INTRODUCTION TO PETROLEUM GEOLOGY

REVIEW OF COMPOSITION OF THE GLOBE

Geology is the study of the Earth which is a dynamic system covered by crustal plates that are constantly moving and changing in structure. The crustal plates are driven by deep lying forces that are not yet completely understood. New crustal plates are being formed by magma rising from molten regions deep in the Earth at mid-ocean rifts. Other crustal plates are being consumed as they are drawn downward into the mantle at subduction zones at the edges of some continents, such as the Pacific coasts of North and South America.

Detailed analyses of earthquake wave seismograms, waves that travel on the Earth's surface, gravity and magnetic differences, heat flow from the interior, and electrical conductivity have been used to develop a composite picture of the globe. Four distinct zones have been identified:

1. The lithosphere which includes the continental and ocean crusts
2. Underlying the lithosphere is the mantle which is readily recognized because the seismic (earthquake) waves increase in velocity at the boundary known as the Mohorovicic discontinuity in honor of its discoverer (generally called the Moho discontinuity)
3. A liquid outer core composed principally of nickel and iron
4. The solid inner core.

More than 100,000 detectable earthquakes occur each year around the globe and most of these originate at specific focal points (a point of maximum intensity within the crust) [1–3]. Two types of waves emanate from the focal point of the earthquake, compression and shear waves. Compression waves travel through all materials by moving particles forward and backward. Shear waves, however, can propagate only through solids by moving the particles back and forth perpendicular to the direction of travel. A worldwide network of seismographs records the paths and velocities of these waves making it possible to locate the focal point of any earthquake and to infer the composition of the interior of the Earth.

Compression waves (*P*-waves) travel at a velocity approximately two times the velocity of the shear waves (*S*-waves). The velocities are functions of the elastic properties and density of the materials through which they travel:

$$u_c = \left[\frac{(B + 4G/3)}{\rho} \right]^{1/2} \tag{2.1}$$

$$u_s = \left[\frac{B}{\rho} \right]^{1/2} \tag{2.2}$$

where:

u_c = velocity of the compression wave, m/s
u_s = velocity of the shear wave, m/s
B = bulk modulus, Pa
G = shear modulus, Pa
ρ = density of material, kg/m^3.

EXAMPLE

Calculate the velocities of the compression and shear waves through limestone: ($B = 7.0336 \times 10^{10}$ Pa; $G = 3.1026 \times 10^{10}$ Pa, $\rho = 2710.6$ kg/m^3):

$$u_c = \left\{ \frac{[7.0336 + (4/3)(3.1026)] \times 10^{10}}{2710.6} \right\}^{1/2} = 6419.5 \text{ m/s}$$

$$u_s = \left\{ \frac{3.1026 \times 10^{10}}{2710.6} \right\}^{1/2} = 3383.2 \text{ m/s}$$

In the crustal plates, the *P-wave* velocity ranges from about 6.4 km/s to 7 km/s. At the Moho discontinuity, where the *P-waves* enter the mantle, the velocity increases to about 8 km/s. The velocity ranges from 9 km/s to 10 km/s in the upper mantle, 12-13 in the middle mantle, and peaks at 13.7 at about 2800 km depth. When the P and S waves encounter the liquid core, the *P*-wave velocity decreases sharply to about 8 km/s and the S waves disappear because a liquid cannot support a shear wave. At the inner solid core of the Earth the P-wave velocity increases once more to about 11.3 km/s.

Crust is the term that originated for the outer solid shell of the Earth when it was generally believed that the interior was completely molten, and it is still used to designate the outer shell which has different properties from the underlying mantle. The crust varies in thickness and composition. The continental masses are composed of a veneer of sediments over a layer of light-colored granitic rocks. The granite-type layer is called the *SIAL* layer because its most abundant components are silicon and aluminum with an average density of 2.7 g/cm^3. Below the *SIAL* layer, there is a layer of dark rocks resembling basalt and gabbro which is known as the *SIMA* layer because its principal constituents are silicon and magnesium. The density of *SIMA* is slightly higher than that of the *SIAL* layer, about 2.9 g/cm^3. Under the oceans, the SIMA layer is covered only by a thin layer of soft sediments (Figure 2.1).

The mantle is a shell, which is apparently a plastic-like solid that extends inward about 2900 km deep from the Moho discontinuity to the liquid core. The movement of crustal plates and continents on top of the mantle is partially explained by the theory of convective currents within the mantle. Theoretically, the mantle responds to continuous stresses created by heat rising from the interior of the globe by developing current cells of very slowly ascending and descending material. Continental masses accumulate over the descending zones and the ocean basins lie over the ascending zones. Thus the slow movement of the mantle, as a plastic material, could be the mechanism causing the drift of the continental masses and spreading of the ocean floor at mid-ocean rifts around the globe. Continuous drifting motion of the crustal plates also may be influenced by body forces generated by gravitational Earth tides and by the rotation of the Earth.
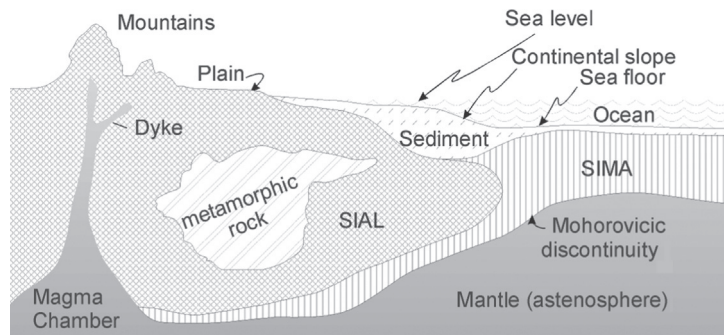
FIGURE 2.1

Cross-section of the crust at a continental shelf showing the relationship between the SIAL (granite rocks) and SIMA (basalt) layers under the continents and oceans [2].

Rocks and magma at volcanic eruptions that have come from the upper mantle are basic in composition, and rich in magnesium and iron. The density of the mantle is greater than the lithosphere, approximately 3.3 g/cm^3.

The boundary at the base of the mantle where the *S-waves* disappear and the *P-wave* velocity decrease marks the beginning of the outer liquid core. The fact that the *P-waves* increase in velocity once more at a depth of 5000 km suggests that the inner core is a solid. It is believed to be composed principally of nickel and iron with a density of about 10.7 g/cm^3, which is more than twice as dense as the mantle. The Earth's magnetic field is assumed to be created by an electric field resulting from circulation of currents within the liquid core [1–5].

PLATE TECTONICS

Theories of plate tectonics relate spreading of the sea floor at mid-ocean rifts to the motion, or drift, of the continents. The Earth's lithosphere is composed of six major plates whose boundaries are outlined by zones of high seismic activity [4]. The continents appear to be moved by the convection currents within the mantle at rates of 5.1-7.6 cm (2-3 in.) per year. The convection cells apparently occur in pairs and thus provide the kinetic energy for movement of the continental masses.

Mid-ocean ridges form a network of about 65,000 km of steep mountains with branches circling the globe. Some of the mountains are as high as 5500 m above the ocean floor, and some emerge above the ocean as islands.

The crustal plates are manufactured from magma rising to the surface through rifts at the sites of the mid-ocean ridges. Material from the mantle liquefies as it nears the surface and is relieved of a great part of its pressure. The liquid, or magma, rises to the crust and adds to the mass of the plate. As the plate moves across the ocean floor, it accumulates a layer of sediments that was eroded from the continents. The sedimentary layer that accumulates on the ocean floor is thin in comparison to the sedimentary layers on the continents because the ocean floor is very young. Driven by convective, rotational and gravity forces the plates move around until they are eventually drawn into the mantle at subduction zones, before sedimentation has time to form thick layers [1,2,6],

If two ocean plates of equal density collide, they will slowly deform each other at the edges forming a range of mountains. If the colliding forces remain active long enough the range of mountains will rise above sea level. The Alp Mountains in Switzerland are examples of this process due to a collision between Eurasia and Africa that began about 80 million years ago when the region was covered by a sea. Marine sediments can be found high in the Alpine regions.

India was once a separate continent riding on a plate moving in a northerly direction. The plate carrying the Indian continent was diving under the Asian continental plate carrying the lighter Indian continent with it. Eventually India collided with Asia and pushed up the massive Himalayan mountain range [3,4].

