene
		Di benzothiophene
		Naphthobenzothiophene
Fig. 1.15. Nomenclature and Types of Organic Sulfur Compounds		

The presence of sulfur compounds in finished petroleum products often produces harmful effects. For example, in gasoline, sulfur compounds are believed to promote corrosion of engine parts, especially under winter conditions, when water containing sulfur dioxide from the combustion may accumulate in the crankcase. In addition, mercaptans in hydrocarbon solution cause the corrosion of copper and brass in the presence of air and also affect lead susceptibility and color stability. Free sulfur is also corrosive, as are sulfides, disulfides, and thiophenes, which are detrimental to the octane number response to tetraethyllead. However, gasoline with a sulfur content between 0.2 and 0.5% has been used without obvious harmful effect. In diesel fuels, sulfur compounds increase wear and can contribute to the formation of engine deposits, and although a high sulfur content can sometimes be tolerated in industrial fuel oils, the situation for lubricating oils is that a high content of sulfur compounds in lubricating oils seems to lower resistance to oxidation and increases the deposition of solids.
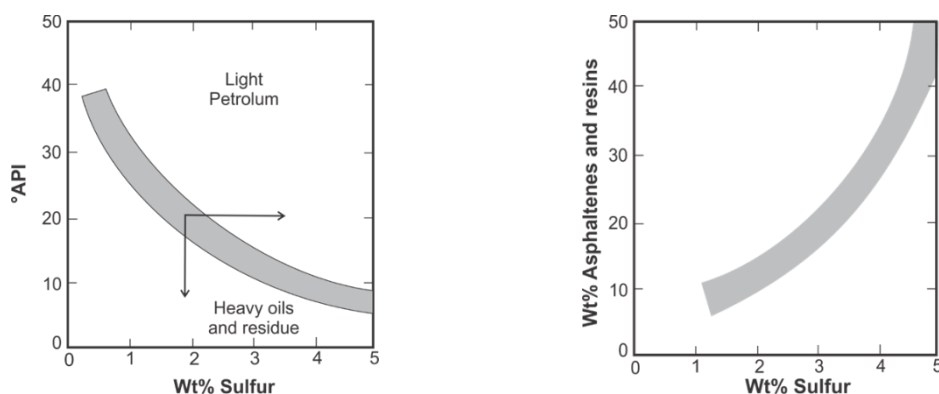
Fig. 1.16. Generalized relationship of (left) sulfur content to API gravity and (right) sulfur content to asphaltic (asphaltenes plus resins) content.

The distribution of sulfur in the various fractions of crude oils has been studied many times, beginning in 1891. Although it is generally true that the proportion of sulfur increases with the boiling point during distillation, the middle fractions may actually contain more sulfur than higher boiling fractions as a result of decomposition of the higher molecular weight compounds during the distillation. A high sulfur content is generally considered harmful in most petroleum products, and the removal of sulfur compounds or their conversion to less deleterious types is an important part of refinery practice. The distribution of the various types of sulfur compounds varies markedly among crudes of diverse origin, but fortunately some of the sulfur compounds in petroleum undergo thermal reactions at relatively low temperatures. If elemental sulfur is present in the oil, a reaction, with the evolution of hydrogen sulfide, begins at about 150°C (300°F) and is very rapid at 220°C (430°F), but organically bound sulfur compounds do not yield hydrogen sulfide until higher temperatures are reached . Hydrogen sulfide is, however, a common constituent of many crude oils, and some crude oils with >1% sulfur are often accompanied by a gas having substantial properties of hydrogen sulfide.

The identification of sulfur-containing constituents of crude oils has been the subject of many investigations with the result that many of the sulfur compound types that occur in crude oils are now known (Tbl. 1.12; see also Thompson et al., 1976). These vary from the simple thiols, to the simple sulfides, and the polycyclic sulfides, such as compounds with two condensed rings which have all been isolated from petroleum. Various thiophenes, such as have also been isolated from a variety of crude oils; benzothiophene derivatives, are not regarded as true constituents of crude oil but are generally formed by oxidation of thiols during processing:

$$2R - SH \xrightarrow{[O]} R - S - S - R + H_2O$$
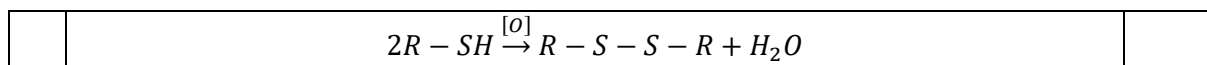
Although sulfur is the most important heteroatom (i .e ., nonhydrocarbon) present in petroleum with respect to the current context, other nonhydrocarbon atoms can exert a substantial influence not only on the nature and properties of the products but also on the nature and efficiency of the process. Such atoms are nitrogen, oxygen, and metals, and because of their influence on the process, some discussion of each is warranted here.

Tbl. 1.12 Sulfur Compounds in a Texas Crude Oil

Sulfur Compound Name	Boiling point (°C)	Wasson Texas Crude oil (Wt%)
Methanethiol	5.96	0.00240
Ethanethiol	35.00	0.00530
2-Thiapropane	37.31	0.00088
2-Propanethiol	52.56	0.00199
2-Methyl-2-propanethiol	64.22	0.00055
2-Thiabutane	66.65	0.00222
1-Propanethiol	67.5	0.00041
3-Methyl-2-thiabutane	84.81	0.00064
2-Butanethiol	85.15	0.00386
2-Methyl-1-propanethiol	88.72	0.00003
3-Thiapentane	92.10	0.00075
2-Thiapentane	95.52	0.00030
1-Butanethiol	98.4	Trace
2-Methyl-2-butanethiol	99.0	0.00064
3,3-Dimethyl-2-thiabutane	99.0	
2-Methyl-3-thiapentane	107.4	
3-Methyl-2-butanethiol	109.8	
2-Pentanethiol	112.9	0.0014
3-Pentanethiol	113.9	0.00057
3-Thiahexane	118.50	0.00012
2,4-Dimethyl-3-thiapentane	120.02	0.00053
2,2-Dimethyl-3-thiapentane	120.41	0.000058
Thiacyclopentane	121.12	0.000077
2-Thiahexane	123.2	0.000077
2-Methyl-3-thiahexane	132.05	0.000078
Cyclopentanethiol	132.2	
2-Methylthiacyclopentane	133.23	0.0023
4-Methyl-3-thiahexane	133.65	0 .00050
3-Methylthiacyclopentane	138.67	0.00046
2-Hexanethiol	138.9	0.0028
Thiacyclohexane	141. 75	0.00032
trans-2,5-Dimethylthiacyclopentane	142 .0	0.0025
cis-2,5-Dimethylthiacyclopentane	142.28	0.0024
3-Thiaheptane	144.24	0.000078
2-Methylthiacyclohexane	153.04	0.0029
3-Methy lthiacyclohexane	158.04	0.000024
4-Methylthiacyclohexane	158.64	0.000048
Cyclohexanethiol	158.8	0.0012

1.3.2.2. Oxygen Compounds

Oxygen in organic compounds can occur in a variety of forms (Fig. 1.17), and it is not surprising that the more common oxygen-containing compounds occur in petroleum. The surprising that the more common oxygen-containing compounds occur in petroleum. The total oxygen content of petroleums is usually less than 2%, although larger amounts have been reported, but when the oxygen content is phenomenally high it may be that the oil has suffered prolonged exposure to the atmosphere either during or after production. However, the oxygen content of petroleum increases with the boiling point of the fractions examined; in fact, the nonvolatile residua may have oxygen contents up to 8% by weight. Although these high-molecular-weight compounds contain most of the oxygen in petroleum, little is known concerning their structure, but those of lower molecular weight have been investigated with considerably more success and have been shown to contain carboxylic acids and phenols.

The presence of acid substances in petroleum first appears to have been reported in 1874, and it was established 9 years later that these substances contained carboxyl groups and were carboxylic acids. These were termed naphthenic acids. Although alicyclic (naphthenic) acids appear to be the more prevalent, it is now well known that aliphatic acids are also present (Tbl. 1.13). In addition to the carboxylic acids, alkaline extracts from petroleum contain phenols.

