CHAPTER

2

The Physical and Chemical Properties of Petroleum

Petroleum exploration is largely concerned with the search for oil and gas, two of the chemically and physically diverse group of compounds termed the *hydrocarbons*. Physically, hydrocarbons grade from gases, via liquids and plastic substances, to solids. The hydrocarbon gases include dry gas (methane) and the wet gases (ethane, propane, butane, etc.). Condensates are hydrocarbons that are gaseous in the subsurface, but condense to liquid when they are cooled at the surface. Liquid hydrocarbons are termed *oil, crude oil,* or just *crude,* to differentiate them from refined petroleum products. The plastic hydrocarbons include asphalt and related substances. Solid hydrocarbons include coal and kerogen. Gas hydrates are ice crystals with peculiarly structured atomic lattices, which contain molecules of methane and other gases. This chapter describes the physical and chemical properties of natural gas, oil, and the gas hydrates; it is a necessary prerequisite to Chapter 5, which deals with petroleum generation and migration. The plastic and solid hydrocarbons are discussed in Chapter 9, which covers the tar sands and oil shales.

The earth's atmosphere is composed of natural gas. In the oil industry, however, natural gas is defined as "a mixture of hydrocarbons and varying quantities of nonhydrocarbons that exist either in the gaseous phase or in solution with crude oil in natural underground reservoirs." The foregoing is the definition adopted by the American Petroleum Institute (API), the American Association of Petroleum Geologists (AAPG), and the Society of Petroleum Engineers (SPE). The same authorities subclassify natural gas into dissolved, associated, and nonassociated gas. Dissolved gas is in solution in crude oil in the reservoir. Associated gas, commonly known as gas cap gas, overlies and is in contact with crude oil in the reservoir. Nonassociated gas is in reservoirs that do not contain significant quantities of crude oil. Natural gas liquids, or NGLs, are the portions of the reservoir gas that are liquefied at the surface in lease operations, field facilities, or gas processing plants. NGLs include, but are not limited to, ethane, propane, butane, pentane, natural gasoline, and condensate. Basically, natural gases encountered in the subsurface can be classified into two groups: those of organic origin and those of inorganic origin (Table 2.1).

Gases are classified as *dry* or *wet* according to the amount of liquid vapor that they contain. A dry gas may be arbitrarily defined as one with less than 0.1 gal/1000 ft^3 of condensate; chemically, dry gas is largely methane. A wet gas is one with more than 0.3 gal/1000 ft^3 of

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TABLE 2.1 Natural Gases and Their Dominant Modes of Formation

Gas			Dominant source
Inert gases	Helium		Inorganic
	Argon		
	Krypton		
	Radon		
	Nitrogen		
	Carbon dioxide		Mixed
	Hydrogen sulfide		
	Hydrogen		Mainly organic
Hydrocarbons	Methane	dry gas	
	Ethane	wet gases	
	Propane		
	Butane		

condensate; chemically, these gases contain ethane, butane, and propane. Gases are also described as *sweet* or *sour*, based on the absence or presence, respectively, of hydrogen sulfide.

2.1 NATURAL GASES

2.1.1 Hydrocarbon Gases

The major constituents of natural gas are the hydrocarbons of the paraffin series (Table 2.2). The heavier members of the series decline in abundance with increasing molecular weight. Methane is the most abundant; ethane, butane, and propane are quite common, and paraffins with a molecular weight greater than pentane are the least common. Methane (CH_4) is also known as *marsh gas* if found at the surface or *fire damp* if present down a coal mine. Traces of methane are commonly recorded as shale gas or background gas during the drilling of all but the driest of dry wells. Methane is a colorless, flammable gas, which is produced (along with other fluids) by the destructive distillation of coal. As such, it was commonly used for domestic purposes in Europe until replaced by natural gas, itself largely composed of methane. Methane is the first member of the paraffin series. It is chemically nonreactive, sparingly soluble in water, and lighter than air (0.554 relative density).

Methane forms in three ways. It may be derived from the mantle, it may form from the thermal maturation of buried organic matter, and it may form by the bacterial degradation of organic matter at shallow depths. Geochemical and isotope analysis can differentiate the source of methane in a reservoir. Mantle-derived methane is differentiated from biogenically sourced methane from the carbon 12:13 ratio. Methane occurs as a by-product of bacterial

TABLE 2.2 Significant Data of the Paraffin Series

Name	Formula	Molecular weight	Boiling point at atmospheric pressure (°C)	Solubility (g/10°g water)
Methane	CH_4	16.04	−162	24.4
Ethane	C_2H_6	30.07	−89	60.4
Propane	C_3H_8	44.09	−42	62.4
Isobutane	C_4H_{10}	58.12	−12	48.9
n-Butane	C_4H_{10}	58.12	−1	61.4
Isopentane	C_5H_{12}	72.15	30	47.8
n-Pentane	C_5H_{12}	72.15	36	38.5
n-Hexane	C_6H_{14}	86.17	69	9.5

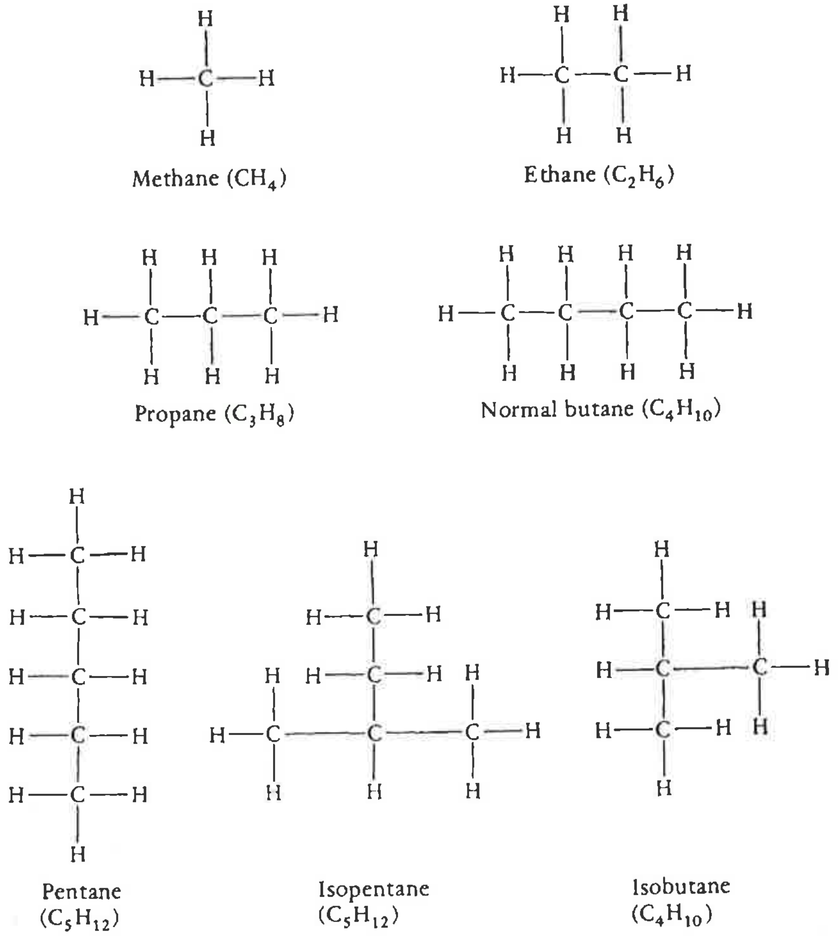
decay of organic matter at normal temperatures and pressures. This biogenic methane has considerable potential as a source of energy. It has been calculated that some 20% of the natural gas produced today is of biogenic origin (Rice and Claypool, 1981). In the nineteenth century, eminent Victorians debated the possibility of lighting the streets of London with methane from the sewers. Today's avant-garde agriculturalists acquire much of the energy needed for their farms by collecting the gas generated by the maturation of manure. Methane generated by waste fills (garbage) is now pumped into the domestic gas grid in many countries. Biogenic methane is commonly formed in the shallow subsurface by the bacterial decay of organic-rich sediments. As the burial depth and temperature increase, however, this process diminishes and the bacterial action is extinguished. The methane encountered in deep reservoirs is produced by thermal maturation of organic matter. This process is discussed in detail later in Chapter 5.

The other major hydrocarbons that occur in natural gas are ethane, propane, butane, and occasionally pentane. Their chemical formulas and molecular structure are shown in Fig. 2.1. Their occurrence in various gas reservoirs is given in Table 2.3. Unlike methane these heavier members of the paraffin series do not form biogenically. They are only produced by the thermal maturation of organic matter. If their presence is recorded by a gas detector during the drilling of a well, it often indicates proximity to a significant petroleum accumulation or source rock.