Island arcs, such as those that have developed in the Pacific Ocean east of Asia, also occur as a result of plate collisions. The Asian plate is more or less stationary with respect to the Pacific Ocean plate that is slipping under the large land mass forming a range of offshore islands. As the denser ocean plate returns to the high temperature mantle, selective melting of some of its material takes place, and the lighter materials are squeezed upward as rising columns called diapirs. The diapirs are pushed through the overriding plate and form chains of offshore volcanoes that eventually rise above sea level to form the islands. Lavas from the island arc volcanoes are generally intermediate in composition between granitic continental rocks and basaltic rocks. Deep-focused earthquakes occur along the arcs, indicating deep fracture zones between the continent and ocean plates.

The plates also may slip laterally with respect to each other, forming transform faults. The faults may be very long (hundreds of miles) such as the San Andreas Fault of California where the Pacific plate abuts the North American continental plate. The Pacific plate is moving in a northwest direction with respect to the American plate, which is moving west. The difference in the relative motions of the plates produces a shear-type phenomena at the junction resulting in a transform fault, many thrust faults parallel to the Earth's surface, and devastating earthquakes.

The ancient supercontinent known as Pangaea was formed by the union of a number of other continents. North America apparently moved east about 500 million years ago to collide into Pangaea and the collision brought about the formation of the Appalachian mountain range. This movement of North America crushed a chain of ancient island arcs and welded them onto the continent because layers that appear to be crushed island arcs have been located east of the Appalachian mountain range. The junction between Pangaea and North America was apparently weak, leading to development of a line of rising magma between them with the formation of spreading ocean plates on both sides that gradually pushed the two continental masses apart and formed the Atlantic Ocean [1,2,6,7].

The convolutions of old crustal plates and sediments at the continental margins provide conditions for entrapment of hydrocarbons in porous sedimentary rocks under impermeable layers that seal the oil in place. Continental margins bordering on a sea with restricted circulation of ocean water permits the collection of sediments and salt deposits which are associated with the genesis, migration, and trapping of oil. Margins that are separating from one another also are zones where oil is formed and trapped. Usually if oil is formed on one side of a continental margin, it also will be found across the gulf, or ocean, on the margin of the other continent. Divergent, convergent and transformed continental margins provide the necessary conditions for sedimentation and accumulation of hydrocarbon deposits [1,8–10].

GEOLOGIC TIME

Geologic time scales in use today were developed by numerous geologists working independently. Different methods for subdividing the records of flora, fauna, minerals, and radioactive decay found in sedimentary rocks were suggested: some were repeatedly used and have been generally accepted. Table 2.1 shows the subdivisions of geologic time, approximate dates in millions of years, and

Table 2.1 Subdivisions of the Three Geologic Eras and the Estimated Times of Major Events [5]

Subdivisions Based on Strata/Time				
Era	Systems/Periods	Series/Epochs	Radiometric Dates (Millions of Years Ago)	In Physical History
Cenozonic	Quaternary	Recent or Holocene	0	Several glacial ages
		Pleistocene	2	
	Tertiary	Pliocene	6	Colorado River begins
		Miocene	22	Mountains and basins in Nevada
		Oligocene	36	Yellowstone Park volcanism
		Eocene	58	
		Paleocene	63	Rocky Mountains begin
				Lower Mississippi River begins
Mesozonic	Cretaceous	(Many)	145	Atlantic Ocean begins
	Jurassic		210	Appalachian Mountains climax
	Triassic		255	
Paleozonic	Permian		280	
	Pennsylvanian (Upper Carboniferous)		320	
	Mississippian (Lower Carboniferous)		360	
	Devonian		415	Appalachian Mountains begin
	Silurian		465	
	Ordovician		520	
	Cambrian		580	
Precambrian (mainly igneous and metamorphic rocks, no worldwide subdivisions)			1,000	
			2,000	
			3,000	Oldest dated rocks
Birth of Planet Earth			4,650	

recognized physical events that took place during the long record of geologic history. The Earth is estimated to be about 4.5 billion years old. The Paleozoic Era begins 580 million years ago; therefore, approximately 87% of the Earth's history occurred during the Precambrian age. The approximate dates of most of the boundaries in the geologic time column are established from extensive analyses of radioactive isotopes and the flora and fauna records in sedimentary rocks. Isotopic dating also allows estimates of the rates of mountain building and sea-level changes [5].

The age of the Earth has been determined from uranium decay to lead isotope analyses of several meteorites. Radioactive dating of terrestrial rocks is not considered to be accurate because daughter nuclides may have been lost by leaching or otherwise displaced from the rock by weathering or plate tectonic motions. However, meteorites were formed at the same time as the Earth and have remained undisturbed.

Lead on Earth contains four isotopes: Pb-204, -206, -207 and -208. Lead isotope Pb-204 does not originate from the decay of thorium and uranium; therefore, the other isotopes were accumulated over time in the lead sample from the decay of the radioactive nucli. Hence, a comparison of the ratios of the isotopes in the Earth-bound sample to the ratios in the meteorites allows calculation of the Earth's age (Amelin *et al.* 2002).

Geologic age dating using radioisotopes is conducted by determining the amount of the specific daughter isotope present with the radioactive element and then multiplying by the rate of decay of the parent element (Table 2.2). The rate of radioactive element decay is exponential and is characterized by the following equation:

$$C \times t_{1/2} = \ln(N_o/N_t)$$

$$C \times t_{1/2} = \ln(1.0/0.5) = 0.693 \qquad (2.3)$$

where:

C = radioactive decay constant
N_o = original amount of parent element
N_t = amount of daughter isotope currently present
t = age, years
$t_{1/2}$ = half-life of the parent element

Dating early events from the decay of carbon-14 is possible because the radiocarbon is formed in the atmosphere by the collision of cosmic rays with nitrogen. The carbon dioxide in the atmosphere thus contains a small amount of radiocarbon and therefore all plants and animals contain carbon-14 along with the

Table 2.2 Radioactive Elements, Their Half-Lives and Radioactive Decay "Daughter" Elements [3]

Element	Half-Life	Stable Daughter
Carbon-14	5710 years	Nitrogen-14
Potassium-40	1.3 billion years	Argon-40
Thorium-232	13.9 billion years	Lead-208
Uranium-235	0.71 billion years	Lead-207
Uranium-238	4.5 billion years	Lead-206

stable carbon-12. When the plant or animal dies, the accumulation of carbon-14 stops and its content or radiocarbon decays steadily. The carbon dating is then made possible by measuring the ratio of ^{14}C to ^{12}C in the remains of organisms and comparing them to the ratio of these isotopes in current living plants or animals, for example: if the relative radiocarbon content of a specimen of bone $[(^{14}C/^{12}C)_{dead}/(^{14}C/^{12}C)_{living}]$ is one-fourth that of the modern specimen, the age of the specimen is 11,420 years. This is because $1/4 = 1/2 \times 1/2$ of two half-lives old (2 half-lives $\times$ 5710 years/half-life $=$ 11,420 years).

EXAMPLE

If 0.35 g of Lead-206 per 100 g of Uranium-238 is found in sediment, determine the age of the sediment.

Solution

Age $=(1/C) \times \ln$(Amount of parent element/Amount of isotope)

$$C = \frac{0.693}{5710} = 1.2 \times 10^{-4}$$

$$t = \frac{1}{C} \ln\left(\frac{1.0}{0.35}\right) = \left(8.3 \times 10^3\right)(1.05)$$

Age$(t) = 8723$ years.

Several important events in the geologic history of the Earth have already been mentioned, and others are shown in the geologic column of Table 2.1. The Appalachian Mountains were formed by collision of North America with Pangaea about 500 million years ago, and the climax of their growth coincides with the birth of the Atlantic Ocean at the beginning of the Mesozoic Era at about 255 million years ago. The Mississippi River and the Rocky Mountains began at about the same time (63-65 million years ago) and Yellowstone Park volcanism is estimated to have begun at about 40 million years ago. Several ice ages occurred in the Recent or Holocene Epoch that began about 2 million years ago [3,5].

SEDIMENTARY GEOLOGY

Sedimentary geology is fundamental to exploration and development of petroleum reservoirs. It establishes the criteria for petroleum exploration by providing the geologic evidence for prediction of the location of new petroleum provinces. Petroleum is found in all areas of a variety of sedimentary basins. Hydrocarbons may occur at shallow depth along the edges of the basin, the deep central areas, and in the far edges where tectonic motion may have provided sealed traps for oil and gas [1–10].

BASINS

Sedimentary basins differ in origin and lithology and they are individually unique, but they share several common characteristics. They represent accumulations of clastic and evaporite materials in a geologically depressed area (an area that has undergone subsidence with respect to the surrounding land mass) or an offshore slope. They have thick sedimentary layers in the center that thin toward the edges. The layers represent successive sedimentary episodes.