Tbl. 1.13 Naphthenic Acids in Various Crude Oils

Crude	Type	Fraction	Naphtenic acids (%)
American crude oils			
Pennsylvania	Paraffinic	Kerosene	0.006
Pennsylvania	Paraffinic	Gas oil	0.010
East Texas	Intermediate	Kerosene	0.009
Midcontinent (pipeline mixture)	Intermediate	Kerosene	0.009
		Naphtha	0.01
California	Naphthenic	Kerosene	0.06
		Gas oil	0.36
Texas heavy	Naphthenic	Kerosene	0.075
		Gas oil	0.35
Russian crude oils			
Balakhany light	Naphthenic	Whole crude	1.05
		Kerosene	0.5
Balakhany heavy	Asphaltic	Whole crude	1.10
		Kerosene	0.5
Binagady	Asphaltic	Whole crude	0.85
		Kerosene	0.5
Ramain	Intermediate	Whole crude	0.40
		Kerosene	0.20
Surakhani	Intermediate	Whole crude	0.20
		Kerosene	0.20
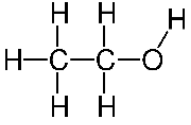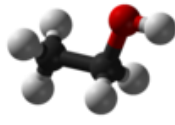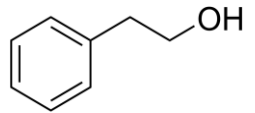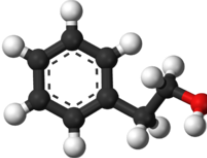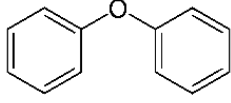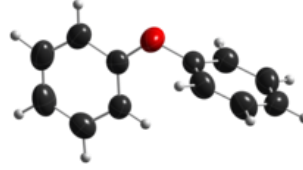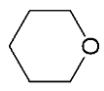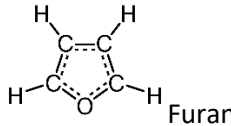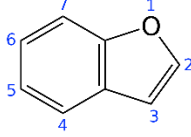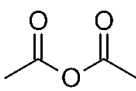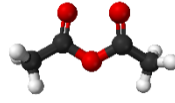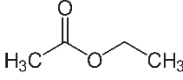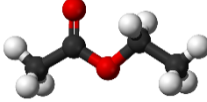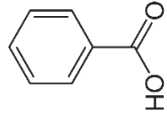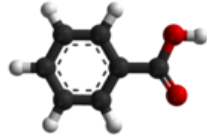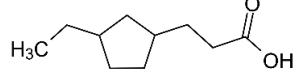
		Ethanol
		Other names Absolute alcohol, alcohol, ethylic alcohol, EtOH, ethyl alcohol, ethylol, grain alcohol hydroxyethane, methylcarbinol
		2-Phenylethan-1-ol
		Other names; 2-Phenylethanol, Phenethyl alcohol Benzyl carbinol, β-Hydroxyethylbenzene Benzeneethanol
		1,1'-Oxydibenzene
		Other names Oxydibenzene, Diphenyl ether Diphenyl oxide, 1,1'-Oxybisbenzene Phenoxybenzene
		Oxane
		Other names: Tetrahydropyran, Oxacyclohexane, 1,5-epoxypentane
Furan		1-Benzofuran
		Other names: Benzofuran, Coumarone, Benzo[b]furan
		Propan-2-one
		Other names: Acetone, Dimethyl ketone 2-Propanone, Ketone propane
		Acetic anhydride
		Ethanoic anhydride
		Other names: Ethanoyl ethanoate, Acetic acid anhydride, Acetyl acetate, Acetyl oxide, Acetic oxide
		Ethyl acetate
		Other names Acetic ester, Acetic ether, Ethyl ester of acetic acid
		Carboxylic acids
		Other names: Carboxybenzene, E210, Dracylic acid Phenylmethanoic acid
		Example of an naphthenic acid component
Fig. 1.17. Common Organic Oxygen Compounds.		

Naphthenic acids (NAs) are a mixture of several cyclopentyl and cyclohexyl carboxylic acids with molecular weight of 120 to well over 700 atomic mass units. The main fraction are carboxylic acids with a carbon backbone of 9 to 20 carbons. McKee et al. claim that "naphthenic acids (NAs) are primarily cycloaliphatic carboxylic acids with 10 to 16 carbons", although acids containing up to 50 carbons have been identified in heavy petroleum.

The term naphthenic acid has roots in the somewhat archaic term "naphthene" (cycloaliphatic but non-aromatic) used to classify hydrocarbons. It was originally used to describe the complex mixture of petroleum-based acids when the analytical methods available in the early 1900s could identify only a few naphthene-type components with accuracy. Today "naphthenic" acid is used in a more generic sense to refer to all of the carboxylic acids present in petroleum, whether cyclic, acyclic, or aromatic compounds, and carboxylic acids containing heteroatoms such as N and S. Although commercial naphthenic acids often contain a majority of cycloaliphatic acids, multiple studies have shown they also contain straight chain and branched aliphatic acids and aromatic acids; some naphthenic acids contain >50% combined aliphatic and aromatic acids.

Naphthenic acids are represented by a general formula $C_nH_{2n-z}O_2$, where n indicates the carbon number and z specifies a homologous series. The z = 0 for saturated, acyclic acids and increases to 2 in monocyclic naphthenic acids, to 4 in bicyclic naphthenic acids, to 6 in tricyclic acids, and to 8 in tetracyclic acids.

Salts of naphthenic acids, called naphthenates, are widely used as hydrophobic sources of metal ions in diverse applications. Aluminium salts of naphthenic acid and palmitic acid were combined during World War II to produce napalm. The word "napalm" is derived from the words naphthenic acid and palmitic acid.

It has generally been concluded that the carboxylic acids in petroleum with fewer than eight carbon atoms per molecule are almost entirely aliphatic in nature. Monocyclic acids begin at C6 and predominate above C14. This indicates that the structures of the carboxylic acids correspond with those of the hydrocarbons, with which they are associated in the crude oil. That is, in the range in which paraffins are the prevailing type of hydrocarbon, the aliphatic acids may be expected to predominate. Similarly, in the ranges in which monocycloparaffins and dicycloparaffins prevail, one may expect to find principally monocyclic and dicyclic acids, respectively.
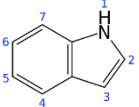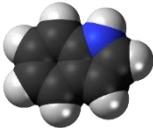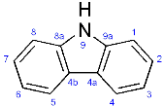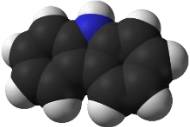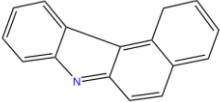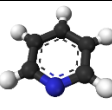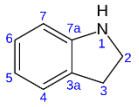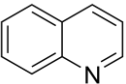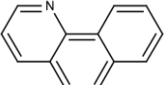
In addition to the carboxylic acids and phenolic compounds, the presence of ketones, esters, ethers, and anhydrides has been claimed for a variety of petroleums. However, the precise identification of these compounds is difficult because most of them occur in the higher molecular weight nonvolatile residue. They are claimed to be products of the air blowing of the residue, and their existence in virgin petroleum may yet need to be substantiated.

Although comparisons are frequently made between the sulfur and nitrogen contents and such physical properties as the API gravity, it is not the same with the oxygen contents of crude oils. Indeed, even though it may be possible to postulate, and show, that such relationships exist,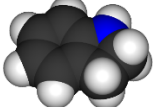 the ease with which some of the crude oil constituents can react with oxygen (aerial or dissolved) to incorporate oxygen functions into their molecular structure often renders the exercise somewhat futile if meaningful deductions are to be made.