2.1.2 Nonhydrocarbon Gases

2.1.2.1 Inert Gases

Helium is a common minor accessory in many natural gases, and traces of argon and radon have also been found in the subsurface. Helium occurs in the atmosphere at 5 ppm and has also been recorded in mines, hot springs, and fumaroles. It has been found in oil field gases in amounts of up to 8% (Dobbin, 1935). In North America helium-enriched natural gases occur in the Four Corners area and Texas panhandle of the United States and in Alberta



Methane (CH_4)

Ethane (C_2H_6)

Propane (C_3H_8)

Normal butane (C_4H_{10})

Pentane (C_5H_{12})

Isopentane (C_5H_{12})

Isobutane (C_4H_{10})

FIGURE 2.1 Molecular structures of the more common hydrocarbon gases.

and Saskatchewan, Canada (Lee, 1963; Hitchon, 1963). In Canada the major concentrations occur along areas of crustal tension, such as the Peace River and Sweetwater arches, and the foothills of the Rocky Mountains. Other regions containing helium-enriched natural gases include Poland, Alsace, and Queensland in Australia. Helium is known to be produced by the decay of various radioactive elements, principally uranium, thorium, and radium. The rates of helium production for these elements are shown in Table 2.4. Rogers (1921) calculated that between 282 and 1.06 billion ft^3 of helium are generated annually. Based on these data, the helium found in natural gas is widely believed to have emanated from deep-seated basement rocks, especially granite. Although the actual rate of production is slow and steady, the expulsion of gas into the overlying sediment cover may occur rapidly when the basement is subjected to thermal activity or fracturing by crustal arching.

Ideally it would be useful to demonstrate a correlation between helium-enriched natural gases and radioactive basement rocks. This correlation is generally difficult to establish

TABLE 2.3 Chemical Composition of Various Gas Fields

	Composition									
Field and area	**Methane**	**Ethane**	**Propane**	**Butane**	**Pentane$^+$**	**Co$_2$**	**N**	**H_2S**	**He**	**References**
SOUTHERN N. SEA BASIN										
Groningen	81.3	2.9	0.4	0.1	0.1	0.9	14.3	Tr[a]	Tr	Cooper (1977, 1975)
Hewett	83.2	5.3	2.1	0.4	0.5	0.1	8.4	Tr	Tr	Cumming and Wyndham (1975)
West Sole	94.4	3.1	0.5	0.2	0.2	0.5	1.1			Butler (1975)
ALGERIA										
Hassi-R'Mel	83.5	7.0	2.0	0.8	0.4	0.2	6.1			Maglione (1970)
FRANCE										
Lacq	69.3	3.1	1.1	0.6	0.7	9.6	0.4	15.2		Cooper (1977)
CANADA										
Turner Valley	92.6	4.1	2.5	0.7	0.13					Slipper (1935)
U.S.A.										
Panhandle	91.3	3.2	1.7	0.9	0.56	0.1			0.5	Cotner and Crum (1935)
Hugoton	74.3	5.8	3.5	1.5	0.6				Av.[b]	Keplinger et al. (1949)
TRINIDAD										
Barrackpore	95.65	2.25	1.55	0.80	0.25					Suter (1952)
VENEZUELA										
La Concepcion	70.9	8.2	8.2	6.2	3.7	2.8				Anon (1948)
Cumarebo	63.89	9.49	14.41	8.8	5.4					Payne (1951)
NEW ZEALAND										
Kapuni	46.2	5.2	2.0	0.6	44.9	1.0				Cooper (1975)
RUSSIA										
Baku	88.0	2.26	0.7	0.5	6.5					Shimkin (1950)
ABU DHABI										
Zakum	76.0	11.4	5.4	2.2	1.3	2.3	1.1	0.3.3		Cooper (1975)
IRAN										
Agha Jari	66.0	14.0	10.5	5.0	2.0	1.5	1.0			Cooper (1975)

[a] *Tr = trace.*

[b] *Av. = average.*

TABLE 2.4 Production Rates of Helium from Various Radioactive Elements

Radioactive substance	Helium production [g/(year)(mm^3)]
Uranium	2.75×10^{-5}
Uranium in equilibrium with its products	11.0×10^{-5}
Thorium in equilibrium with its products	3.1×10^{-5}
Radium in equilibrium with emanation, radium A, and radium C	158

From: Geology of Petroleum by Levorsen. © 1967 by W. H. Freeman and Company. Used with permission.

because helium tends to occur in deep, rather than shallow, wells, and there is seldom sufficient well control to map the geology of the basement. The major source of helium in the United States is the Panhandle·Hugoton field in Texas. This field locally contains up to 1.86% helium, and an extraction plant has been working since 1929 (Pippin, 1970). It is significant that this field produces helium from sediments pinching out over a major granitic fault block. Helium also occurs from the breakdown of uranium ore bodies within sedimentary sequences, for example, at Castlegate in Central Utah. Apart from helium, traces of other inert gases have been found in the subsurface. Argon occurs in the Panhandle Hugoton field (as does radon) and in Japan. Argon and radon are by-products of the radioactive disintegration of potassium and radium, respectively, and are believed to have an origin similar to that of helium.

Helium is of considerable economic significance because it is lighter than air and, because it is inert, is safer than hydrogen for use in dirigibles. Argon and radon are of little economic significance. Radon is a considerable environmental hazard, however, because its inhalation is a cause of lung cancer. Thus, regional maps of radon gas are prepared, and steps are taken to ameliorate radon gas invasion into houses by the use of impermeable membrane foundations. Radon health hazards are highest in areas of basement in general, and granites in particular (Durrance, 1986). The highest radon reading in the United Kingdom was recorded in the lavatory of a health center on the Dartmoor Granite of Devon.

Nitrogen is another nonhydrocarbon gas that frequently occurs naturally in the earth's crust. It is commonly associated both with the inert gases just described and with hydrocarbons. Nitrogen is found in North America in a belt stretching from New Mexico to Alberta and Saskatchewan. The Rattlesnake gas field of New Mexico is a noted example (Hinson, 1947) and has the following composition:

Nitrogen	72.6%
Methane	14.2%
Helium	7.6%
Ethane	2.8%
Carbon dioxide	2.8%
	100.0%

Note the association of nitrogen with helium. Nitrogen is also a common constituent of the Rotliegendes gases of the southern North Sea basin. Published accounts show ranges from 1 to 14% in the West Sole and Groningen fields, respectively (Butler, 1975; Stauble and Milius, 1970). Individual wells in the German offshore sector are reported to have encountered far higher quantities. The origin of nitrogen is less straightforward than that of the inert gases. Nitrogen has been recorded from volcanic emanations, but some studies have suggested that it may form organically, for example, by the bacterial degradation of nitrates via ammonia. Although chemically feasible, such biogenic nitrogen is likely to be produced only in shallow conditions, whereas in nature it occurs in deep hydrocarbon reservoirs. It has also been suggested that the thermal metamorphism of bituminous carbonates could generate both nitrogen and carbon dioxide. This mechanism has been postulated for the Beaverhill Lake formation of Alberta and Saskatchewan (Hitchon, 1963).

Several pieces of information suggest that the major source of nitrogen is basement, or more specifically, igneous rock. First, the association of nitrogen with basement-derived inert gases has been already noted. Second, in the southern North Sea basin nitrogen content is unrelated to the variation of the coal rank of the Carboniferous beds that sourced the hydrocarbon gases (Eames, 1975). The amount of nitrogen in Rotliegendes reservoirs appears to increase eastward across the basin in the direction of increased igneous intrusives. Another significant case has been described from southwestern Saskatchewan by Burwash and Cumming (1974). Natural gas produced from basal Paleozoic clastics contains 97% nitrogen, 2% helium, and 1% carbon dioxide. No associated hydrocarbons are found. The accumulation overlies an upstanding volcanic plug in metamorphic basement (Fig. 2.2). Taken together, these various lines of evidence suggest that nitrogen in natural gases are predominantly of inorganic origin, although organic processes may be significant generators of atmospheric and shallow nitrogen. Furthermore, some atmospheric nitrogen may have been trapped in sediments during deposition, occurring now as connate gas.