Dynamic sedimentary basins exist when sediment accumulation occurs simultaneously with subsidence of the basin area. The forces producing localized subsidence are not fully understood, but have

been related to isotactic adjustment of unbalanced gravitational forces. The theory of isotactic equilibrium is that the outer, lighter SIAL, crust of the Earth is essentially floating on a plastic-type mantle in a state of equilibrium. Therefore, part of the Earth's crust can gradually subside into the plastic mantle while an adjacent area is slowly uplifted.

No earthquake foci have been recorded deeper than about 1600 km, where the pressure and temperature are probably great enough to transform the mantle into a plastic-type material that can develop slow convective currents and gradually move to adjust for changing gravitational loads on the crust. The Great Lakes area of the United Stated, Canada, and the Scandinavian Peninsula are still gradually rising in response to the melting of the Pleistocene glaciers.

Continental masses have stable interiors known as cratons, or shields, which are composed of ancient metamorphosed rocks. Examples are the Canadian, Brazilian, Fennoscandia, and Indian Shields that form the nuclei of the respective continents. Sedimentary deposits from the cratons have accumulated to form much of the dry land of the Earth's surface, filling depressions and accumulating on the shelves of continental margins.

DIVERGENT CONTINENTAL MARGINS

Sediments accumulated on the shelves at the margins of the continents form several types of geologic structures that are the result of the direction and stress imposed on them by motion of the drifting crustal plates. Divergent continental margins develop on the sides of continents that are moving away from a spreading ocean rifts. Examples are the east coasts of North and South America and the west coasts of Europe and Africa which were originally joined together at the mid-ocean rift. The continents are extending leaving wide, shallow, subsea continental shelves where carbonate sediments originate from reefs in the shallow areas and clastic sediments from the wash of clastics from the land surface.

In considering sedimentation and the attributes of a sedimentary basin one must include the entire regional area which has furnished the detrital materials that have accumulated in the basin as sediments, and the environmental conditions of the various episodes of sedimentation. Chapman [9], defined this as the physiographic basin, an area undergoing erosion which will furnish material for the sediments accumulating in a depositional basin or depression on the surface of the land or sea floor. Thus the nature of the sediments is determined by the geology of the peripheral areas of weathering and erosion, and by the physiography and climate of the entire interacting area.

CONVERGENT CONTINENTAL MARGINS

Convergent continental margins develop when two crustal plates collide. When an ocean plate collides with a less dense continental plate a marginal basin forms between the island arc and the continent. This basin fills with carbonate deposits from marine animals and clastics from the land mass forming large areas for accumulation of hydrocarbons such as the oilfields of Southeast Asia.

Continual movement of the plates against each other will result in formation of a long narrow trough (several hundreds of miles long) called a geosyncline. The resulting trough is filled with great thicknesses of sediments that may become uplifted and folded as mountain building (orogeny) begins accompanied by volcanic activity. The Appalachian Mountains in eastern United States and the Ural Mountains in Russia are examples of the result of convergent continental margins where sediments

accumulated and were then uplifted in an orogenic period to form the stable mountains that are eroding today and furnishing sediments to the low land areas on both sides of the mountains.

Some of the petroleum that may have accumulated in the sediments is lost during the orogenic period because the seals holding the oil in geologic traps are destroyed allowing the hydrocarbons to migrate to the surface. Folding and faulting of the sediments, however, also produces structural traps in other areas of the region.

TRANSFORM CONTINENTAL MARGINS

When two crustal plates slide past each other they create a long transform fault with branches at 30° to the main fault creating fault blocks at the edge of the transform fault. Numerous sealed reservoirs result along the fault where clastic sediments have accumulated. An example is the San Andreas Fault in California and its associated oilfields. Transform faults on the ocean floor are sites of sea mounts, some of which project above the ocean floor accompanied by volcanic activity [9].

TRANSGRESSIVE-REGRESSIVE CYCLES

A transgressive phase occurs when the sea level is rising, or the basin is subsiding. During this period, the volume created by subsidence generally exceeds the volume of sediments entering the basin and hence the depth of the sea increases. As the sea advances over the land surface, the depositional facies also migrate inland creating a shallow, low energy, environment along the shore that tends to accumulate fine grained particles. The fine grained sediments have low permeability and are potential petroleum source rocks rather than reservoirs [9].

During a regressive phase in the formation of a basin, the basin is becoming shallower and the depositional facies migrate seaward into a high-energy environment. A regressive sequence may develop because the supply of sediments is greater than the amount accumulating in the basin can be removed by the available energy. This occurs in river deltas where growth of the delta occurs because the supply of sediments to the delta is greater than the amount of sediments that are being removed from the area by the action of currents and waves of the sea. Thus one of two elements may be active: (1) the sea level may be decreasing or (2) the sediment supply may exceed the capacity for removal and redistribution. The sediments accumulating during the regressive phase tend to be coarse grained because of the higher energy level in the depositional basin during this period. The rocks of this sequence therefore have relatively high permeabilities and are potential reservoirs layed down on top of potential source rocks deposited during the transgressive phase.

The transgressive-regressive stages tend to accumulate sequences of sediments that are either shale/sand or shale/carbonate-evaporite. The carbonate-evaporite sequences are associated with some, but not all, of the transgressive phases resulting in periodic accumulations of carbonate-evaporite lithologies. The low-energy environment of the shallow shelves provides opportunities for development of abundant shell-fish life whose shells become beds of calcite. Calcium and magnesium tend to precipitate from the shallow seas resulting in depositions of limestone ($CaCO_3$) and dolomite [$CaMg(CO_3)$]. Porosity is developed by dolomitization, chemical leaching by percolating waters (solution porosity), and mechanical fissuring from structural movements leading to jointing and vertical cracks. Carbonates also are deposited as reefs at the edge of continental shelves and along the continental slope.

ACCUMULATION OF SEDIMENTS

The accumulation of sediments in a given area depends on equilibrium between the energy of the environment and the inertia of the sedimentary particles. For example, sediments transported to the mouth of a river may be moved by wave and currents to another location where the environmental energy is not high enough to move the particles. This is the concept of base level [9]. Sediments of a given size and density will accumulate in an area which is at their base level of energy, but finer grades of the material cannot accumulate in that location and are carried in suspension to an area of less energy which is equivalent to their base level. This is the process that leads to sorting with accumulation of sand grains in one area and silt and clay in another area. The base level of a given area fluctuates with time; thus, during one period of accumulation sand particles are deposited and later finer particles of silt and clay are deposited on top of the sand. This sequence may be repeated many times leading to alternate deposition of sand and shale and the formation of sand-shale sequences.

Pirson identifies three types of physiographic areas that lead to the accumulation of either quartzose, graywacke, or arkose sedimentary particles in basins [11]. Each depends on the relief of the land mass and thus the time available for the chemical weathering of the rocks and particles prior to accumulation in the sedimentary basin. This is a simplification of the sedimentary process which is a complex interplay of the numerous depositional situations including those idealized by Pirson. Nevertheless the simplifications present a clear explanation of sedimentary accumulations that lead to deposition of different lithologies.

During periods of negligible orogenic activity in flat plains bordered by shallow seas, erosion of the land mass is at a minimum whereas chemical weathering is occurring at a rapid rate because the residence time of interstitial fluids at and near the surface is relatively long. Under these conditions weathering processes go to completion furnishing stable components from igneous and metamorphic rocks, such as quartz and zircon, for clastic sediments. These materials are carried into the depression forming the sea and are accumulated as clean, well sorted, sediments with uniform composition and texture. The sediments may remain as unconsolidated sand formations, or the grains may be cemented by carbonate and silica compounds precipitated from the sea, or from the interstitial waters percolating gradually through the deposits at some later stage (Figure 2.2). Changes of the climatic conditions of the physiographic area can change the type of sediments accumulating in the basin from clean grandular material to mixtures of silt, clay and organic materials. These become shale beds that can serve as source rocks for hydrocarbons as well as impermeable cap rocks.

Well sorted, granular, quartzose, reservoirs exhibit high vertical permeability (k_v) with respect to the horizontal permeability (k_h); however, k_h is still higher than k_v. Therefore primary oil recovery will be relatively high while secondary recovery will be very low due to severe fingering and early water breakthrough. Pirson lists the Oriskany sandstone in Pennsylvania, the St Peter Sandstone in Illinois, the Wilcox Sandstone in Oklahoma, and the Tensleep Sandstone in Wyoming as examples of quartzose-type reservoirs [11].