1.3.2.3. Nitrogen Compounds

The nitrogen content in petroleum are in general low and typically in the range from 0.1 to 0. 9%, although some crude oils have been reported to contain up to 2% nitrogen. Crude oils with no detectable nitrogen or even trace amounts are not uncommon.

Nitrogen in petroleum may be classified arbitrarily as basic and non-basic. The basic nitrogen compounds (Fig. 1.18), which are composed mainly of pyridine homologs and occur throughout the boiling ranges, have a decided tendency to exist in the higher boiling fractions and residues. The non-basic nitrogen compounds, which are usually of the pyrrole, indole, and carbazole types, also occur in the higher boiling fractions and residues.

Non-basic		
		Pyrrole
		Indole
		Carbazole
		Benzo(c)carbazole
Basic		
		Pyridine
		Indoline
		Quinoline
		7, 8 Benzoquinoline
Fig. 1.18. Nomenclature and Types of Common Organic Nitrogen Compounds.		

Generally, with more asphaltic oil, the nitrogen content increases, and as an approximate correlation exists between the sulfur content and API gravity of crude oils (Fig. 1.16), there also exists a correlation between nitrogen content and the API gravity of crude oil (Fig. 1.19). It also follows that there is an approximate correlation between the nitrogen content and the carbon residue: the higher the carbon

residue, the higher the nitrogen content. The presence of nitrogen in petroleum is of much greater significance in refinery operations than might be expected from the small amounts present.
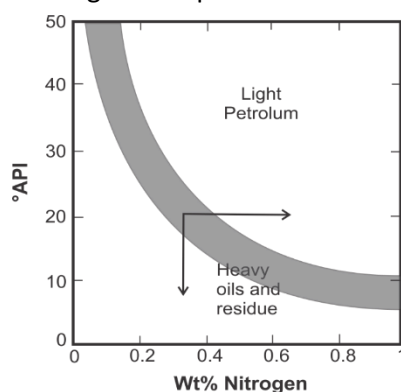

Fig. 1.19. Generalized relationship of nitrogen content to API gravity.

Nitrogen compounds can be responsible for the poisoning of cracking catalysts, and they also contribute to gum formation in such products as domestic fuel oil. The trend in recent years toward cutting deeper into the crude to obtain stocks for catalytic cracking has accentuated the harmful effects of the nitrogen compounds, which are concentrated largely in the higher boiling portions.

Basic nitrogen compounds with a relatively low molecular weight can be extracted with dilute mineral acids; equally strong bases of higher molecular weight remain un-extracted because of unfavorable partitioning between the oil and aqueous phases. A method has been developed in which the nitrogen compounds are classified as basic or non-basic, depending on whether they can be titrated with per chloric acid in a 50: 50 solution of glacial acetic acid and benzene;

Applicatition of this method has shown that the ratio of basic to total nitrogen is approximately constant (0.3 +/- 0.05) irrespective of the source of the crude. Indeed, the ratio of basic to total nitrogen was found to be approximately constant throughout the entire range of distillate and residual fractions. . Nitrogen compounds extractable with dilute mineral acids from petroleum distillates were found to consist of pyridines, quinolines, and isoquinolines carrying alkyl substituents, as well as a few pyridines in which the substituents was a cyclopentyl or cyclohexyl group. The compounds that cannot be extracted with dilute mineral acids contain the greater part of the nitrogen in petroleum and are generally of the carbazole, indole, and pyrrole types.

1.3.2.4. Porphyrins

Porphyrins are a naturally occurring chemical species that have been known to exist in petroleum for more than 50 years. They are given separate consideration in this section because of their uniqueness as separate and distinct chemical entities. They are not usually considered among the usual nitrogen-containing constituents of petroleum, nor are they considered a metallo-containing organic material that also occurs in some crude oils. As a result of these early investigations there arose the concept of porphyrins as biomarkers that could establish a link between compounds found in the geosphere and their corresponding biological precursors [15]; see also [16]

Porphyrins usually occur in the nonbasic portion of the nitrogen-containing concentrate. The simplest porphyrin is porphine and consists of four pyrrole molecules joined by methine (–CH=) bridges (Fig. 1.20). The methine bridges establish conjugated linkages between the component pyrrole nuclei, forming a more extended resonance system. Although the resulting structure retains much of the inherent character of the pyrrole components, the larger conjugated system gives increased aromatic character to the porphine molecule [17, 18].
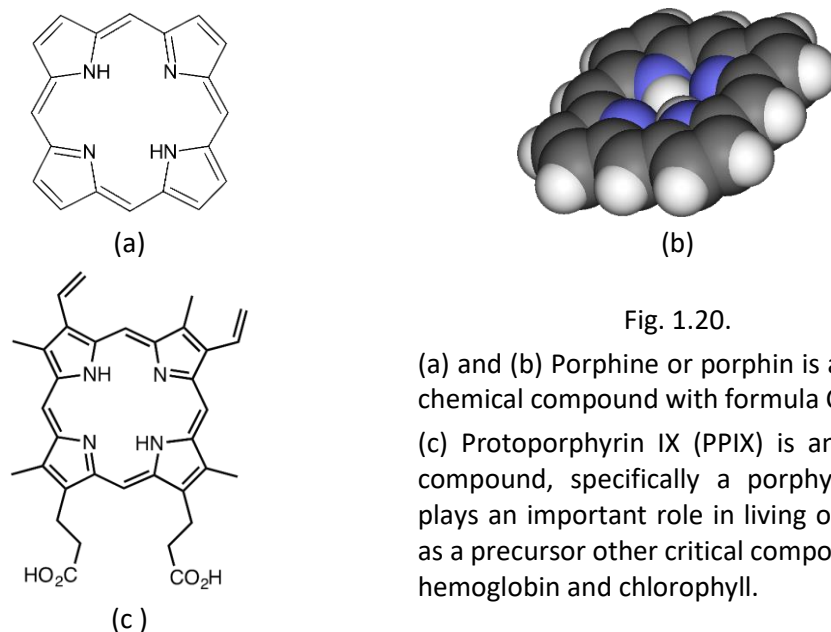
(a)

(b)

(c)

Fig. 1.20.

(a) and (b) Porphine or porphin is a organic chemical compound with formula $C_{20}H_{14}N_4$.

(c) Protoporphyrin IX (PPIX) is an organic compound, specifically a porphyrin, that plays an important role in living organisms as a precursor other critical compounds like hemoglobin and chlorophyll.

A large number of different porphyrin compounds exist in nature or have been synthesized. Most of these compounds have substituents other than hydrogen on many of the ring carbons. The nature of the substituents on porphyrin rings determines the classification of a specific porphyrin compound into one of various types according to one common system of nomenclature (see Fig. 1.21) [19]. Porphyrins also have wellknown trivial names or acronyms that are often in more common usage than the formal system of nomenclature.

When one or two double bonds of a porphyrin are hydrogenated, a chlorin or a phlorin is the result. Chlorins are components of chlorophylls and possess an iso-cyclic ring formed by two methylene groups bridging a pyrrolic carbon to a methine carbon. Geological porphyrins that contain this structural feature are assumed to be derived from chlorophylls. Etioporphyrins are also commonly found in geological materials and have no substituents (other than hydrogen) on the methine carbons. Benzoporphyrins and tetrahydrobenzoporphyrins also have been identified in geological materials. These compounds have either a benzene ring or a hydrogenated benzene ring fused onto a pyrrole unit.