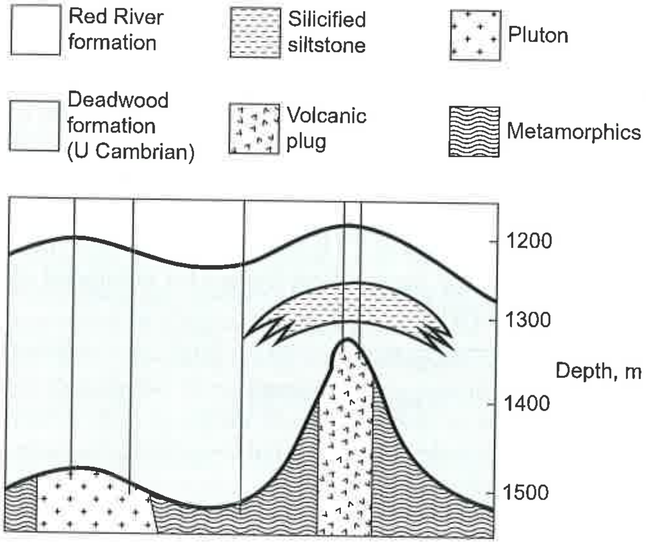


FIGURE 2.2 Cross section of the accumulation of nitrogen, helium, and carbon dioxide gases over a buried volcanic plug in southwestern Saskatchewan, Canada. *From Burwash and Cumming (1974), with permission from the Canadian Society of Petroleum Geologists.*

2.1.2.2 *Hydrogen*

Free hydrogen gas rarely occurs in the subsurface, partly because of its reactivity and partly because of its mobility. Nonetheless, one or two instances are known. More than 1.36 trillion ft^3 of hydrogen gas has been discovered in Mississippian rocks of the Forest City basin, Kansas. Analysis of the gas discovered revealed a composition of 40% hydrogen, 60% nitrogen, and traces of carbon dioxide, argon, and methane (Anonymous, 1948). Hydrogen is commonly dissolved in subsurface waters and in petroleum as traces, but it is seldom recorded in conventional analyses (Hunt, 1979, 1996). Subsurface hydrogen is probably produced by the thermal maturation of organic matter.

2.1.2.3 *Carbon Dioxide*

Carbon dioxide (CO_2) is often found as a minor accessory in hydrocarbon natural gases. It is also associated with nitrogen and helium, as shown by previously presented data. Natural gas accumulations in which carbon dioxide is the major constituent are common in areas of extensive volcanic activity, such as Sicily, Japan, New Zealand, and the Cordilleran chain of North America, from Alaska to Mexico. Levorsen (1967) cites a specific example from the Tensleep Sandstone (Pennsylvanian) of the Wertz Dome field, Wyoming:

Carbon dioxide	42.00%
Hydrocarbons	52.80%
Nitrogen	4.09%
Hydrogen sulfide	1.11%
	100.00%

Levorsen also quotes wells in New Mexico capable of producing up to 26 million ft^3/day of 99% pure carbon dioxide. Numerous natural accumulations of CO_2-dominant gas are located in the Colorado Plateau and Southern Rocky Mountain Region (Fig. 2.3). Some of these fields are produced for commercial purposes (e.g., McElmo Dome and Sheep Mountain, Colorado; Farnham Dome, Utah; Springerville, Arizona; Big Piney-LaBarge, Wyoming). The commercial uses of CO_2 include dry ice sales, industrial uses, and subsurface injection to enhance oil recovery. The McElmo Dome Field of the Paradox Basin, Colorado, is one of the world's largest known accumulations of nearly pure CO_2. The field produces from the Mississippian Leadville Limestone at average depths of 2100 m from approximately 60 wells. The field has produced over 3.3 trillion ft^3 and has reserves of 17 trillion ft^3. At present, more than 1.1 billion ft^3/day can be delivered to the Permian Basin (West Texas) for enhanced oil operations. The gas composition at McElmo Dome Field, Colorado, is:

Carbon dioxide	98.2%
Hydrocarbons	0.2%
Nitrogen	1.6%
	100.00%

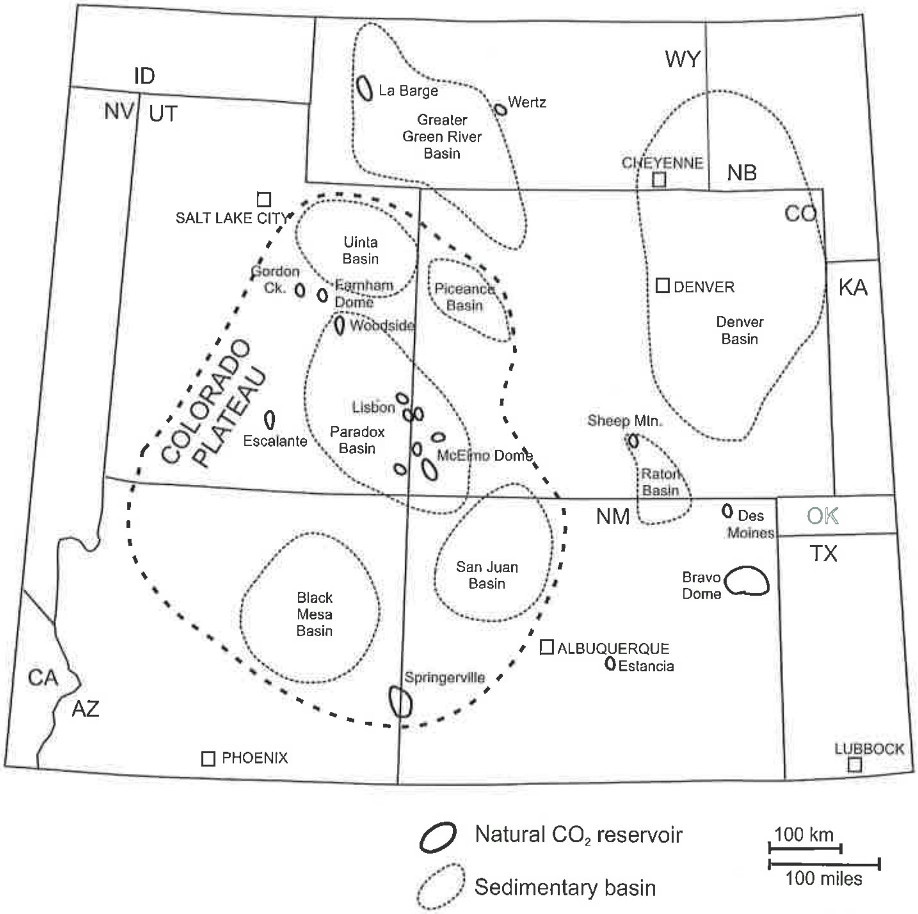


FIGURE 2.3 Natural CO_2 fields around the Colorado Plateau. *Modified from Allis et al. (2001).*

Both organic and inorganic processes can undoubtedly generate significant amounts of carbon dioxide in the earth's crust. Carbon dioxide is commonly recorded in natural gasess (Sugisaki et al., 1983). It may also be generated where igneous intrusives metamorphose carbonate sediments. Permeable limestones and dolomites can also yield carbon dioxide when they are invaded and leached by acid waters of either meteoric or connate origin. As described in Chapter 5, carbon dioxide is a normal product of the thermal maturation of kerogen, generally being expelled in advance of the petroleum. Carbon dioxide is also given off during the fermentation of organic matter as well as by the oxidation of mature organic matter due to either fluid invasion or bacterial degradation. Specifically, methane in the presence of oxygenated water may yield carbon dioxide and water:

$$3CH_4 + 6O_2 = 3CO_2 + 6H_2O.$$

Much of the carbon dioxide will remain in solution as carbonic acid. A duplex origin for carbon dioxide thus seems highly probable. In the past, carbon dioxide was generally of limited economic value, being used principally for dry ice. The recent application of carbon dioxide to enhance oil recovery has increased its usefulness (Taylor, 1983).

2.1.2.4 *Hydrogen Sulfide*

Hydrogen sulfide (H_2S) occurs in the subsurface both as free gas and, because of its high solubility, in solution with oil and brine. It is a poisonous, evil-smelling gas, whose presence causes operational problems in both oil and gas fields. It is highly corrosive to steel, quickly attacking production pipes, valves, and flowlines. Gas or oil containing significant traces of H_2S are referred to as *sour*—in contrast to sweet, which refers to oil or gas without hydrogen sulfide. Small amounts of H_2S are economically deleterious in oil or gas because a washing plant must be installed to remove them, both to prevent corrosion and to render the residual gas safe for domestic combustion. Extensive reserves of sour gas can be turned to an advantage, however, since it may be processed as a source of free sulfur. One analysis of a H_2S-rich gas from Emory, Texas, yielded the following composition (Anonymous, 1951):

Hydrogen sulfide	42.40%
Hydrocarbons	53.10%
Carbon dioxide	4.50%
	100.00%

Hydrogen sulfide is commonly expelled together with sulfur dioxide from volcanic eruptions. It is also produced in modern sediments in euxinic environments, such as the Dead Sea and the Black Sea. This process is achieved by sulfate-reducing bacteria working on metallic sulfates, principally iron, according to the following reaction:

$$2C + MeSO_4 + H_2O = MeCO_3 + CO_2 + H_2S,$$

where Me = metal. Note that sour gas generally occurs in hydrocarbon provinces where large amounts of evaporites are present. Notable examples include the Devonian basin of Alberta, the Paradox basin of Colorado, southwest Mexico, and extensive areas of the Middle East. Anhydrite may be converted to calcite in the presence of organic matter, the reaction leading to the generation of H_2S according to the following equation:

$$CaSO_4 + 2CH_2O = CaCO_3 + H_2O + CO_2 + H_2S,$$

where $2CH_2O$ = organic matter. There is a further interesting point about sour gas. Not only is it associated with evaporites but it is frequently associated with carbonates, generally reefal and lead–zinc sulfide ore bodies. A genetic link has long been postulated between these telethermal ores and evaporites (Davidson, 1965). Dunsmore (1973) has shown that the reduction of anhydrite to calcite and sour gas can occur inorganically, without the aid of bacteria. The reaction is an exothermic one, which may generate the high temperatures needed to mobilize the metallic sulfides.