In conditions where the uplifted land areas bordering seas are steep enough to prevent total chemical weathering of the exposed rocks to stable minerals such as quartz, the detrital material accumulating in the basin will be composed of mixed rock fragments, or graywacke sediments. The sedimentary particles are irregular in shape and poorly sorted with variable amounts of intergranular clay particles. Changes of the climatic conditions of the physiographic area result in variable episodes of fine clastic deposition on top of the coarse particles forming the layers that become the cap rocks of the reservoirs (Figure 2.3).
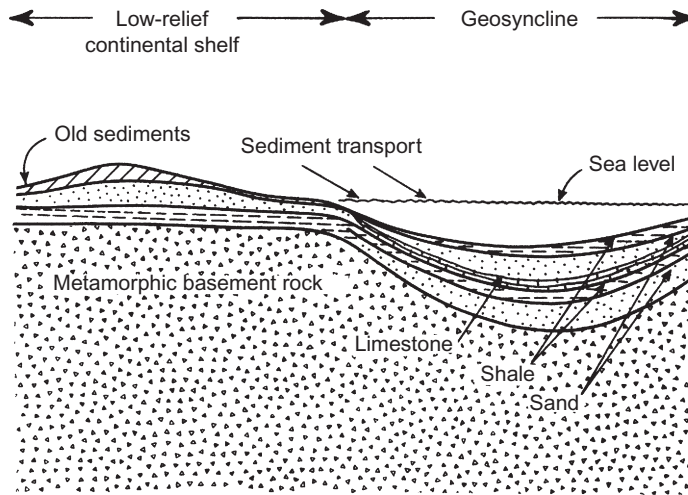
FIGURE 2.2

Accumulation of quartzose-type sediments in a basin from a low relief continental shelf. On a low relief land surface, erosion is at a minimum and chemical degradation of rocks to quartz is at a maximum [11].
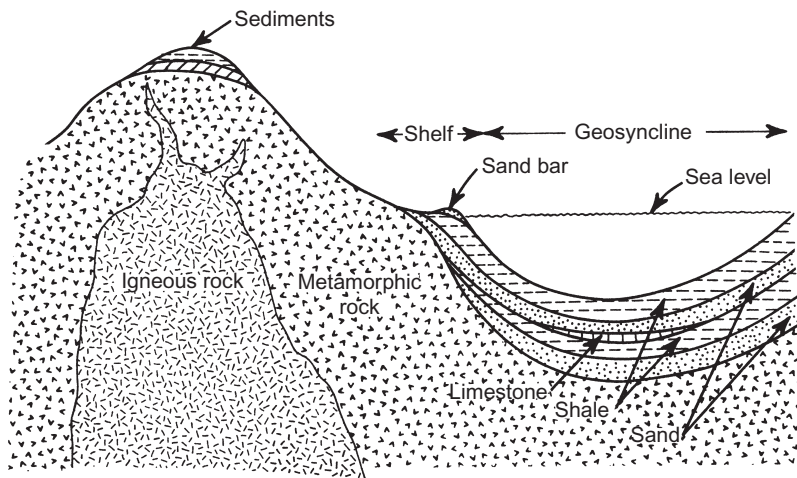

FIGURE 2.3

Accumulation of graywacke-type sediments in a geosyncline adjacent to a land mass of moderate relief [11].

The permeabilities of these reservoirs vary considerably over short distances, and the vertical permeability is usually much less than the horizontal permeability. The permeability variation is one reason why graywacke-type reservoirs do not produce as well during primary production as the quartzose-type reservoirs, but exhibit excellent secondary recovery. Due to the mixed sediments containing clay minerals, the reservoirs are generally subject to water sensitivity problems (clay swelling and particle movement).
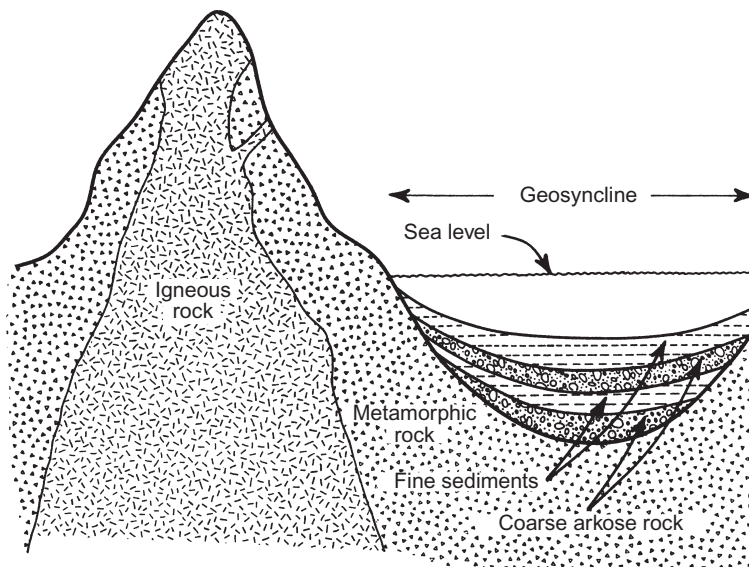
FIGURE 2.4

Idealized conditions that lead to deposition of arkose-type sediments. Steep land relief results in incomplete chemical weathering that yields arkose-type sediments [11].

The Bradford Sandstone in Pennsylvania and the Bartlesville Sandstone in Oklahoma are examples of graywacke sandstone formations.

A third general class of clastics, arkose-type sediments, will accumulate in basins, or dendritic canyons, adjacent to land areas of steep relief. Due to the steep relief chemical weathering of the sediments is incomplete resulting in deposition of angular grains with considerable size variation. Reactive clays and unstable minerals such as feldspars are mixed with the grains and make up a large portion of the cementing agents. Variable climatic conditions of the physiographic area result in a period of deposition of coarse clastics followed by fine sediments that eventually become the cap rocks of reservoirs (Figure 2.4). Thick reservoirs are formed, but the permeability is extremely variable, both vertically and horizontally. Consequently both primary and secondary production may be poor and the reactive clays produce severe water sensitivity. Examples of arkose-type formations are the Kern River formation in California and the Granite Wash in the Oklahoma-Texas Panhandle area [11].

HYDROCARBON TRAPS

Hydrocarbon traps may be illustrated by considering a porous, permeable, formation that has been folded into an anticlinal trap by diastrophism (processes of deformation) and is enclosed between impermeable rocks (Figure 2.5). The closure of the trap is the distance between the crest and the spill point (lowest point of the trap that can contain hydrocarbons). In most cases the hydrocarbon trap is not filled to the spill point. It may contain a gas cap if the oil contains light hydrocarbons and the
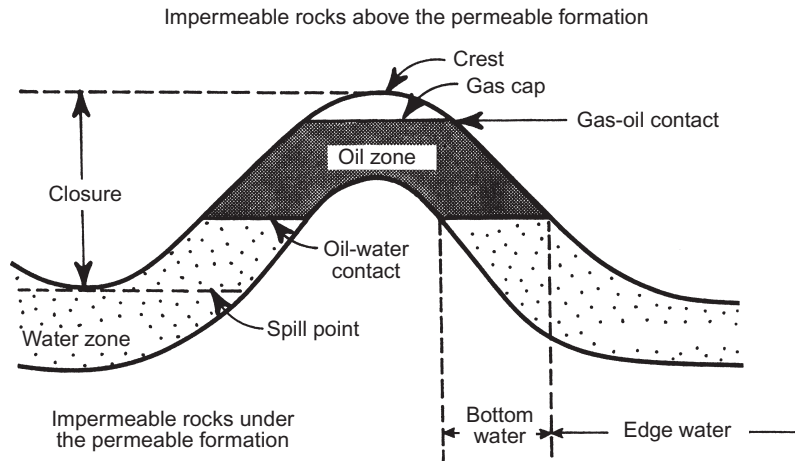
FIGURE 2.5

Idealized cross-section through an anticlinal trap formed by a porous, permeable, formation surrounded by impermeable rocks. Oil and gas are trapped at the top of the anticline.

pressure-temperature relationship of the zone permits the existence of a distinct gas zone at the top of the reservoir. If a gas cap exists, the gas-oil contact is the deepest level of producible gas. Likewise, the oil-water contact is the lower level of producible oil. Transition zones exist that are graded from high oil saturation to hydrocarbon free water. For example: the water zone immediately below the oil-water contact is the bottom water and edge water is the water which is laterally adjacent to the oil zone. The gas-oil and water-oil contacts are generally planar, but they may be tilted due to the hydrodynamic flow of the fluids, a large permeability contrast between opposite sides of the reservoir, or unequal production of the reservoir.