Almost all crude oils and bitumens contain detectable amounts of vanadyl and nickel porphyrins. More mature, lighter crudes usually contain only small amounts of these compounds. Heavy oils may contain large amounts of vanadyl and nickel porphyrins. Vanadium concentrations of over 1000 ppm are known for some crudes, and a substantial amount of the vanadium in these crudes is chelated with porphyrins. In high-sulfur crudes of marine origin, vanadyl porphyrins are more abundant than nickel porphyrins. Low sulfur crudes of lacustrine origin usually contain more nickel porphyrins than vanadyl porphyrins. Of all the metals in the periodic table, only vanadium and nickel have been proven definitely to exist as chelates in significant amounts in a large number of crude oils and tar sand bitumens. The existence of iron porphyrins in some crudes has been claimed ([20]. Geochemical reasons for the absence of substantial quantities of porphyrins chelated with metals other than nickel and vanadium in most crude oils and tar sand bitumens have been advanced [21, 22, 23, 24, 25, 26].
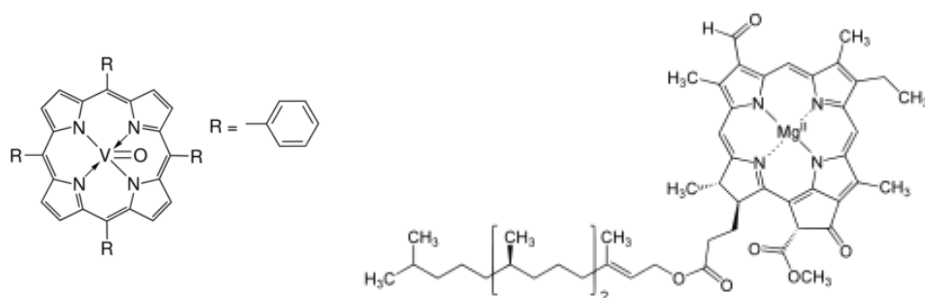
Fig. 1.21. (left) Almost all crude oils and bitumens contain detectable amounts of vanadyl or nickel porphyrins. (right) There are several types of chlorophyll, but all share the chlorin magnesium ligand which forms the right side of this diagram [19]

If the vanadium and nickel contents of crudes are measured and compared with porphyrin concentrations, it is usually found that not all the metal content can be accounted for as porphyrins (Tbl. 1.14) [27]. In some crudes, as little as 10% of total metals appears to be chelated with porphyrins. Only rarely can all measured nickel and vanadium in a crude oil be accounted for as porphyrinic [28]. Currently some investigators believe that part of the vanadium and nickel in crude oils is chelated with ligands that are not porphyrins. These metal chelates are referred to as nonporphyrin metal chelates or complexes [29, 30, 31]. On the other hand, the issue of nonporphyrin metal in crude oils has been questioned [32]. There is the possibility that in such systems as the heavy crude oils, in which intermolecular associations are important, measurement of the porphyrin concentrations are unreliable and there is a tendency to undercount the actual values. However, for the purposes of this chapter it is assumed that nonporphyrin chelates exist in fossil fuels but the relative amount is as yet unknown.

Finally, during the fractionation of petroleum the metallic constituents (metalloporphyrin and no porphyrin metal chelates) are concentrated in the asphaltene fraction. The de-asphaltened oils (petrolenes and maltenes; see Chapter 1) contain smaller concentrations of porphyrins than the parent materials and usually very small concentrations of nonporphyrin metals.

Tbl. 1.14. Porphyrin Concentrations in Petroleum [27]

Source	Porphyrins (ppm)	Vanadium and nickel		
		Complexed (%)	V (ppm)	Ni (ppm)
Bachaquero, Venezuela	380	8.5	430	53
Boscan, Venezuela	1680	18 .7	900	66
Coleville, Canada	110	9.6	94	32
Lagunillas, Venezuela	170	5.1	317	41
North Belridge, California	390	44.6	23	83
Rhodes, Kansas	135	8.8	133	33
Santa Maria, California	300	8.1	280	130
Tatums, Oklahoma	165	8.4	148	71
Tia Juana, Venezuela	60	3.2	187	24
West Texas, Texas	12	4.7	23	5
Wilmington, California	200	21.6	46	60

1.3.2.5. Metallic Constituents

The occurrence of metallic constituents in crude oil is of considerably greater interest to the petroleum industry than might be expected from the very small amounts present. Even minute amounts of iron, copper, and particularly nickel and vanadium in the charging stocks for catalytic cracking affect the activity of the catalyst and result in increased gas and coke formation and reduced yields of gasoline. In high-temperature power generators, such as oil-fired gas turbines, the presence of metallic constituents, particularly vanadium in the fuel, may lead to ash deposits on the turbine rotors, thus reducing clearances and disturbing their balance. More particularly, damage by corrosion may be very severe. The ash resulting from the combustion of fuels containing sodium and especially vanadium reacts with refractory furnace linings to lower their fusion points and so cause their deterioration.

Thus, the ash residue left after burning of a crude oil is due to the presence of these metallic constituents, part of which occur as inorganic water-soluble salts (mainly chlorides and sulfates of sodium, potassium, magnesium, and calcium) in the water phase of crude oil emulsions. These are removed in the desalting operations, either by evaporation of the water and subsequent water washing or by breaking the emulsion, thereby causing the original mineral content of the crude to be substantially reduced. Other metals are present in the form of oil-soluble organometallic compounds as complexes, metallic soaps, or in the form of colloidal suspensions, and the total ash from desalted crudes is of the order of 0.1 - 100 mg/liter.

Two groups of elements appear in significant concentrations in the original crude oil associated with well-defined types of compounds. Zinc, titanium, calcium, and magnesium appear in the form of organometallic soaps with surface-active properties adsorbed in the water/oil interfaces and act as emulsion stabilizers. However, vanadium, copper, nickel, and part of the iron found in crude oils seem to be in a different class and are present as oil-soluble compounds. These metals are capable of complexing with pyrrole pigment compounds derived from chlorophyll and hemoglobin and are almost certain to have been present in plant and animal source materials. It is easy to sunnise that the metals in question are present in such fonn, ending in the ash content. Evidence for the presence of several other metals in oil-soluble fonn has been produced, and thus zinc, titanium, calcium, and magnesium compounds have been identified in addition to vanadium, nickel , iron, and copper (Tbl. 1.15). Examination of the analyses of a number of crudes for iron, nickel, vanadium, and copper (Tbl. 1.16) indicates a relatively high vanadium content, which usually exceeds that of nickel, although the reverse can also occur.

Distillation concentrates the metallic constituents in the residues, although some can appear in the higher boiling distillates, but the latter may be due in part to entrainment. Nevertheless, there is evidence that a portion of the metallic constituents may occur in the distillates by volatilization of the organometallic compounds present in the petroleum. In fact , as the percentage of overhead obtained by vacuum distillation of a reduced crude is increased, the amount of metallic constituents in the overhead oil is also increased. The majority of the vanadium, nickel, iron, and copper in residual stocks may be precipitated along with the asphaltenes by hydrocarbon solvents. Thus, removal of the asphaltenes with n-pentane reduces the vanadium content of the oil by up to 95% with substantial reductions in the amounts of iron and nickel.

Tbl. 1.15. Trace Elements Found in Petroleum

Element	Range in Petroleum (ppm)
Cu	0. 2- 12.0
Ca	1.0- 2.5
Mg	1.0- 2.5
Ba	0.001 - 0.1
Sr	0. 001 - 0. I
Zn	0.5- 1.0
Hg	0.03- 0.1
Ce	0.001 - 0.6
B	0.001 - 0. I
Al	0.5- 1.0
Ga	0.001 - 0.1
Ti	0.001-0.4
Zr	0.001 - 0.4
Si	0. 1- 5.0
Sn	0.1-0.3
Pb	0.001 - 0.2
V	5.0- 1500.0
Fe[*]	0.04-120.0
Co	0.001 - 12.0
Ni	3.0- 120.0

[*]Part may be due to contamination by iron-containing equipment.