2.2 GAS HYDRATES

2.2.1 Composition and Occurrence

Gas hydrates are compounds of frozen water that contain gas molecules (Kvenvolden and McMenamin, 1980). The ice molecules themselves are referred to as *clathrates* (Sloan, 1990). Physically, hydrates look similar to white, powdery snow (Fig. 2.4) and have two types of unit structure. The small structure with a lattice structure of 12 Å holds up to eight methane molecules within 46 water molecules. This clathrate may contain not only methane but also ethane, hydrogen sulfide, and carbon dioxide. The larger clathrate, with a lattice structure of 17.4 Å, consists of unit cells with 136 water molecules. This clathrate can hold the larger hydrocarbon molecules of the pentanes and *n*-butanes (Fig. 2.5).

Gas hydrates occur only in very specific pressure and temperature conditions. They are stable at high pressures and low temperatures, the pressure required for stability increasing logarithmically for a linear thermal gradient (Fig. 2.6). Gas hydrates occur in shallow arctic sediments and in deep oceanic deposits. Gas hydrates in arctic permafrost have been described from Alaska and Siberia. In Alaska they occur between about 750 and 3500 m (Holder et al., 1976). In Siberia, where the geothermal gradient is lower, they extend down to about 3100 m (Makogon et al., 1971; Makogan, 1981).

Hydrates have been found in the sediments of many of the oceans around the world. They have been recovered in the Deep Sea Drilling Project (DSDP) borehole cores, and their presence has been inferred from seismic data (e.g., Moore and Watkins, 1979; MacLeod, 1982). Specifically, they have been recognized from bright spots on seismic lines in water

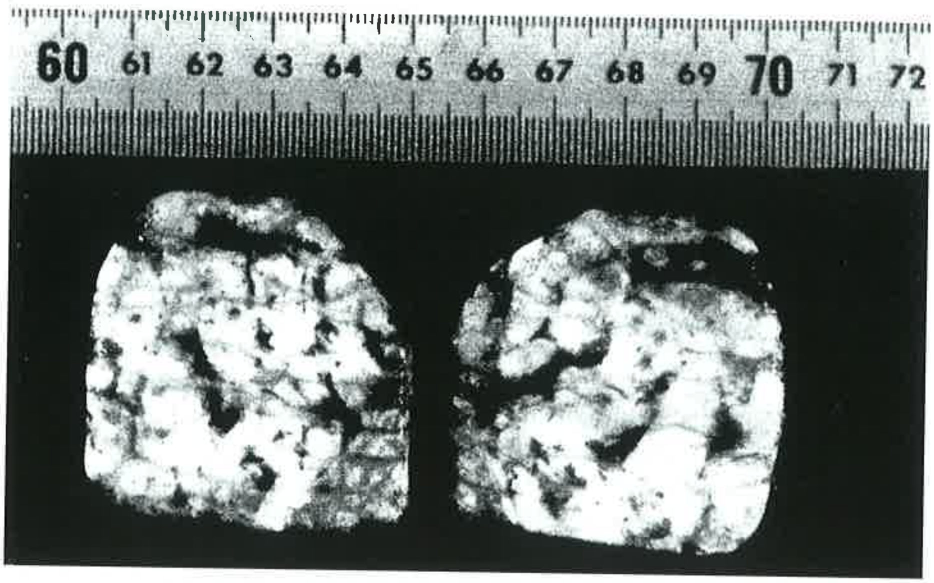


FIGURE 2.4 Samples of massive gas hydrate cored by the Deep Sea Drilling Project. *Courtesy of R. von Huene and J. Aubouin and the Deep Sea Drilling Project, Scripps Institute of Oceanography.*

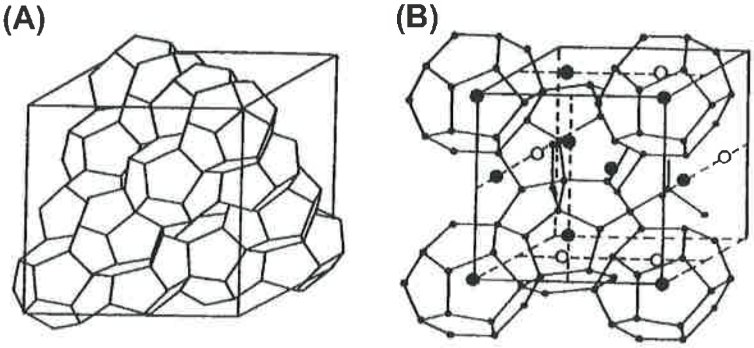


FIGURE 2.5 The two types of lattice structure for gas hydrates: (A) the larger structure with a 17.4-Å lattice and (B) the smaller one with a 12-Å lattice. *From Krason and Ciesnik (1985).*

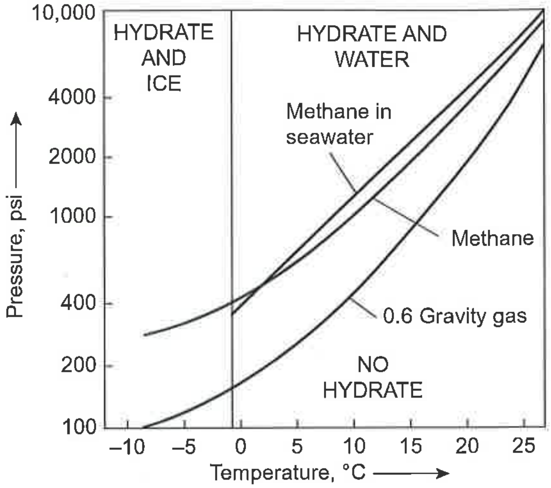


FIGURE 2.6 Pressure–temperature graph showing the stability field of gas hydrates. *After Hunt (1979, 1996), with permission from W. H. Freeman and Company.*

depths of 1000–2500 m off the eastern coast of North Island, New Zealand (Katz, 1981), and in water depths of 1000–4000 m in the western North Atlantic (Dillon et al., 1980). Gas hydrates have been attributed to a shallow biogenic origin (e.g., Hunt, 1979). MacDonald (1983), however, has postulated a crustal inorganic origin for hydrates, based on analysis of their carbon and helium isotope ratios. It is probable that the methane comes from three sources. Some may be derived from the mantle, some from the thermal maturation of kerogen, and some from the bacterial degradation of organic matter at shallow burial depths. This topic is discussed in greater depth in Chapter 5.

Known and inferred locations of gas hydrates are shown in Fig. 2.7. Sedimentary gas hydrates exist in large quantities beneath permafrost and offshore. Recent drilling activity in Japan (Nankai Trough), Canada, the United States, Korea, and India has shown that gas hydrates occur in shallow sediments in the outer continental shelves and in Arctic regions. Sand-dominated gas hydrate reservoirs are considered to be the most viable target for gas hydrate production (Collett et al., 2009; Boswell and Collett, 2011).

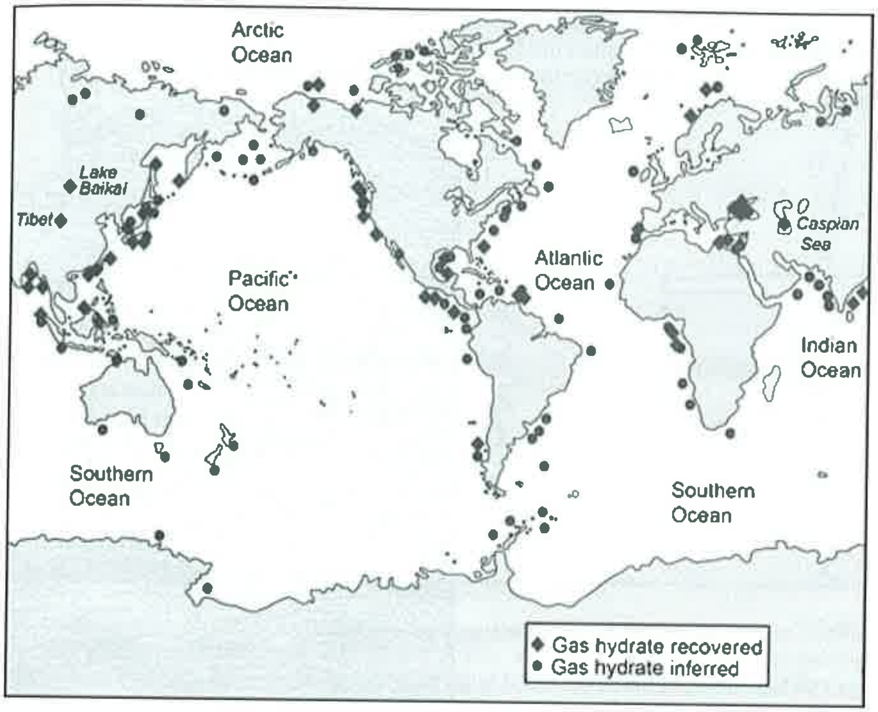


FIGURE 2.7 Known and inferred locations of gas hydrate occurrence. *From USGS gas hydrate primer (2014).*