An anticlinal structure may contain several oil traps, one on top of the other, separated by impermeable rocks. Furthermore, the lithology of the individual traps may vary from sands to limestone and dolomite [9,11].

Hydrocarbon traps are generally classified as either structural or stratigraphic, depending on their origin. Structural traps were formed by tectonic processes acting on sedimentary beds after their deposition. They may generally be considered as distinct geological structures formed by folding and faulting of sedimentary beds. Structural traps may be classified as: (1) fold traps formed by either compression or compaction anticlines, (2) fault traps formed by displacement of blocks of rocks due to unequal tectonic pressure, and (3) diapiric traps produced by intrusion of salt or mud diapirs (Figure 2.6).

Stratigraphic traps are produced by facies changes around the porous, permeable, formation such as pinchouts and lenticular sand bodies surrounded by impermeable shales. Stratigraphic traps may develop from off shore bars, reefs, and river channels. The processes of formation are more complex than those of structural traps because they involve changes of the depositional environment that lead to the isolation of permeable zones by different lithologies. Distinctions are made between those that are associated with unconformities and those that are not [6].
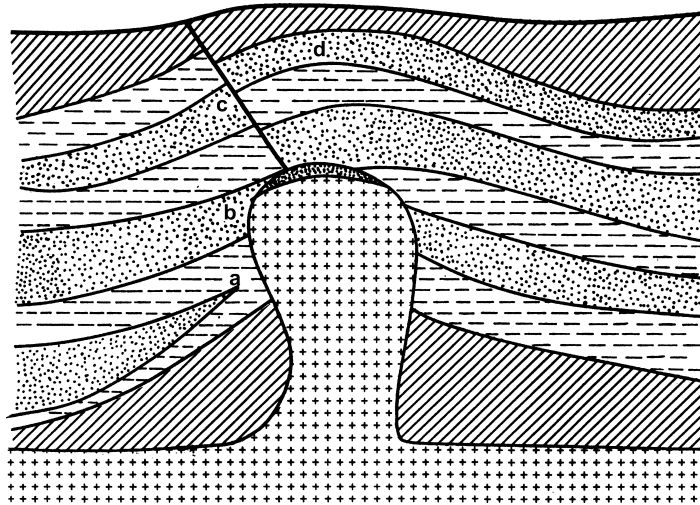
FIGURE 2.6

Illustration of several types of traps: (a) stratigraphic pinch-out trap, (b) trap sealed by the salt dome, (c) trap formed by a normal fault, (d) domal trap.
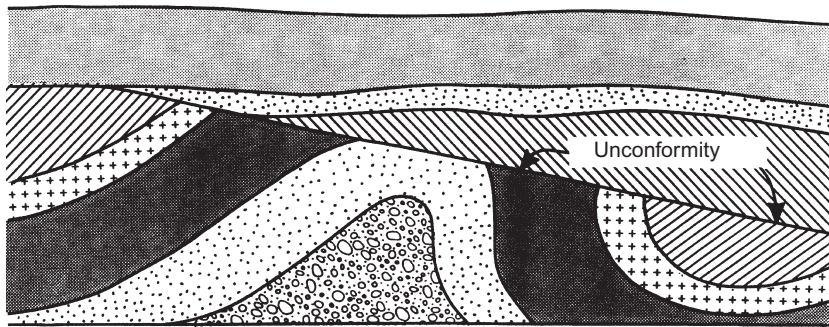

FIGURE 2.7

Unconformity, showing the uplifted, eroded strata overlain unconformably by younger sediments.

Many hydrocarbon accumulations are associated with unconformities. An unconformity forms when a site of sedimentation is uplifted, eroded, and buried again under a new layer of sediment, which may delineate the boundaries of an oil trap, because unconformities generally separate formations that have developed under very different environmental conditions (Figure 2.7). The rocks immediately below an unconformity are likely to be porous and permeable because an unconformity is a zone of erosion that is on the top of a weathering zone where water is percolating through the rocks causing solution of some minerals and precipitation of others as cementing agents. This is especially true of carbonate formations underlying unconformities. In addition, the mixed debris that is deposited on top of an unconformity can form permeable conduits for migration of oil from source rocks to geologic traps [12].

ORIGIN OF PETROLEUM

The biogenic origin of petroleum is widely accepted on the basis of geochemical studies. Petroleum contains compounds that have characteristic chemical structures which are related to plants and animals such as porphyrins, isoprenoids, steranes, and many others. In addition, the source rocks where the precursors of petroleum were originally deposited are the fine-grained sediments that are deposited in shallow marine environments during the low-energy transgressive phases of geologic basin formation. Particulate organic matter is not much denser than water and, therefore, sedimentation along with clay and fine carbonate precipitates will take place slowly in a low-energy environment. Depletion of oxygen takes place in quiet water leading to an anaerobic condition and preservation of organic matter. Anaerobic bacteria tend to reduce organic compounds by removal of oxygen from the molecules in some cases, but they do not attack the carbon-to-carbon bond of hydrocarbons. The evidence for the origin of petroleum in a low-energy, anaerobic environment is supported by the fact that in the opposite condition (a high-energy, aerobic environment) aerobic bacteria decompose organic matter to carbon dioxide and water [9,13,14].

TRANSFORMATION OF ORGANICS INTO KEROGEN

Organic materials from dead plants and animals are either consumed by living organisms or left to be decomposed by bacteria. If the organic material remains in an oxygen-rich, aerobic environment, aerobic bacteria will decompose it to carbon dioxide and water. If the environment is anaerobic, the products of decomposition will be essentially compounds of carbon, hydrogen, and oxygen. The hydrocarbons of crude oils can originate from the fundamental biological molecules: proteins (amino acids), lipids (fats, waxes and oils), carbohydrates (sugars and starches), and lignins (polymeric hydrocarbons related to cellulose) of plants. If these are preserved in a low-energy environment free of oxygen, they can be mixed with the clays and precipitates that are forming the fine-grained sediments characteristic of the low-energy transgressive phase of basin formation. Therefore, to be preserved, this organic matter must be buried as it is supplied with fine-grained sediments. The source rocks of petroleum are, therefore, those rocks formed from fine-grained sediments mixed with organic materials. Not all fine-grained sediments are source rocks for petroleum, which implies that a necessary criterion is the availability of abundant organic matter in an area of fine grain deposition. This implies a sedimentary basin along a gentle continental slope and the presence of aquatic life (plankton, algae, etc.), in addition to copious terrestrial plant life. Land vertebrates are not a very likely source for organic matter in shallow marine sediments.

Higher-order land plants contain abundant quantities of cellulose and lignin yielding aromatic-type compounds with a low hydrogen-to-carbon ratio (1.0-1.5). Marine algae contain proteins, lipids and carbohydrates; these are aliphatic in character with a high hydrogen to carbon ratio of 1.7-1.9. (The hydrogen to carbon ratios of specific compounds are: benzene-1.0; cyclohexane-2.0; and *n*-pentane-2.4).

The organic materials, fine-grained sediments, and bacteria that are mixed together and deposited in the quiet, low-energy environments are not in thermodynamic equilibrium. The system approaches thermodynamic equilibrium during initial burial while it is undergoing digenetic transformations. Inasmuch as burial is shallow during this stage, the temperature of the environment is low, and the sediment undergoes digenetic changes slowly under mild conditions. The first 3 m or so of sediment represents an interface where the biosphere passes into the geosphere. The residence time in this shallow sediment, before deeper burial, may range from 1000 to 10,000 years. During this time, organic matter

is subjected to both microbial and chemical action which transforms it from the biopolymers (proteins, etc.) to more stable polycondensed compounds, which are the precursors of kerogen. In time the sediments are buried deeper where the anaerobic environment prevails and where the organic matter continues to transform to more insoluble high-molecular-weight polymers due principally to the increase of pore fluid pressure and temperature.

Anaerobic bacteria reduce sulfates to hydrogen sulfide and may remove oxygen from some low-molecular-weight organic compounds, but otherwise they add to the total biomass rather than depleting it, which occurs in the aerobic regions. Some organically produced compounds of calcium and silica dissolve in the water and later are precipitated with the mixture of clay minerals and organics as they reach saturation in the aqueous layer. The organic matter is gradually transformed into new polymeric organic compounds that eventually become kerogen. Considerable methane is formed and released—mixed with hydrogen sulfide—as marsh gas. Low molecular-weight water-soluble compounds formed during diagenesis are probably lost to the interstitial water percolating upward, leaving behind a solid organic mass compacted into fine kerogen particles.