Tbl. 1.16. Metals Content of Various Crude Oils

Source	Metals (ppm)			
	Fe	Ni	V	Cu
East Texas	3.2	1.7	1.2	0.4
West Texas	5.1	4.8	7.9	0.4
Mirando	7.6	1.9	1.4	0.5
Jackson	4.4	1.8	0.9	0.2
Scurry County	3.4	1.0	0.8	0.2
Wilmington	28	46	41	0.6
Santa Maria	17	97	223	0.3
Kettleman	24	35	34	0.4
Ventura	31	33	49	1.1
Tibu-Petrolea	1.6	9.0	60	0.9
Kuwait	0.7	6.0	22.	0.1
Midcontinent	3.8	4.2	7.9	0.3
Kansas	5.8	5.8	20.8	0.4
Morocco		0.8	0.6	0.1
Redwater	3.4	10.6	4.5	0.1

1.3.3. Natural Gas

Natural gas contains constituents other than methane; therefore, knowledge of the occurrence and concentration of these constituents in natural gas are a prerequisite to any step in the processing sequence. For example, many wells produce natural gas that contains non hydrocarbon gasses like nitrogen (N_2) carbon dioxide (CO_2) and in some cases hydrogen sulfide (H_2S).

A characteristic feature of natural gas that contains hydrogen sulfide is the presence of carbon dioxide (generally in the range of 1-4% by volume). When the natural gas does not contain hydrogen sulfide, there is usually a relative lack of carbon dioxide also.

Sales gas specifications for natural gas include one or more of the following: water content, hydrocarbon content, heating value, specific gravity, acid gas content, temperature, and pressure. As with any property measurement, the value of any specification depends on the availability of reliable test methods to determine the specific property. The hydrocarbon content of natural gas is usually obtained indirectly by either measurement of the heating value (ASTM D 1826) or the specific gravity (ASTM D 1070 and ASTM D 3588). However, it must be remembered that the composition of natural gas can vary widely, but because natural gas is a multicomponent system, neither property may be changed significantly.

In some instances, the hydrocarbon dew points may be specified or limits may be placed on gas enrichment with reference to specific components. Of particular importance in this respect are the hexanes and higher molecular weight hydrocarbons, which may condense in the gas-gathering and/or distribution systems. If significant amounts of carbon dioxide or nitrogen are present in the natural gas, neither gravity nor heating value alon indicates hydrocarbon content. If both these properties are measured, the presence of either carbon dioxide or nitrogen is reflected in a higher specific gravity and lower heating value.

The water content of natural gas is usually expressed as pounds of water per million cubic feet of gas or by use of dew point and dew point pressure (ASTM D 1142). The two methods have a definite relationship, as shown by curves of water content as a function of saturation temperature and pressure. Common specifications are I, 4, or 7 pounds gas (i.e., 1 pound water per Mscf gas) depending on the conditions to which the gas will be exposed.

Hydrogen sulfide and carbon dioxide are the acid gases associated with natural gas. They are termed acid gases because solutions of these gases in water are acid in nature. Besides emitting a foul odor at low concentrations, hydrogen sulfide is deadly poisonous, and at concentrations above 600 ppm it can be fatal in a matter of minutes and has a toxicity comparable to that of hydrogen cyanide. Thus it cannot be tolerated in gas that will be used as domestic fuel. In addition , hydrogen sulfide is corrosive to all metals normally associated with gas-transporting, processing, and handling systems (although it is less corrosive to stainless steel) and may lead to premature failure of most such systems. On combustion, it forms sulfur dioxide:which is usually highly toxic and corrosive. Hydrogen sulfide and other sulfur compounds can also cause catalyst poisoning in refinery processes.

Acid gas content is specified according to the particular impurity. The usual acid gas specification is for hydrogen sulfide (ASTM D 2420, ASTM D 2725, and ASTM D 4048). Sulfur compounds may also be present in natural gas (ASTM D 3031) but may not often present a major problem if they are present only in small amounts since mercaptans are added as a warning odorant for natural gas. Carbon dioxide content may also be specified (ASTM D 1945 and ASTM D 1946); an upper limit is commonly 5% by volume in sales gas.

There are also a few reported cases of carbonyl sulfide (also called carboxy sulfide, COS) in natural gas.

Alterations of organic substances by methanogenic bacteria, the thermal degradation of kerogen and coal, and the cracking of oil in reservoirs are the primary formation mechanisms for hydrocarbon gases (HC), and sour gasses as CO_2 and H_2S.

Natural gas is usually considered methane (CH_4), and hence natural gas liquids are the higher molecular weight hydrocarbons. They are not true liquids in the sense that they are not usually in the liquid form at ambient temperature and pressure. Thus, natural gas liquids are defined as

(1) ethane

(2) liquefied petroleum gas

(3) natural gasoline.

The liquefied petroleum gas is usually composed of propane (C_3H_8), butanes (C_4H_{10}), and/or mixtures thereof; small amounts of ethane and pentane may also be present as impurities. On the other hand, natural gasoline (like refinery gasoline) consists mostly of pentane (C_5H_{12}) and higher molecular weight hydrocarbons. The term "natural gasoline" has also on occasion in the gas industry been applied to mixtures of liquefied petroleum gas, pentanes, and higher molecular weight hydrocarbons. Caution should be taken not to confuse the term "natural gasoline" with the term "straight-run gasoline" (often also incorrectly referred to as natural gasoline), which is the gasoline distilled unchanged from petroleum.

There are also standards for the liquid content of natural gas that are usually set by mutual agreement between the buyer and the seller, but such specifications vary widely and can only be given approximate limits. For example, ethane may have a maximum methane content of 1.5% by volume and a maximum carbon dioxide content of 0.28% by volume. On the other hand, propane is specified to have a minimum of 95% propane by volume, a maximum of 1 - 2% butane, and a maximum vapor pressure that limits ethane content. For butane, the percentage of one of the butane isomers is usually specified along with the maximum amounts of propane and pentane.

Other properties that may be specified are vapor pressure, specific gravity, corrosivity, dryness, and sulfur content. The specifications for the propane-butane mixtures have limits on the amount of the nonhydrocarbons, and in addition the maximum isopentane content is usually stated.

Natural gasoline may be sold on the basis of vapor pressure or on the basis of actual composition, which is determined from the Reid vapor pressure-composition curves prepared for each product source (ASTM D 323).

1.3.3.2. Inorganic gasses

Nitrogen (N_2)

Nitrogen (N_2) gas are present in most natural gas reservoirs.

Nitrogen is the chemical element with the symbol N and atomic number 7. Nitrogen is the lightest member of group 15 of the periodic table, often called the pnictogens. It is a common element in the universe, estimated at about seventh in total abundance in the Milky Way and the Solar System.

At standard temperature and pressure, two atoms of the element bind to form dinitrogen, a colorless and odorless diatomic gas with the formula N_2. Dinitrogen forms about 78% of Earth's atmosphere, making it the most abundant uncombined element, Fig. 1.22.

Nitrogen occurs in all organisms, primarily in amino acids (and thus proteins), in the nucleic acids (DNA and RNA) and in the energy transfer molecule adenosine triphosphate.

The human body contains about 3% nitrogen by mass, the fourth most abundant element in the body after oxygen, carbon, and hydrogen. The nitrogen cycle describes movement of the element from the air, into the biosphere and organic compounds, then back into the atmosphere.
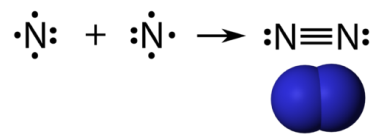

Fig. 1.22. Nitrogen molecule structure

Many industrially important compounds, such as ammonia, nitric acid, organic nitrates (propellants and explosives), and cyanides, contain nitrogen. The extremely strong triple bond in elemental nitrogen (N≡N), the second strongest bond in any diatomic molecule after carbon monoxide (CO), dominates nitrogen chemistry. This causes difficulty for both organisms and industry in converting N_2 into useful compounds, but at the same time means that burning, exploding, or decomposing nitrogen compounds to form nitrogen gas releases large amounts of often useful energy. Synthetically produced ammonia and nitrates are key industrial fertilizers, and fertilizer nitrates are key pollutants in the eutrophication of water systems.

Origin of nitrogen molecules in natural gas

Nitrogen is one of the most common non-hydrocarbons in natural gas, whose physical properties are much like hydrocarbons rather than other non-hydrocarbons. In the 1950s, the majority of research efforts were on the composition and occurrence of nitrogen in natural gas. Then the origin of nitrogen molecules, depending on the gas and isotope geochemical methods, attracted a lot of attention, followed by the discovery of numerous high N_2 gas reservoirs [33, 43, 35].