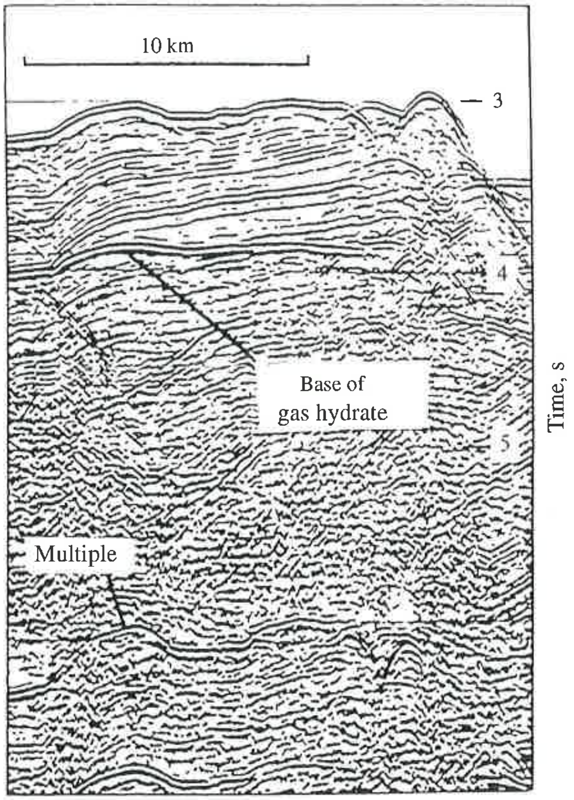
2.2.2 Identification and Economic Significance

As just noted, the presence of gas hydrates can be suspected, but not proved, from seismic data. The lower limit of hydrate-cemented sediment is often concordant with bathymetry, because the velocity contrast between the gas-hydrate-cemented sediment and underlying noncemented sediment is large enough to generate a detectable reflecting horizon. The bottom simulating reflector may appear as a bright spot, which cross-cuts bedding-related reflectors. Care must be taken to distinguish gas hydrate bottom reflectors from ordinary seabed multiples (Fig. 2.8). Basal hydrate reflectors commonly increase in subbottom depth with increasing water depth because of the decreasing temperature of the water above the sea floor.

The presence of gas hydrates can only be proved, however, by engineering data. The penetration rate of the bit is low when drilling clathrate-cemented sediments. Pressure core barrels provide the ultimate proof, since gas hydrates show a characteristic pressure decline when pressure cells are brought to the surface and opened (Stoll et al., 1971). Gas hydrates also show certain characteristic log responses (Bily and Dick, 1974). They have high resistivity and acoustic velocity, coupled with low density (Fig. 2.9).

Large areas of the arctic permafrost and of the ocean floors contain vast reserves of hydrocarbon gas locked up in clathrate deposits. Clathrates can hold six times as much gas as can an open, free, gas-filled pore system and are a potential energy resource of great significance (McIver, 1981; Max and Lowrie, 1996). Detailed studies have been carried out on 12 selected areas of known gas hydrate occurrence (Finley and Krason, 1989; Krason, 1994). These

FIGURE 2.8 Seismic line from offshore New Zealand showing bright spot, which is interpreted as the lower surface of a gas hydrate accumulation. *From Katz (1981).*



studies have revealed that these 12 areas contain well in excess of 100,000 Trillion Cubic Feet (TCF) of gas within the hydrate-cemented sediment, and more than 4000 TCF of gas trapped beneath the hydrate seal (Table 2.5). Unfortunately, gas hydrates present considerable production problems that are yet to be overcome. These problems are due, in part, to the low permeability of the reservoir and, in part, to chemical problems concerning the release of gas from the crystals. Clathrate deposits may be of indirect economic significance, however, by acting as cap rocks. Because of their low permeability, they form seals that prevent the upward movement of free gas. Some gas is produced from gas hydrates in Western Siberia, where they pose some interesting engineering problems (Krason and Finley, 1992).

Production methods for producing gas hydrates include thermal stimulation, depressurization, and chemical inhibition (Fig. 2.10). Production tests at the permafrost Mallik and Mt. Elbert wells and laboratory simulations on sediment cores have produced important data on gas production (Ruppel, 2011). Thermal stimulation involves injection of heated fluids into the formation or directly heating the formation. Thermal stimulation introduces heat into the marine gas hydrate-bearing sediments (GHBS), changes the gas hydrate stability zone, and dissociates gas hydrate. Depressurization through drilling, perforating, and producing lowers the pressure in the gas hydrate-bearing sediments. This also leads to instability in the gas hydrate reservoir and causes gas hydrate to dissociate. Depressuring is the

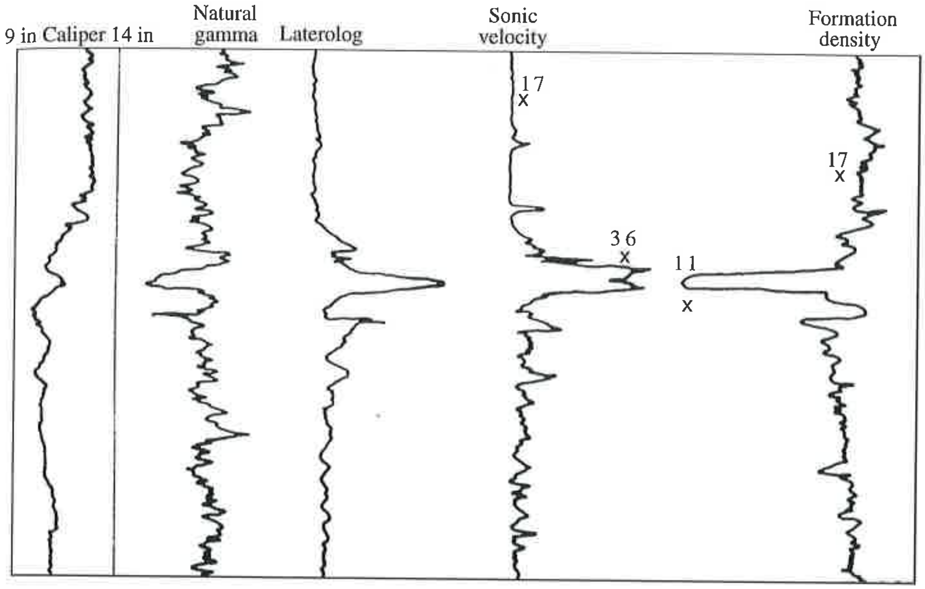


FIGURE 2.9 Wireline log of part of the Deep Sea Drilling Project Site 570, showing a gas hydrate zone. It is characterizd by high resistivity and acoustic velocity, and by low radioactivity and density. Crosses show velocities and densities in hydrate-bearing and normal intervals. *Courtesy of R. von Huene and J. Aubouin and the Deep Sea Drilling Project, Scripps Institute of Oceanography.*

most preferred and most economic method of producing gas from methane hydrates. Gas hydrate stability is inhibited in the presence of organic or ionic (seawater or brine) compounds. Inhibitors shift the gas hydrate stability boundary toward lower temperatures. Thus, injection of an inhibitor will dissociate gas hydrate near the wellbore.

It has also been suggested that gas hydrates may be of considerable importance in understanding climatic change, both the rapid rise in global temperature at the end of the Paleocene (Dickens et al., 1995) and more recent Quaternary climatic fluctuations (Nisbet, 1990). During glacial maxima vast quantities of methane, of whatever origin, become trapped within permafrost and submarine clathrate-cemented sediment. As the climate warms, a critical temperature will be reached at which point the clathrate will destabilize and huge amounts of methane gas will be released. This sudden release of gas may trigger mud volcanoes and pock marks on the sea bed, and pingos in permafrost. The huge increase of a greenhouse gas into the atmosphere may be responsible for the sudden increases in global temperatures observed at the end of glacial maxima.