TRANSFORMATION OF KEROGEN INTO OIL AND GAS

Consecutive deposition of sediments in the basin leads to deeper burial reaching several thousand feet deep, which imposes an increase of temperature and pressure on the kerogen mixed with the fine-grained sediments. The increase of temperature with burial places the materials once more out of thermodynamic equilibrium which induces further reactions and transformations (catagenetic stage). During the catagenesis, are catalyzed to some extent by the inorganic matrix. While the organic material is undergoing major transformations, the sediments are being compacted with expulsion of water and decrease of porosity and permeability. The kerogen evolves through liquid bitumen to liquid petroleum. If the petroleum remains in the compacted source rock undergoing deeper burial with continued heating, the kerogen is ultimately reduced to graphite and methane.

The thermodynamic stability of the organic matter is never reached because of the gradual increase of temperature as burial proceeds. Chilingarian and Yen [15] describe the approximate depths for the various digenetic and catagenetic changes (Figure 2.8):

1. The zone of change to humic materials is 3-10 m (10-20 ft)
2. Diagenic changes take place between 6 and 450 m (20-1500 ft)
3. Catagenic changes and formation of oil from kerogen occur between 450 and 1800 m (1500-6000 ft)
4. The metageneic changes to graphite and methane take place below 1800 m (6000 ft).

MIGRATION AND ACCUMULATION OF PETROLEUM

The genesis of petroleum occurs in compacted clay and shale beds which are essentially impermeable to fluid flow. Therefore, the processes by which hydrocarbons migrate from the source rock to a porous, permeable, reservoir (called primary migration) are not completely understood. Numerous theories have been advanced to explain the processes. Possibly, several different mechanisms may be operative under different environmental and geological conditions. Some of these are:

1. Transport in colloidal solutions as micells
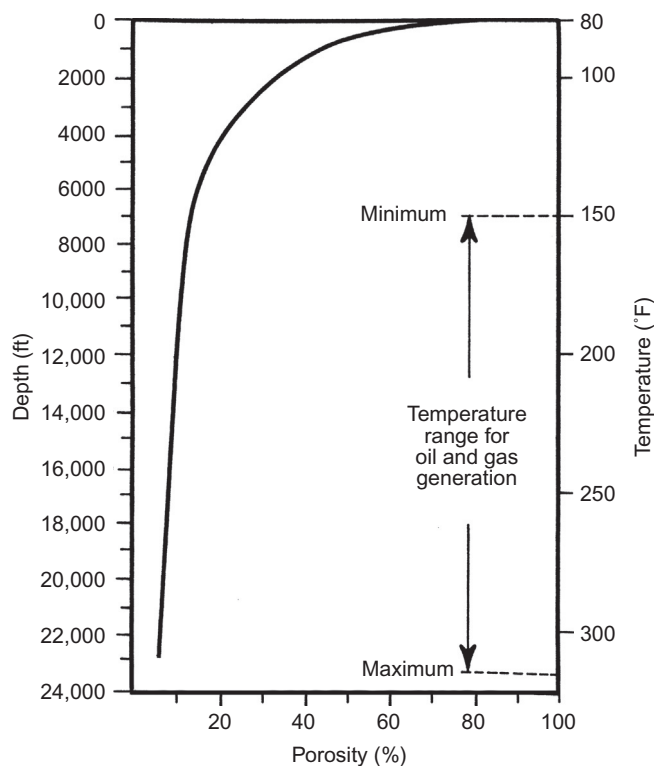2. Transport as a continuous hydrocarbon phase

FIGURE 2.8

Average relationship between porosity and depth of burial for shales, and the temperatures and depths for the genesis of oil and gas [15].

3. Buoyant movement of individual droplets
4. Solution of hydrocarbons in water moving out of the source rock
5. Transport by mechanical forces during clay diagenesis
6. Movement through microfractures in the source rock.

After leaving the source rock, the hydrocarbons migrate upward through permeable beds until it reaches a sealed hydrocarbon trap where accumulation occurs forming a hydrocarbon reservoir. This process has been labeled secondary migration which is governed principally by buoyancy and hydrodynamic flow [9].

PRIMARY MIGRATION

The geochemical evidence of the generation of petroleum shows that hydrocarbons do not generally originate in the structural and stratigraphic traps in which they are found. The petroleum reservoirs are porous, permeable geologic structures, whereas the source rocks have been identified as compacted, impermeable, shales. The source rocks are impermeable; therefore, the method of expulsion of oil from the shales where it is generated is not obvious. Considerable data on the expulsion of water from shale

during compaction show that most of the pore water is squeezed out during burial before the temperature required for the generation of petroleum is attained (Figure 2.8) [15,16].

Compaction of sediments begins as soon as the sediments begin to accumulate. During original accumulation the loose-grained sediments contain more than 50% water. As they are buried deeper, due to subsidence and continued deposition of sediments on top, the interstitial water from the deeper sediments is expelled, resulting in a decrease of porosity and increase of density. The material acquires cohesive strength as the grains are pressed together tightly. Chemical changes occurring in the interstitial fluids produce precipitates that cement the grains into an even more cohesive formation [16].

The major oil generation occurs well below the depth at which compaction of the shale is almost complete. Consequently, the displacement of oil from most source rocks could not have taken place when the shales were being compacted [6]. Expulsion of oil during compaction may have taken place in a few isolated cases where rapid burial resulted in the development of abnormally high pore pressures, or zones of abnormally high temperatures were present at shallow depths. Barker contends that petroleum may be expelled from the top and bottom of source rocks due to the pressure gradient that develops during deep burial [16]. After expulsion of the pore water, petroleum forming in the organically rich shale may produce a continuous network of fine thread-like channels in response to the applied physical stress [13].

Some clay minerals (smectites in general) contain bound water within the lattice structure of the clay particles. This bound water is expelled when the smectites are transformed to illite which begins at a temperature of about 200°F. This temperature is well within the temperature range for the generation of petroleum and thus may assist in the primary migration of oil when smectites are present in the shale body [6].

SECONDARY MIGRATION

Inasmuch as petroleum reservoirs exist in an environment of water, the migration of hydrocarbons from the point of release from a source rock to the top of the trap is intimately associated with capillary pressure phenomena and hydrology. The pore-size distributions, tortuosity of continuous pores, porosity, permeability, and chemical characteristics of reservoir rocks differ widely. Nevertheless, because of the ubiquitous presence of water, capillarity, buoyancy and hydrology apply in all cases [14].

The migration of oil as distinct droplets in a water-saturated rock is opposed by the capillary forces, which are functionally related to the pore size, the interfacial tension between the oil and water, and the adhesion of the oil to the mineral surface (wettability). This is expressed through a contact angle for a capillary of uniform size as:

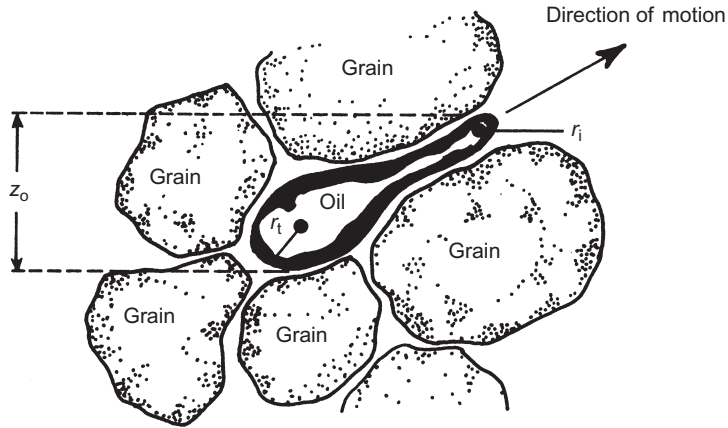$$P_c = (2\sigma \cos\theta)/r_c \qquad (2.4)$$

where:

P_c = capillary pressure, Pa
σ = interfacial tension, $N \times 10^{-3}$/m
θ = contact angle
r_c = radius of the capillary, m

The more usual case is one in which the oil droplet exists within the confines of a large pore containing several smaller sized pore throat exits (Figure 2.9). Under these conditions, the pressure required to

FIGURE 2.9

Displacement of an oil droplet through a pore throat in a water-wet rock.

displace the droplet from the large pore through the constriction of a pore throat (the displacement pressure) is the difference between the capillary pressures of the leading (l) and trailing (t) pores [6]:

$$P_d = 2\sigma \left(\frac{\cos \theta_l}{r_1} - \frac{\cos \theta_t}{r_2} \right) \tag{2.5}$$

where:

P_d = displacement pressure, Pa
θ_l = contact angle of the leading edge
θ_t = contact angle of the trailing edge
r_1 = radius of the leading pore, m
r_t = radius of the trailing pore, m

The two forces in a reservoir that are most likely to be operating on the droplet are buoyancy and hydrodynamic pressure, neither of which is normally sufficient to dislodge an isolated droplet of oil.