Overall, nitrogen in natural gases has been studied based on their constituents, volume ratio of components, stable isotopes and associated geological settings [36, 37]. For example, Dai et al. [38] compared 1000 gas samples and discovered that 76% of them have less than 4% nitrogen content, and 86% of them have less than 8% nitrogen.

Nitrogen and methane, whose molecular weight are smaller than those of heavy hydrocarbons (C2+), are easily transported and preserved during the process of gas-forming reservoirs [39], which greatly facilitates the discovery of giant scale gas reservoirs with high N_2 content. In addition, the increasing attention paid to non-hydrocarbons in natural gas will help to solve a series of problems in geological theories and reduce the investment risks encountered with high content non-hydrocarbons in exploration and production.

As the largest oil and gas inland basin in China, Tarim Basin has relatively high N_2 content (i.e., in Donghetang gas field) and complex N_2 distribution in its natural gas, which may lead to high risk of exploration. Therefore, it is important to classify the genetic types and regional distribution of nitrogen for the natural gas in the area.

107 natural gas samples from Tarim Basin were collected and measured their chemical and isotopic compositions. The N_2 contents vary widely.

Based on the carbon isotopic composition of gas hydrocarbons, the natural gases were classified into two genetic types: (1) coal-type and (2) oil-type gases, and the latter have consistently higher nitrogen contents than the former. Furthermore, according to the N_2 content, stable carbon and nitrogen isotope composition, three groups of N_2 sources were identified:

(I) Coal-type gas in Cenozoic reservoirs has low N_2 contents ($N_2 < 5\%$), less depleted carbon and nitrogen isotope compositions ($\delta^{13}C_2 > -26‰$, $\delta^{15}N > +5.0‰$). These nitrogen molecules likely come from ammonium montmorillonites and thermal degradation of aromatic and heterocyclic structures of anthracite.

(II) Oil-type gas with moderate N_2 contents ($5\% < N_2 < 20\%$) and relatively depleted carbon isotopes ($\delta^{13}C_2 = -36‰$ to $-29‰$, $\delta^{15}N = -6.0‰$ to $+6.0‰$), distributed in the gas fields of Yakela, Hetianhe, Lungu, Jiefagnqu, Jilake, etc. and preserved in Paleozoic and Mesozoic, with N_2 likely originating from ammonium clays, evaporate and thermal decomposition of organic matter at the high- and over-mature stage.

(III) Oil-type gas with high N_2 content ($N_2 > 20\%$), depleted carbon ($\delta^{13}C_2 < -34‰$) and widely varying nitrogen isotope compositions ($-15‰ < \delta^{15}N < +15‰$), located in Paleozoic and Mesozoic intervals such as Tazhong, Donghetang, Hade and Lunnan gas fields, etc. This high concentration of N_2 is mainly derived from Cambria–Ordovician shale carbonates at mature and highly mature stages, and the N_2 contents tend to increase with increasing thermal stress.

A broad correlation between N_2 content and $^3He/^4He$ ratio and helium concentration was also provided which indicates that a deep N_2 gas source may be relevant.

Hydrogen sulfide (H_2S)

Hydrogen sulfide is the chemical compound with the formula H_2S. It is a colorless chalcogen hydride gas with the characteristic foul odor of rotten eggs. It is very poisonous, corrosive, and flammable, Fig. 1.23.
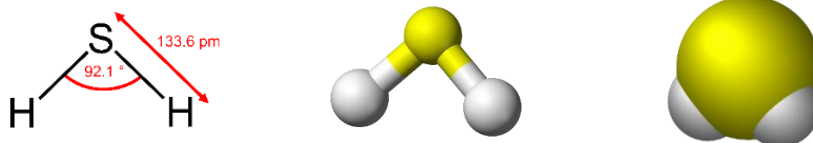

Fig. 1.23. Chemical structure of hydrogen sulfide (H_2S)

Hydrogen sulfide is often produced from the microbial breakdown of organic matter in the absence of oxygen gas, such as in swamps and sewers; this process is commonly known as anaerobic digestion which is done by sulfate-reducing microorganisms. H_2S also occurs in volcanic gases, natural gas, and in some sources of well water. The human body produces small amounts of H_2S and uses it as a signaling molecule. Natural gases containing hydrogen sulfide are, like petroleum products that contain hydrogen sulfide or mercaptans, termed "sour". H_2S in water will create an acidic environment and could influence the initial reservoir pH.

$$H_2S + H_2O \longrightarrow H_3O^+ + HS^-$$
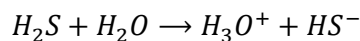
Dissolution of gasses in water increases with increasing pressure, while the dissolution decreases with increasing temperature.

Those natural gases that are free of hydrogen sulfide are called "sweet."

Hydrogen sulfide is most commonly obtained by its separation from sour gas, which is natural gas with a high content of H_2S. It can also be produced by treating hydrogen with molten elemental sulfur at about 450 °C. Hydrocarbons can serve as a source of hydrogen in this process. Sulfate-reducing (resp. sulfur-reducing) bacteria generate usable energy under low-oxygen conditions by using sulfates (resp. elemental sulfur) to oxidize organic compounds or hydrogen; this produces hydrogen sulfide as a waste product.

The hydrogen sulfide concentration in natural gas usually varies from barely detectable quantities to more than 0.3% (3000 ppm). Other sulfur derivatives are not usually present in insignificant quantities and may occur in only trace amounts. Thus, a sulfur removal process must be very precise since natural gas contains only a small amount: most consumers of natural gas require less than 4 ppm (parts per million) in the gas.

In the atmosphere, H_2S could be oxidized to Sulfur dioxide (SO_2) in the presence of water (H_2O);

$$2H_2S + O_2 \longrightarrow 2H_2O + 2SO_2$$
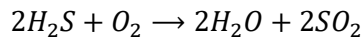
It is a toxic gas responsible for the smell of burnt matches. It is released naturally by volcanic activity and is produced as a by-product of copper extraction and the burning of fossil fuels contaminated with sulfur compounds. Sulfur dioxide is fairly soluble in water, and by both IR and Raman spectroscopy; the hypothetical sulfurous acid, H_2SO_3, is not present to any extent. However, such solutions do show spectra of the hydrogen sulfite ion, HSO_3^-, by reaction with water, and it is in fact the actual reducing agent present:

$$2SO_2 + H_2O \longrightarrow HSO_3^- + H^+$$
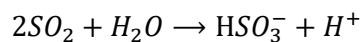
Sulfur dioxide is a major air pollutant and has significant impacts upon human health. In addition, the concentration of sulfur dioxide in the atmosphere can influence the habitat suitability for plant communities, as well as animal life. Sulfur dioxide emissions are a precursor to acid rain and atmospheric particulates. Due largely to the US EPA's Acid Rain Program, the U.S. has had a 33% decrease in emissions between 1983 and 2002. This improvement resulted in part from flue-gas desulfurization, a technology that enables SO_2 to be chemically bound in power plants burning sulfur-containing coal or oil. In particular, calcium oxide (lime) reacts with sulfur dioxide to form calcium sulfite:

$$CaO + SO_2 + H_2O \longrightarrow CaSO_3 + H^+$$
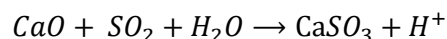
Aerobic oxidation of the $CaSO_3$ gives $CaSO_4$, anhydrite. Most gypsum sold in Europe comes from flue-gas desulfurization.

Origin of Hydrogen sulfide in HC gasses:

Hydrogen sulfide is generally an undesirable component of natural gas and is highly toxic and corrosive to production equipment.