2.3 CRUDE OIL

Crude oil is defined as "a mixture of hydrocarbons that existed in the liquid phase in natural underground reservoirs and remains liquid at atmospheric pressure after passing through surface separating facilities" (joint API, AAPG, and SPE definition). In appearance

TABLE 2.5 Estimated Potential Gas Resources in Gas Hydrates[a]

	I-m hydrate zone		10-m hydrate zone	
Study region	**TCF**	**m^3**	**TCF**	**m^3**
Offshore Labrador	25	0.71×10^{12}	250	7.1×10^{12}
Baltimore Canyon	38	1.08×10^{12}	380	10.8×10^{12}
Blake Outer Ridge	66	1.88×10^{12}	660	18.8×10^{12}
Gulf of Mexico	90	2.57×10^{12}	900	25.7×10^{12}
Colombia Basin	120	3.42×10^{12}	1200	34.2×10^{12}
Panama Basin	30	0.85×10^{12}	300	8.5×10^{12}
Middle America Trench	92	2.62×10^{12}	470	13.4×10^{12}
Northern California	5	0.14×10^{12}	50	1.4×10^{12}
Aleutian Trench	10	0.28×10^{12}	100	2.8×10^{12}
Beaufort Sea	240	6.85×10^{12}	725	20.7×10^{12}
Nankai Trough	15	0.42×10^{12}	150	4.2×10^{12}
Black Sea	3	0.08×10^{12}	30	0.8×10^{12}
Total	730	21.0×10^{12}	5200	149.0×10^{12}
		2.1×10^{13}		1.5×10^{14}

[a] *Estimated gas resources in gas hydrates in selected offshore areas. In most of the regions cited, the gas hydrate zone is much thicker than 10 m, and often extends down to several 100 m. Total estimated offshore gas hydrate resources potential is 100,000 TCF. Total estimated gas trapped beneath hydrates is 4000 TCF. TCF; Trillion Cubic Feet.*

From Krason (1994).

crude oils vary from straw yellow, green, and brown to dark brown or black in color. Oils are naturally oily in texture and have widely varying viscosities. Oils on the surface tend to be more viscous than oils in warm subsurface reservoirs. Surface viscosity values range from 1.4 to 19,400 cSt and vary not only with temperature but also with the age and depth of the oil.

Most oils are lighter than water. Although the density of oil may be measured as the difference between its specific gravity and that of water, it is often expressed in gravity units defined by the API according to the following formula:

$$^{\circ}\mathrm{API} = \frac{141.5}{\text{specific gravity } 60/60^{\circ}\mathrm{F}} - 131.5$$

where 60/60 °F is the specific gravity of the oil at 60 °F compared with that of water at 60 °F. Note that API degrees are inversely proportional to density. Thus light oils have API gravities of more than 40° (0.83 specific gravity), whereas heavy oils have API gravities of less than 10° (1.0 specific gravity). Heavy oils are thus defined as those oils that are denser than water. Variations of oil gravity with age and depth are discussed in Chapter 8. Oil viscosity and API gravity are generally inversely proportional to one another.

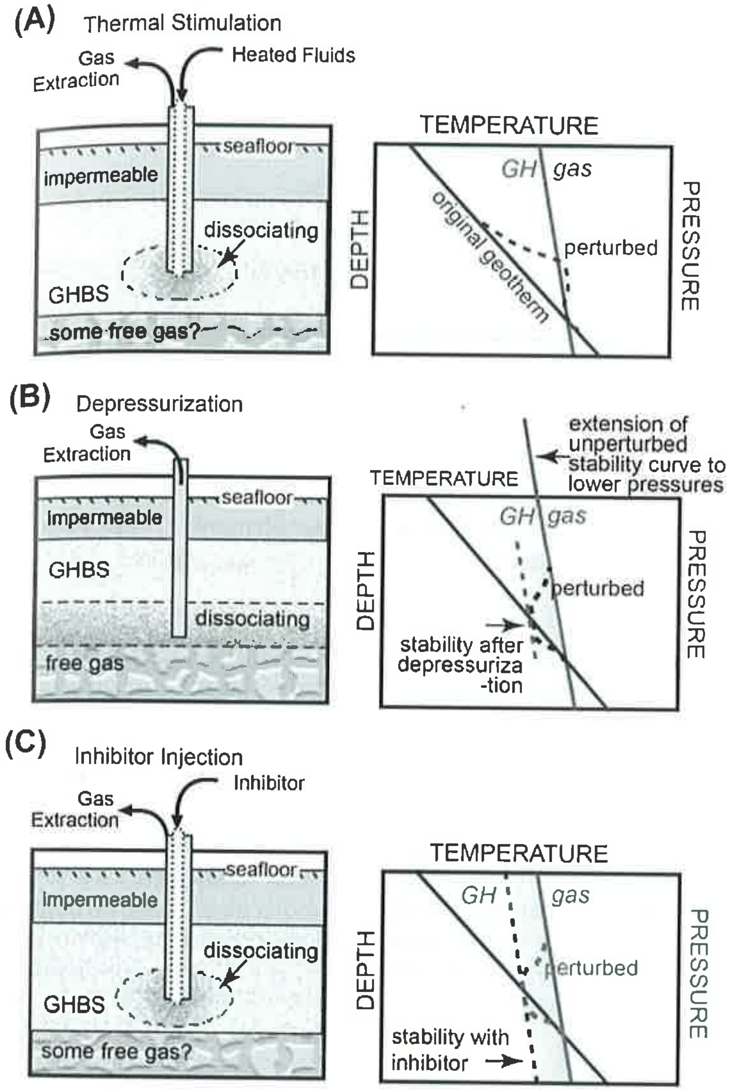


FIGURE 2.10 Possible methods for producing gas from marine gas hydrate-bearing sediments (GHBS). (A) Illustrates thermal stimulation. (B) Illustrates depressuring. (C) Illustrates inhibitor injection. In each case the stability field for the gas hydrate-bearing sediment is perturbed or shifted causing dissociation of gas. *From Ruppel (2011).*

2.3.1 Chemistry

In terms of elemental chemistry, oil consists largely of carbon and hydrogen with traces of vanadium, nickel, and other elements (see Table 2.6). Although the elemental composition of oils is relatively straightforward, there may be an immense number of molecular compounds. No two oils are identical either in the compounds contained or in the various proportions present. However, certain compositional trends are related to the age, depth, source, and geographical location of the oil. Conoco's Ponca City crude oil from Oklahoma, for

TABLE 2.6 Elemental Composition of Crude Oils by Weight %

Element	Minimum	Maximum
Carbon	82.2	87.1
Hydrogen	11.8	14.7
Sulfur	0.1	5.5
Oxygen	0.1	4.5
Nitrogen	0.1	1.5
Other	Trace	0.1

From: Geology of Petroleum by Levorsen. © 1967 by W. H. Freeman and Company. Used with permission.

example, contains at least 234 compounds (Rossini, 1960). For convenience the compounds found in oil may be divided into two major groups: (1) the hydrocarbons, which contain three major subgroups and (2) the heterocompounds, which contain other elements. These various compounds are described in the following sections.

2.3.1.1 *Paraffins*

The paraffins, often called alkanes, are saturated hydrocarbons, with a general formula C_nH_{2n+2}. For values of $n < 5$ the paraffins are gaseous at normal temperatures and pressures. These compounds (methane, ethane, propane, and butane) are discussed in the section on natural gas earlier in this chapter. For values of $n = 5$ (pentane, C_5H_{12}) to $n = 15$ (pentadecane, $C_{15}H_{32}$) the paraffins are liquid at normal temperatures and pressures; and for values of $n > 15$ they grade from viscous liquids to solid waxes. Two types of paraffin molecules are present within the series, both having similar atomic compositions (isomers), which increase in molecular weight along the series by the addition of CH_2 molecules. One series consists of straight-chain molecules, the other of branched-chain molecules. These structural differences are illustrated in Fig. 2.11. The paraffins occur abundantly in crude oil, the normal straight-chain varieties dominating over the branched-chain structures. Individual members

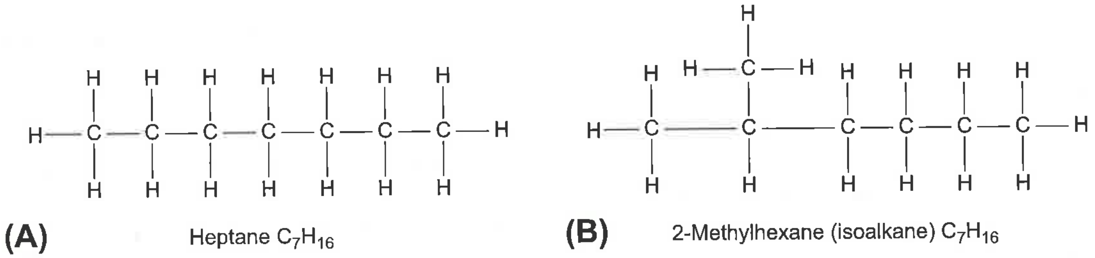
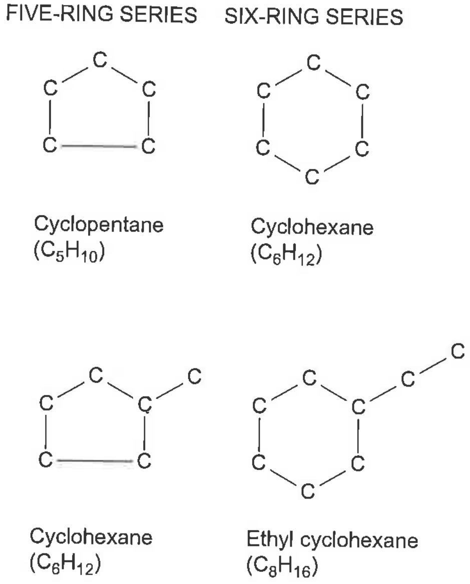


FIGURE 2.11 The isomeric structure of the paraffin series. Octane may have a normal chain structure (A) or a branched chain isomer (B).