The displacement pressure due to buoyancy is expressed as:

$$P_d = Z_0 g_c (\rho_w - \rho_o) \tag{2.6}$$

where:

Z_o = height of the oil column
g_c = gravitational constant, 9.81 m/s^2
ρ_w = water density, kg/m^3
ρ_o = oil density, kg/m^3
P_d = displacement pressure, Pa

Since the combined buoyant and hydrodynamic pressures acting on an isolated droplet are insufficient to exceed the displacement pressure required by capillary forces, isolated drops of oil cannot migrate under the influence of these forces alone [14].

The movement of oil, over many miles, from a source rock to a petroleum reservoir leaving only a trace amount of hydrocarbon in the porous sediments along the path through which the oil moved has not been adequately explained. For movement of the oil to occur, there must be a source of energy to support the transport; tectonic movement may have provided an inclined region between the source and trap for movement by diffusion, density differences between the fluids, solution of hydrocarbons in mobile ground water at elevated temperature and pressure, expansion of free and dissolved gas and travel through fractures. Another source of energy for transport of fluids in subsurface permeable formations is Earth tides. The tides provide constant diurnal expansion and contraction of subsurface formations. This motion has been detected in deep wells as a diurnal rise and fall of the fluid level in the pipes, and the phase-lag between the tidal force and the hydraulic motion in the well has been recorded. The periodic fluctuation of fluid in the well is out of phase with the periodic change of gravity due to drag-forces caused by viscosity, density, compressibility, etc. If the path from the source rock to the oil trap is an inclined and permeable formation, the constant motion of the water and oil will produce segregated movement of the water and oil by buoyant forces and film drainage. A 0.1% reciprocating change of porosity in a 10-m thick, 100-m radius of a reservoir will produce an oscillating motion of 47 m^3 (294 bbl) of fluid. In geologic periods of more than a million years, this motion could move all but a trace of hydrocarbons from the source rock to the oil trap [17].

As the oil leaves the source rock under the forces of compaction, large saturations develop at the entry to the reservoir rock. The oil then begins to migrate upward as a continuous phase in long filaments within the pores. Under these circumstances sufficient buoyant and hydrodynamic forces can develop to cause migration of the oil.

It also has been suggested that oil migration may occur by molecular solution of oil in water which is in motion, and by colloidal solution brought about by surfactants that are present in petroleum. Both theories have been challenged because the solubility of oil molecules in water is extremely low and the actual concentration of surfactant-type molecules in crude oils is very small [9,18,19]. Leaching of sand containing discrete droplets of oil is, however, possible if the sand is flushed with large quantities of hot water. These processes may help account for the oil free sand found below many hydrocarbon saturations in reservoirs, given the enormous amount of geologic time accompanied by changes of temperature and diastrophism.

Secondary migration of petroleum ends in the accumulation in a structural or stratigraphic trap, and sometimes in a trap which is a complex combination of the two. Levorsen observed that oil has been found in traps that were not developed until the Pleistocene epoch, which implies that the minimum time for migration and accumulation is about 1,000,000 years [19]. The hydrocarbons accumulate at the highest point of the trap and the fluids are stratified in accord with their densities, which shows that individual hydrocarbon molecules are free to move within the reservoir. Inasmuch as sedimentary accumulation may have developed during the Cretaceous period or earlier, it is entirely possible that the oil accumulation may have been disturbed by diastrophism, and many changes of temperature and pressure. The petroleum accumulation may (1) become exposed by an outcrop and develop an oil seep, or (2) become uplifted and eroded to form a tar pit. In addition, petroleum may be transported to another sedimentary sequence as a result of rapid erosion and clastic transport. Levorsen identifies this type of secondary accumulation as recycle oil which should be low in paraffin compounds because of attack by aerobic bacteria [19]. Thus, the geologic history of an oil reservoir may have been quite varied and knowledge of the sedimentary history, origin, migration, and accumulation, and reservoir history is

valuable for the overall understanding of oil recovery processes and formation damage that may develop during production of the oil.

The cap-rock, or oil trap seal, may not be absolutely impermeable to light hydrocarbons. The capillary pressure relationship of the rocks overlying the oil trap may form an effective vertical seal for liquid petroleum constituents (C_5+ compounds), but the seal may not be completely effective in retaining the lighter hydrocarbons.

PROPERTIES OF SUBSURFACE FLUIDS

A basic knowledge of the physics and chemistry of subsurface waters and petroleum is essential for petroleum engineers because many problems associated with exploration, formation damage or production problems, enhanced oil recovery, wettability, and others, are directly associated with the physical and chemical behavior of subsurface waters and petroleum as a whole, or as groups of constituents, such as paraffins, asphaltenes, etc.

HYDROSTATIC PRESSURE GRADIENT

An important physical property of reservoir fluids is the density and its relationship to the hydrostatic gradient (the increase of the fluid pressure with increasing depth due to the increasing weight of the overlying fluid). Density measurements are made relative to the maximum density of water which is 1.0 g/cm^3 at 15°C (60°F) and 1 atm of pressure. When the specific weight (or mass) of any substance is divided by the specific weight (or mass) of an equal volume of water at 15°C and 1 atm of pressure, the resulting dimensionless value is described as the specific gravity relative to water (SG $= \rho_{fluid}/\rho_{water}$ at 15°C). The pressure gradient (G_p) of any fluid is determined from the specific gravity as follows:

$$G_p = \rho \cdot g \cdot d \cdot SG = \left(\frac{1000 \text{ kg}}{m^3}\right)\left(\frac{9.81 \text{ m}}{s^2}\right)(m) = (9.81 \text{ kPa/m})SG = (0.433 \text{ psi/f})SG \tag{2.7}$$

The hydrostatic gradient of subsurface waters is greater than 9.81 kPa per meter of depth because the brines contain dissolved solids that increase the specific gravity of the fluids. The gradient also is affected by temperature and in some areas by dissolved gas, both of which decrease the hydrostatic pressure gradient. An average hydrostatic gradient of 10.53 kPa/m (0.465 psi/ft) generally is used in the literature for subsurface brines [20]. This value corresponds to about 80,000 ppm of dissolved solids at 25°C (specific gravity $= 1.074$).

LITHOSTATIC PRESSURE GRADIENT

The lithostatic pressure gradient is caused by the density of the rocks and is transmitted through the grain-to-grain contacts of successive layers of rocks. The lithostatic weight, however, is supported by the pressure of the subsurface fluids in the pore spaces. Thus, the overburden pressure is equal to the grain-to-grain lithostatic pressure plus the fluid pressure of the porous formation times the depth, yielding an average overburden pressure gradient of 22.7 kPa per meter of depth (1.0 psi/ft) which corresponds to an overall bulk specific gravity of the rocks plus the interstitial fluids equal to 2.31 (Figure 2.10):

$$p_{ob} = \frac{\text{mass of rock matrix} + \text{fluid}}{\text{area}} \times d = \frac{(1-\phi)\rho_m + \phi \cdot \rho_f}{\text{area}} \times d \tag{2.8}$$
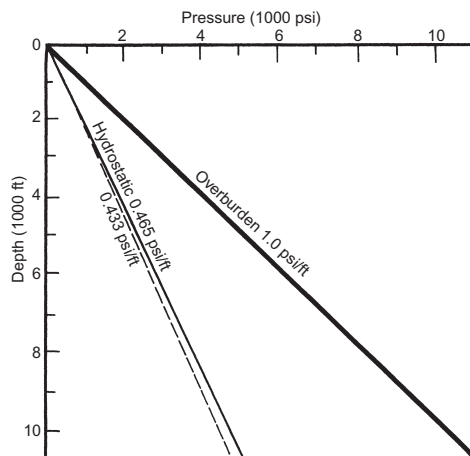
FIGURE 2.10

Subsurface pressure gradients.

When the hydrostatic pressure gradient for any region is approximately 10.53 kPa/m, it is known as the normal pressure gradient, abnormal pressure gradients may be either abnormally low or high. Abnormally high hydrostatic pressure gradients of 21.5 kPa per meter (0.95 psi/ft) have been encountered in a geopressure/geothermal zone along the Gulf Coast of the United States extending from New Orleans into Mexico, the Niger delta and the North Sea [6,21]. Abnormally low pressures have been encountered, in some gas fields of Pennsylvania and the Morrow formation in N.W. Oklahoma.