Different mechanisms have been suggested for H_2S formation [40–53]. Bacterial sulfate reduction (BSR) and thermochemical sulfate reduction (TSR) are the two main processes resulting in high H_2S production in oil and gas fields although mantle and volcanic outgassing kerogen decomposition, oil thermal cracking, and asphaltene thermal degradation may also contribute. Under appropriate temperatures, salinities, oxygen content, and nutrient levels, H_2S can be formed in small amounts by bacteria (BSR) [54–56]. H_2S can also be of organic origin and upon thermal maturation formed from the sulfur in kerogen or oil [57–59]

As a result of the reaction of anhydrite with petroleum fluids or methane at temperatures of 120 – 145°C, H_2S is additionally formed by TSR [56].

Carbon dioxide (CO₂)

CO_2 is a colorless gas with a density about 60% higher than that of dry air. Carbon dioxide is odorless at normally encountered concentrations. However, at high concentrations, it has a sharp and acidic odor. Carbon dioxide consists of a carbon atom covalently double bonded to two oxygen atoms, Fig. 1.24.

It occurs naturally in Earth's atmosphere as a trace gas. The current concentration is about 0.04% (410 ppm) by volume, having risen from pre-industrial levels of 280 ppm. Natural sources include volcanoes, hot springs and geysers, and it is freed from carbonate rocks by dissolution in water and acids. Because carbon dioxide is soluble in water, it occurs naturally in groundwater, rivers and lakes, ice caps, glaciers and seawater. It is present in deposits of petroleum and natural gas.
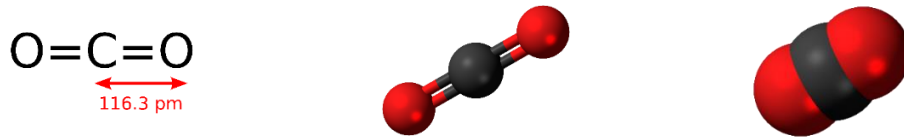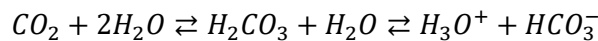

O=C=O
116.3 pm

Fig. 1.24. Chemical structure of Carbon dioxide

Most HC reservoir fluids contain some CO_2, and the dissolution of CO_2 in water or brines increases with increasing pressure and decreases with increasing temperature. Carbon dioxide dissolved in water will give Carbonic Acid (H_2CO_3) and will influence reservoir pH.

$$CO_2 + 2H_2O \rightleftarrows H_2CO_3 + H_2O \rightleftarrows H_3O^+ + HCO_3^-$$

Carbon dioxide has no heating value, and its removal may be required in some instances (when acid properties are of a lesser issue) to increase the energy content (Btu/ scf) of the gas. For gas being sent to cryogenic plants (LNG), removal of carbon dioxide is necessary to prevent solidification of the carbon dioxide.

Origin of Carbon dioxide in HC gasses:

Origin of CO_2 in natural gas can be divided into two types, organic and inorganic.

CO_2 of organic origin is derived mainly from the decomposition of organic matters and the bacterial activities, whereas that of inorganic origin is mainly derived from the magmatism, thermal decomposition [60,61], and the dissolution of carbonate rocks [62].

CO_2 formation can be related to the degradation of organic matter, the thermal decarbonation of calcite at 200- 250°C, and/or the decomposition of carbonate or reactions between certain minerals at 230- 320°C [63] (Petrucci et al., 1994); it can also be of mantle origin [64] (Javoy et al., 1986). Zhu et al. [53] proposed a mixed origin for CO_2 from TSR and carbonate decomposition through acidolysis.

Hydrate formation

Both hydrogen sulfide and carbon dioxide promote hydrate formation, and the presence of carbon dioxide may be less desirable for this reason.

Removal of CO_2 and H_2S could reduce Hydrate potential and should be encountered for during design of production systems.

Hydrate will be discussed more in detail later in the Gas chapter.

1.4 References

[1] Gruse, W. A. , and Stevens, D. R. (1960). The Chemical Technology of Petroleum, McGraw-Hill, New York.

[2] Charbonnier, R. P., Draper, R. G., Harper, W. H., and Yate s, A. (1969). Analyses and Characteristics of Oil Samples from Alberta, Information Circular IC 232, Department of Energy Mines and Resources, Mines Branch, Ottawa.

[3] Camp, F. W. (1976). The Tar Sands of Alberta, Cameron Engineers, Denver, Colorado.

[4] Bunger, J. W., Thomas, K. P., and Dorrence, S. M. (1979). Fuel 58:183.

[5] Meyer, R. F., and Steele, C. T. (1981). The Future of Heavy Crude and Tar Sands, McGraw-Hill, New York.

[6] Wallace, D., Starr, J., Thomas, K. P., and Dorrence, S. M. (1988). Characterization of Oil Sands Resources, Alberta Oil Sands Technology and Research Authority, Edmonton, Alberta.

[7] Rossini, F. D., Mair, B. J., and Streiff, A. J. (1953). HydrocarbonsfromPetroleum, Reinhold, New York.

[8] Brooks, B. T., Kurtz, S. S., Jr., Boord, C. E., and Schmerling, L. (1954). The Chemistry of Petroleum Hydrocarbons, Reinhold, New York.

[9] Lochte, H. L., and Littmann, E. R. (1955). The Petroleum Acids and Bases, Chemical Publishing, New York.

[10] Schwartz, R. D., and Brasseaux, D. J. (1958). Anal. Chem. 30:1999.

[11] Brandenburg, C. R., and Latham, D. R. (1968). J. Chem. Eng. Data 13:391.

[12] Rall, H. T., Thompson, C. J., Coleman, H. J., and Hopkins, R. L. (1 972). Bulletin 659, Bureau of Mines, U.S. Department of the Interior, Washington, D. C.

[13] Rossini, F. D., and Mair, B. J. (1959). Proc. Fifth World Petroleum Cong., 5:223.

[14] Bestougeff, M. A. (1961). J. Etudes Methodes Separation Immediate Chromatogr. C. R .. Paris, p. 55.

[15] Treibs, A. (1934). Ana/en 509: 103.

[16] Glebovskaya, F. A., and Volkenshtein, M. V. (1948). J. Gen. Chem. USSR 18: 1440- 1451.

[17] Falk, J.E. (1964). Porphyrins and Metalloporphyrins, Elsevier, New York.

[18] Smith, K. M. (1975). Porphyrins and Metalloporphyrins, Elsevier, New York.

[19] Bonnett, R. (1978). In The Porphyrins, Vol. I. Structure and Synthesis, Part A. (D. Dolphin, ed.), Academic Press, New York.

[20] Franceskin, P. J., Gonzalez-Jiminez, M. G., DaRosa, F., Adams, 0 ., and Katan, L. (1986). Hyperfine Interactions 28:825- 828.

[21] Hodgson, G. W., Baker, B. L., and Peake, E. (1967). Fundamental Aspects of Petroleum Geochemistry (B . Nagy and U. Columbo, eds.), Elsevier, Amsterdam, p. 177.

[22] Baker, E. W. (1969). Organic Geochemistry (G. Eglinton and M. T. J. Murphy, eds.), SpringerVerlag, New York.

[23] Baker, E. W., and Palmer, S. E. (1978). The Porphyrins, Vol. I, Structure and Synthesis, Part A (D. Dolphin, ed.), Academic Press, New York.

[24] Baker, E. W., and Louda, J. W. (1986). Biological Markers in the Sedimentary Record (R. B. Johns, ed.), Elsevier, Amsterdam.

[25] Filby, R. H., and Van Berke!, G. J. (1987). Metal Complexes in Fossil Fuels (R. H. Filby and J. F. Branthaver, eds.), Symposium Series No. 344, American Chemical Society, Washington, D.C., p. 2 .

[26] Quirke, J.M. E. (1987). Metal Complexes in Fossil Fuels (R. H. Filby and J. F. Branthaver, eds.), Symposium Series No. 344, American Chemical Society, Washington, D.C., p. 74.

[27] Dunning, H. N., Moore, J. W., Bieber, H., and Williams, R. B. (1960). J. Chem. Eng. Data 5:547.