Cyclopentane (C_5H_{10})

Cyclohexane (C_6H_{12})

Cyclohexane (C_6H_{12})

Ethyl cyclohexane (C_8H_{16})

FIGURE 2.12 Examples of the molecular structures of five- and six-ring naphthenes (cycloalkanes). For convenience the accompanying hydrocarbon atoms are not shown.

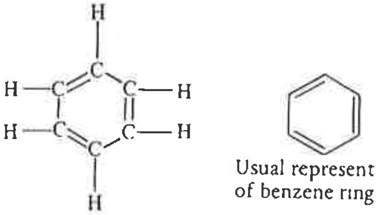
of the series have been recorded up to $C_{78}H_{158}$. For a given molecular weight, the normal paraffins have higher boiling points than do equivalent weight isoparaffins.

2.3.1.2 *Naphthenes*

The second major group of hydrocarbons found in crude oils is the naphthenes or cycloalkanes. This group has a general formula C_nH_{2n}. Like the paraffins they occur in a homologous series consisting of five- and six-membered carbon rings termed the cyclopentanes and cyclohexanes, respectively (Fig. 2.12). Unlike the paraffins all the naphthenes are liquid at normal temperatures and pressures. They make up about 40% of both light and heavy crude oil.

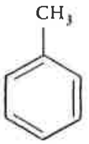
2.3.1.3 *Aromatics*

Aromatic compounds are the third major group of hydrocarbons commonly found in crude oil. Their molecular structure is based on a ring of six carbon atoms. The simplest member of the family is benzene (C_6H_6), whose structure is shown in Fig. 2.13. One major series of the aromatic compounds is formed by substituting hydrogen atoms with alkane (C_nH_{2n+2}) molecules. This alkyl benzene series includes ethyl benzene (C_6H_5, C_2H_5) and toluene ($C_6H_5CH_3$). Another series is formed by straight- or branched-chain carbon rings. This series includes naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$). The aromatic hydrocarbons include asphaltic compounds. These compounds are divided into the resins, which are soluble in *n*-pentane, and the asphaltenes, which are not. The aromatic hydrocarbons are liquid at normal temperatures and pressures (the boiling point of benzene is 80.5 °C).

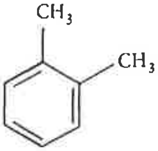


Benzene (C_6H_6)

Usual representation of benzene ring



Toluene ($C_6H_5CH_3$)



Dimethyl benzene
(one of three isomers of xylene)

FIGURE 2.13 Molecular structures of aromatic hydrocarbons commonly found in crude oil.

They are present in relatively minor amounts (about 10%) in light oils, but increase in quantity with decreasing API gravity to more than 30% in heavy oils. Toluene ($C_6H_5CH_3$) is the most common aromatic component of crude oil, followed by the xylenes ($C_6H_4(CH_3)_2$) and benzene.

2.3.1.4 Heterocompounds

Crude oil contains many different heterocompounds that contain elements other than hydrogen and carbon. The principal ones are oxygen, nitrogen, and sulfur, together with rare metal atoms, commonly nickel and vanadium. The oxygen compounds range between 0.06% and 0.4% by weight of most crudes. They include acids, esters, ketones, phenols, and alcohols. The acids are especially common in young, immature oils and include fatty acids, isoprenoids, and naphthenic and carboxylic acids. The presence of steranes in some crudes is an important indication of their organic origin. Nitrogen compounds range between 0.01% and 0.9% by weight of most crudes. They include amides, pyridines, indoles, and pyroles.

Sulfur compounds range from 0.1% to 7.0% by weight in crude oils. This figure represents genuine sulfur-containing carbon molecules; it does not include H_2S gas or native sulfur.

Elemental sulfur occurs in young, shallow oils (above 100 °C sulfur combines with hydrogen to form hydrogen sulfide). Five main series of sulfur-bearing compounds in crude oil are: alkane thiols (mercaptans), the thio alkanes (sulfides), thio cycloalkanes, dithio alkanes, and cyclic sulfides.

Traces of numerous other elements have been found in crude oils, but determining whether they occur in genuine organic compounds or whether they are contaminants from the reservoir rock, formation waters, or production equipment is difficult. Hobson and Tiratsoo (1975) have tabulated many of these trace elements. Their lists include common rock-forming elements, such as silicon, calcium, and magnesium, together with numerous metals, such as iron, aluminum, copper, lead, tin, gold, and silver. Of particular interest is the almost ubiquitous presence of nickel and vanadium. Unlike the other metals it can be proved that nickel and vanadium occur, not as contaminants, but as actual organometallic compounds, generally in porphyrin molecules. The porphyrins contain carbon, nitrogen, and oxygen, as well as a metal radical. The presence of porphyrins in crude oil is of particular genetic interest because they may be derived either from the chlorophyll of plants or the hemoglobin of blood. Data compiled by Tissot and Welte (1978) show that the average vanadium and nickel content of 64 crude oils is 63 and 18 ppm, respectively. The known maximum values are 1200 ppm vanadium and 150 ppm nickel in the Boscan crude of Venezuela.

Metals tend to be associated with resin, sulfur, and asphaltene fractions of crude oils. Metals are rare in old, deep marine oils and are relatively abundant in shallow, young, or degraded crudes.

2.3.1.5 Chemical Composition of Crude Oil

Crude oil is separated into useful products by distillation. Refiners are interested in the various valuable petroleum products that can be formed in a refinery (e.g., naphtha, gasoline, diesel fuel, asphalt base, heating oil, kerosene, liquefied petroleum gas, etc.). Petroleum products have different boiling points that allow them to be separated by distillation. Modern refiners distill thousands of barrels of crude through distillation towers (Fig. 2.14). Crude oil is heated to very high temperatures until the petroleum is converted into a gas phase that contains a variety of hydrocarbons. The hydrocarbon gases rise in the distillation tower until they reach their unique condensing temperature. Vapor distilled from one of the chambers rises to the chamber above. The vapor passes through condensed liquid of the overlying chamber. Each overlying chamber condenses smaller and lighter molecules. Light gasoline is present at the top of the distillation tower whereas residuum is found at the base. Products are taken out at various levels in the distillation tower.

The composition of a typical crude oil is shown in Table 2.7. The typical oil has more aromatics and asphaltics in the residuum and more paraffins in the gasoline fraction.

Figure 2.15 illustrates the abundance of the various hydrocarbon compounds with boiling range occurring in naphthenic crude oils.

2.3.2 Classification

Many schemes have been proposed to classify the various types of crude oils. Broadly speaking, the classifications fall into two categories: (1) those proposed by chemical engineers

FIGURE 2.14 Distillation Tower. Vapor distilled from one of the chambers rises to the chamber above and passes through condensed liquid of the overlying chamber. Each overlying chamber in the tower condenses lighter and smaller molecules.

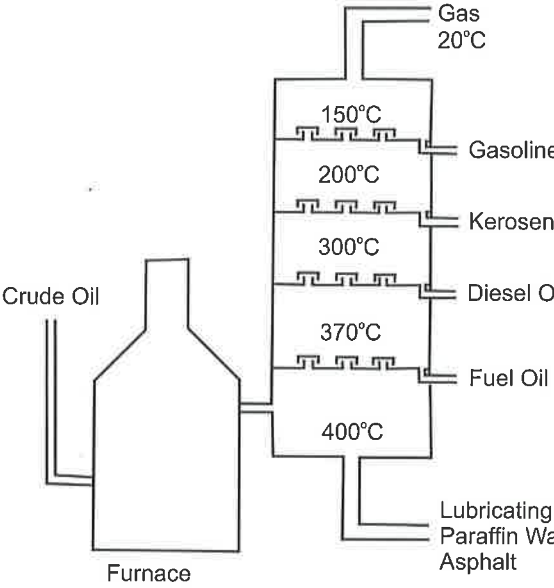


TABLE 2.7 Composition of a 35° API Gravity Crude Oil

Molecular size	Volume percent
Gasoline (C_5 to C_{10})	27
Kerosene (C_{11} to C_{13})	13
Diesel fuel (C_{14} to C_{18})	12
Heavy gas oil (C_{19} to C_{25})	10
Lubricating oil (C_{26} to C_{40})	20
Residuum ($>C_{40}$)	18
Total	100
Molecular type	**Weight percent**
Paraffins	25
Naphthenes	50
Aromatics	17
Asphaltics	8
Total	100

API, American Petroleum Institute.