[28] Erdman, J. G., and Harju, P. H. (1963). J. Chem. Eng. Data 8:252.

[29] Crouch, F. W., Sommer, C. S., Galobardes, J. F., Kraus, S., Schmauch, E. M., Galobardes, M., Fatmi, A. , Pearsall, K., and Rogers, L.B. (1983). Separation Sci. Technol. 18:603.

[30] Fish, R. H., Konlenic, J. J., and Wines, B. K. (1984). Anal. Chem. 56:2452.

[31] Reynolds, J. G., Biggs, W. E., and Bezman, S. A. (1987). Metal Complexes in Fossil Fuels (R.H. Filby and J. F. Branthaver, eds.), Symposium Series No. 344, American Chemical Society, Washington, D.C., p. 205.

[32] Goulon, J., Retoumard, A., Frient, P., Goulon-Ginet, C., Berthe, C. K., Muller, J. R. , Ponce!, J. L., Guilard, R., Escalier, J. C., and Neff, B. (1984). J. Chem. Soc . Dalton Trans. 1095 .

[33] Hoering, T.C., Moore, H., 1958. The isotopic composition of the nitrogen in natural gases and associated crude oils. Geochim. Cosmochim. Acta 13, 225–232.

[34] Littke, R., Krooss, B.M., Idiz, E., Frielingsdorf, J., 1995. Molecular nitrogen in natural gas accumulations: generation from sedimentary organic matter at high temperatures. AAPG Bull. 79 (3), 410–430.

[35]Stahl, W.J., 1977. Carbon and nitrogen isotope in hydrocarbon research and exploration. Chem. Geol. 20, 121–149.

[36] Krooss, B.M., et al., 1995. Generation of nitrogen and methane from sedimentary organic matter: implications on the dynamics of natural gas accumulations. Chem. Geol. 126 (3–4), 291–318.

[37] Xu, Y., Shen, P., 1996. A study of natural gas origins in China. AAPG Bull. 80 (10), 1604–1614.

[38] Dai, J., Pei, X., Qi, H., 1992. Natural Gas Geology of China. PetroleumIndustry Press, Beijing. (In Chinese).

[39] Getz, F.A., 1977.Molecular nitrogen: clue in coal-derived-methane hunt. Oil Gas J. 75 (17), 220–221.

[40] Krouse, H.R., Viau, C.A., Eliuk, L.S., Ueda, A., Halas, S., 1988. Chemical and isotopic evidence of thermochemical sulfate reduction by light hydrocarbon gases in deep carbonate reservoirs. Nature 333, 415-419.

[41] Machel, H.G., Krouse, H.R., Sassen, R., 1995. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. Appl. Geochem. 10, 373-389.

[42] Worden, R.H., Smalley, P.C., 1996. H2S-producing reactions in deep carbonate reservoirs: Khuff Formation, Abu Dhabi. Chem. Geol. 133, 157-171.

[43] Worden, R.H., Smalley, P.C., Cross, M.M., 2000. The influence of rock fabric and mineralogy on thermochemical sulfate reduction: Khuff Formation, Abu Dhabi. J. Sediment. Res. 70, 1210-1221.

[44] Heydari, E., 1997. The role of burial diagenesis in hydrocarbon destruction and H2S accumulation, upper Jurassic Smackover Formation, Black Creek Field, Mississippi. AAPG Bull. 81, 25e45.

[45] Manzano, B.K., Fowler, M.G., Machel, H.G., 1997. The influence of thermochemical sulfate reduction on hydrocarbon composition in Nisku reservoirs, Brazeau River area, Alberta, Canada. Org. Geochem. 27, 507-521.

[46] Belenitskaya, G.A., 2000. Distribution pattern of hydrogen sulfide-bearing gas in the former Soviet Union. Pet. Geosci. 6, 175-187.

[47] Machel, H.G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings - old and new insights. Sediment. Geol. 140, 143-175.

[48] Cai, K.P.,Wang, Y.R., Yang, Y.M., Zhang, Z.R., 2003. Evaluation of Permian and Triassic hydrocarbon source rock and gas source analysis in Guang-Wang region of northwestern Sichuan Basin. Nat. Gas Ind. 23, 10-14.

[49] Cai, C., Xie, Z., Worden, R.H., Hu, G., Wang, L., He, H., 2004. Methane-dominated thermochemical sulphate reduction in the Triassic Feixiangun Formation East Sichuan Basin, China: towards prediction of fatal H2S concentration. Mar. Pet. Geol. 21, 1265-1279.

[50] Zhang, S.C., Zhu, G.Y., Liang, Y.B., Dai, J.X., Liang, H.B., Li, M.W., 2005. Geochemical characteristics of the Zhaolanzhuang sour gas accumulation and thermochemical sulfate reduction in the Jixian Sag of Bohai Bay Basin. Org. Geochem. 36, 1717-1730.

[51] Zhu, G.Y., Zhang, S.C., Liang, Y.B., Dai, J.X., Li, J., 2005. Isotopic evidence of TSR origin for natural gas bearing high H2S contents within the Feixianguan Formation of the Northeastern Sichuan Basin, southwestern China. Sci. China 48, 1037-1046.

[52] Zhu, G.Y., Zhang, S.C., Liang, Y.B., Zhou, G.Y., Wang, Z.J., 2007. Origin mechanism and controlling factors of natural gas reservoir of Jialingjiang Formation in Eastern Sichuan Basin. Acta Geol. Sin. 81, 805-817.

[53] Zhu, G.Y., Zhang, S.C., Huang, H., Liang, Y.B., Meng, S., Li, Y., 2011. Gas genetic type and origin of hydrogen sulfide in the Zhongba gas field of the western Sichuan Basin, China. Appl. Geochem. 26, 1261-1273.

[54] Hose, D.L., Palmer, A.N., Palmer, M.V., Northup, D.E., Boston, P.J., DuChene, H.R., 2000. Microbiology and geochemistry in a hydrogen-sulphide-rich karst environment. Chem. Geol. 169, 399e423.

[55] Paul, A., Boashun, F., 2000. Microbial sulfate reduction rates and sulfur and oxygen isotope fractionations at oil and gas seeps in deep water Gulf of Mexico. Geochim. Cosmochim. Acta 64, 233-246.

[56] Cai, C., Hu, W., Worden, R., 2001. Thermochemical sulphate reduction in Cambro-Ordovician carbonates in Central Tarim. Mar. Pet. Geol. 18, 729-741.

[57] Orr,W.L.,1974. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation-study of Big Horn Basin paleozoic oils. Part1.AAPGBull.58,2295-2318.

[58] Orr, W.L., 1977. Geologic and geochemical controls on the distribution of hydrogen sulfide in natural gas. In: Campos, R., Goni, J. (Eds.), Advances in Organic Geochemistry. empressa nacional adaro de investigaciones mineras, Madrid, pp. 571-597.

[59] Hunt, J.M., 1996. Petroleum Geochemistry and Geology, second ed. Freeman, San Francisco. New York.

[60] Dai J X, Song Y, Dai C S, et al. Geochemistry and accumulation of carbon dioxide gases in China. AAPG Bull, 1996, 80: 1615−1626

[61] Wycherley H, Fleet A, Shaw H. Some observations on the origins of large volumes of carbon dioxide accumulations in sedimentary basins. Mar Pet Geol, 1999, 16: 489−494

[62] Huang S J, Huang K K, Tong H P, et al. Origin of CO2 in natural gas from the Triassic Feixianguan Formation of Northeast Sichuan Basin. Sci China Earth Sci, 2010, 53: 642−648

[63] Petrucci, E., Gianelli, G., Puxeddu, M., Iacumin, P., 1994. An oxygen study of silicates in the Larderello Gethermal Field, Italy. Geothermics 23, 327e337

[64] Javoy, M., Pineau, F., Delorme, H., 1986. Carbon and nitrogen isotopes in the mantle. Chem. Geol. 57, 41e62.