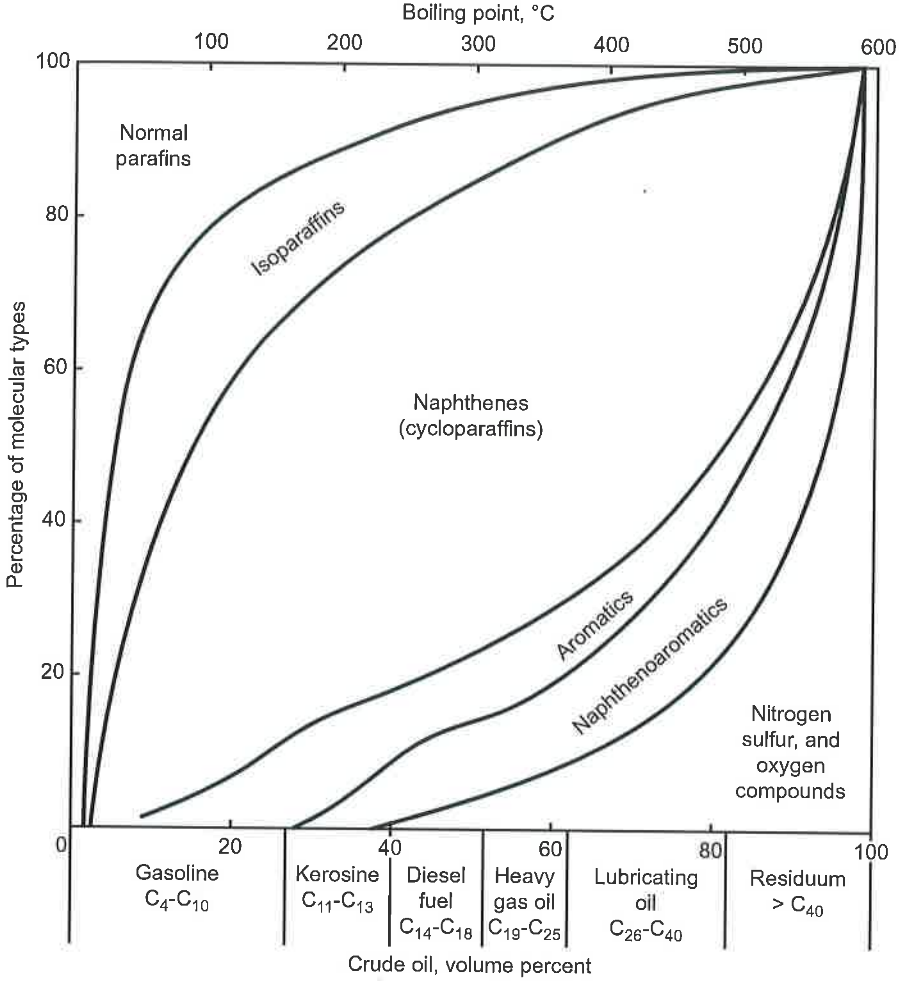


FIGURE 2.15 Chemical composition of naphthenic crude oil. *From: Petroleum Geochemistry and Geology 2/E by Hunt. © 1979 by W. H. Freeman and Company. Used with permission.*

interested in refining crude oil and (2) those devised by geologists and geochemists as an aid to understanding the source, maturation, history, or other geological parameters of crude oil occurrence.

The first type of classification is concerned with the quantities of the various hydrocarbons present in a crude oil and their physical properties, such as viscosity and boiling point. For example, the *n.d.M.* scheme is based on refractive index, density, and molecular weight (n = refractive index, d = density, and M = molecular weight).

Classificatory schemes of interest to geologists are concerned with the molecular structures of oils because these may be the keys to their source and geological history. One of the first schemes was developed in the US Bureau of Mines (Smith, 1927; Lane and Garton, 1935). It

TABLE 2.8 Classification of Crude Oils

Concentration in crude oil (>210 °C)					
S = saturates AA = aromatics +resins +asphaltenes	**P = paraffins N = naphthenes**		**Crude oil type**	**Sulfur content in crude oil (approximate)**	**Number of sampl per class (total =**
S > 50% AA < 50%	P > N and P > 40%		Paraffinic		100
	P ⩽ 40% and N ⩽ 40%		Paraffinic-naphthenic	<1%	217
	N > P and N > 40%		Naphthenic		21
S ⩽ 50% AA ⩾ 50%	P > 10%		Aromatic intermediate	>1%	126
	P ⩾ 10%	N ⩽ 25%	Aromatic asphaltic		41
		N ⩾ 25%	Aromatic naphthenic	Generally S < 1%	36

From Tissot and Welte (1978). Reprinted with permission from Springer-Verlag.

classifies oils into paraffinic, naphthenic, and intermediate types according to their distil fractions at different temperatures and pressures. Later, Sachenen (1945) devised a sch that also included asphaltic and aromatic types of crude.

A more recent scheme by Tissot and Welte (1978) is based on the ratio between paraf naphthenes, and aromatics, including asphaltic compounds (Table 2.8 and Fig. 2.16). great advantage of this classification is that it can also be used to demonstrate the matura and degradation paths of oil in the subsurface. A scheme based more on geological oc rence was proposed by Biederman (1965). This empirical classification is based or arbitrarily defined depth and age:

1. Mesozoic and Cenozoic oil at less than 600 m
2. Mesozoic and Cenozoic oil at over 3000 m
3. Paleozoic oil at less than 600 m
4. Paleozoic oil at more than 3000 m

Essentially, this scheme recognized four classes of oil: young-shallow, young-d old-shallow, and old-deep. A detailed study of many oils by Martin et al. (1963) showe number of statistically significant chemical and physical differences between these gro Young-shallow oils tend to be heavy and viscous. They are generally sulfurous and relati low in paraffins and rich in aromatics. Young-deep oils, on the other hand, are less viscou higher API gravity, more paraffinic, and low in sulfur content. Old-shallow oils are bro

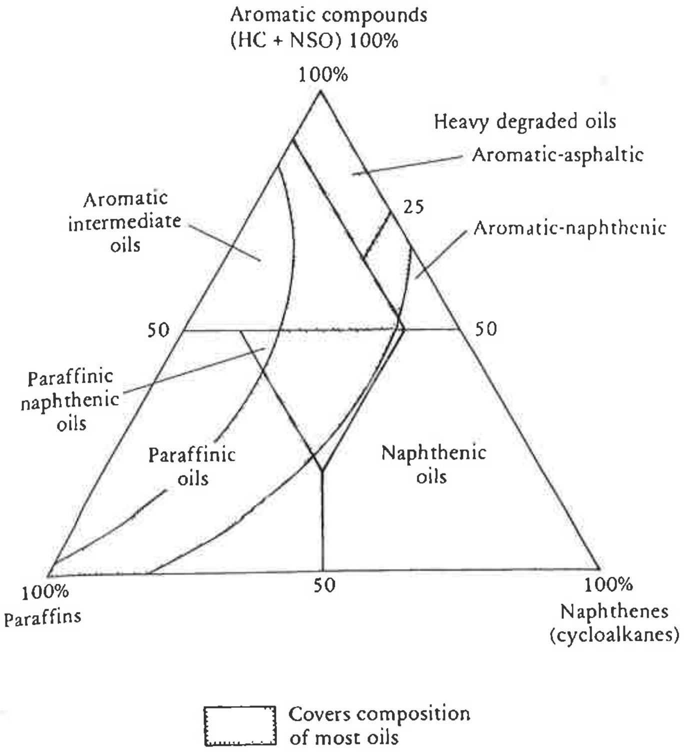


FIGURE 2.16 Ternary diagram showing the classification of oils proposed by Tissot and Welte (1978). *Reprinted with permission from Springer-Verlag.*

comparable to young-deep crudes in purity, viscosity, and paraffinic nature. Like young-shallow oil, however, they tend to be relatively sulfurous. Old-deep oils tend to have the lowest viscosity, density, and sulfur content of the four groups.

This system is very much a rule-of-thumb classification, and the variations of crude oils based on geological parameters are discussed further in Chapter 8. In particular, note that oils vary not only with age and depth, but also with variations in their source rock and the degree of degradation to which they have been subjected. This degradation causes very wide variations, especially in shallow oils.

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