GEOTHERMAL GRADIENT

Heat rising from the mantle produces a heat flux in midcontinent regions ranging from 0.8 to 1.2 µcal/ cm^2 s (3.0-4.4 µBTU/ft^2 s) measured at the surface which results in a geothermal gradient (G_t) [5]. The geothermal gradient varies at different areas on the globe depending on the annual mean surface temperature and the thermal conductivity of the subsurface formations, but an overall average temperature gradient (G_t) of 18.2°C/km (1.0°F/100 ft) depth has been recorded around the world. Using this average value and the region's mean annual surface temperature (T_s), an estimate of subsurface formation temperatures (T_f) can be obtained as follows:

$$T_f = T_s + G_t d \tag{2.9}$$

When the bottom hole temperature (T_f) of a well is accurately measured, the local geothermal gradient may be obtained from Equation (2.9) and used to estimate the temperature of formations at any other depth (d).

EXAMPLE

The bottom hole temperature at 2.2 km was found to be 70°C. The mean surface temperature for the region is 24°C. Determine the geothermal gradient (G_t) and the temperature of a formation at 1700 m.

Solution

Solving for (G_t) from Equation (2.9) we have

$$G_t = \frac{T_f - T_s}{D} = \frac{70 - 24}{2.2} = 20.9°C/km$$

The formation temperature at $D = 1.7$ km is obtained from Equation (2.9).

$$T_f = 24 + 20.9 \times 1.7 = 59.5°C$$

There are zones in various locations on the globe where the geothermal and geopressure gradients are abnormally high. Some areas in the United States where abnormally high pressures and temperatures have been reported are: Gulf Coast Basin post-Cretaceous sediments, Pennsylvanian Period sediments in the Anadarko Basin in Oklahoma, Devonian zone in the Williston Basin in North Dakota, and the Ventura area of California. In areas outside the United States, geopressure/geothermal zones have been reported in the Arctic Islands, Africa (Algeria, Morocco, Mozambique and Nigeria), Europe (Austria, the Carpathian, Ural Mts, and Caucasian region of USSR), Far East (Burma, China, India, Indonesia, Japan, Malaysia, and New Guinea), Middle East (Iran, Iraq, and Pakistan), and South America (Argentina, Colombia, Trinidad, and Venezuela) [19,22]. The pressure and temperature gradients range up to 20 kPa/m (0.9 psi/ft) and 30°C/km (1.7°F/100 ft), respectively, as shown in Figures 2.11 and 2.12.

Many possible causes for the geopressured zones are presented in the literature. Fertl and Timko discuss 17 causes [23]. Among these are sedimentation accompanied by contemporary faulting, which is apparently the greatest contributing cause of the abnormally high pressures found in the Gulf Coast Basin of the United States. Undercompaction of the sediments can occur during rapid sedimentation and burial of soils containing a large quantity of clay minerals. The complete expulsion of water does not occur, leaving the sediments as a loosely bound system of swollen clay particles with interlayered water. Continued sedimentary deposition caused a shear zone to develop by overloading the undercompacted shale. Expulsion of the water was accompanied by subsidence of blocks of sediments. Thus, the contemporaneous fault zone of the Gulf Basin is characterized by the cycle of deposition, temperature increase, expulsion of water, and subsidence of blocks of sediments. As the depth of burial continued, the increase in temperature induced dehydration of the clays within the buried zone and contributed to the shearing stresses. The transformation of illite during digenesis and catagenesis occurs between 65°C and 120°C (150-250°F), releasing an amount of water equal to one half of its volume, leading to undercompaction in the geopressured zone. When the fluid pressure exceeds the lithostatic pressure, the faults act as "valves" for discharge of water upward into the hydropressured aquifers overlying the zone. As the pressure declines, the "valves" closes until the pressure once more exceeds the lithostatic pressure [24,25].

Another contributor to the fluid pressure is the temperature increase that occurs within the geopressured zone. The overlying, normally pressured, sediments that are compacted possess a lower thermal conductivity and act as a "blanket," decreasing the transfer of heat from the mantle. The heat trapped by the blanket above the geopressured zone produces an abnormally high temperature in the formation, which contributes another incremental pressure increase to the fluid [26].
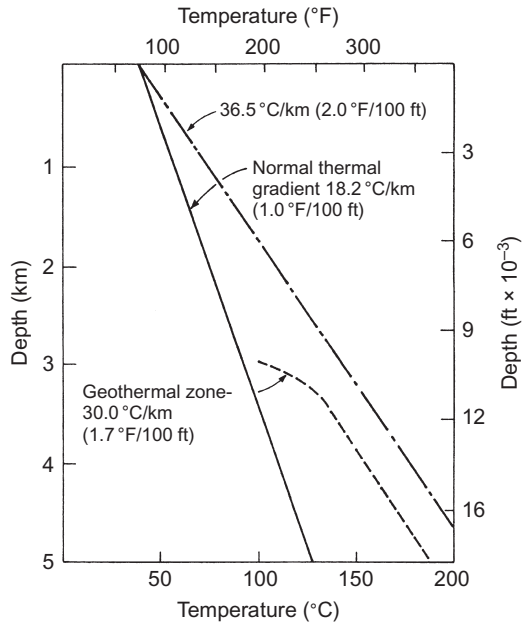
FIGURE 2.11

Subsurface temperature gradient showing the change within the geopressured zone. The 36.5°C/km gradient was included for reference only.
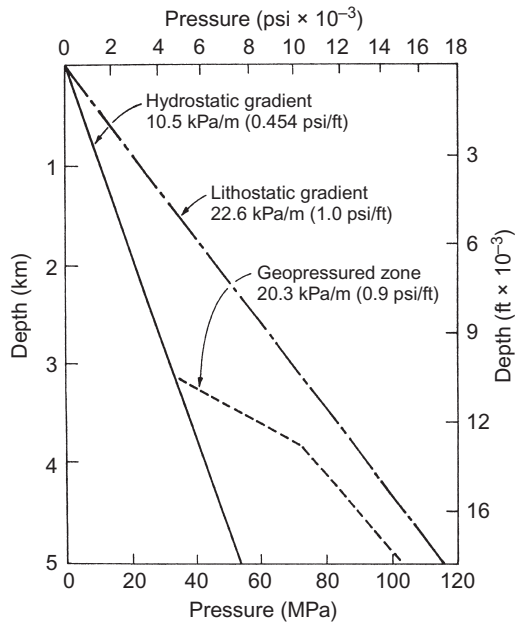

FIGURE 2.12

Subsurface pressure gradients showing the change in hydrostatic pressure gradient within the geopressured zone.

Geopressured zones along the Gulf Coast generally occur at depths below 2500 m (8000 ft) and require careful and expensive drilling technology whenever the zones are penetrated. The zones usually contain about 3.6 cm^3 of methane per cubic meter of brine (20 SCF/bbl).

OILFIELD WATERS

The genesis of petroleum is intimately associated with shallow marine environments, hence it is not surprising that water found associated with oil generally contains dissolved salts, especially sodium and calcium chlorides. Petroleum source rocks that were originally formed from lakes or streams, and the porous sediments that became today's petroleum reservoirs, could have acquired saline waters by later exposure to marine waters. Thus the original waters present in the sediments when they were developed may have been either fresh water or saline marine water. After the original deposition, however, the oilfield sedimentary formations have histories of subsidence, uplift, reburial, erosion, etc. Therefore, the chemistry of the original water may have been mixed with meteoric water, marine water infiltration at a later time, and changes of salt type and concentration due to solution of minerals as subsurface waters moved in response to tectonic events, and precipitation of some salts that may have exceeded equilibrium concentration limits [27].

The origin of deep subsurface waters has not been completely explained. The most plausible explanation is that they were originally derived from sea water. If sea water is trapped in an enclosed basin, it will undergo evaporation resulting in precipitation of the dissolved salts. The least soluble salts will precipitate first leaving concentrated brine, which is deficient in some cations and anions when compared to sea water. The common order of evaporative deposition from sea water in a closed basin is: calcium carbonate (limestone) > calcium magnesium carbonate (dolomite) > calcium sulfate (gypsum) > sodium chloride (halite) > potassium chloride (sylvite). Dolomite begins to precipitate when the removal of calcium from solution increases the Mg/Ca ratio. The residual brines (containing unprecipitated salts at any period) may migrate away from the basin leaving the evaporites behind, or they may become the interstitial water of sediments that are rapidly filling the basin [21]. When the brines are mixed with accumulating clastic sediments, aerobic bacteria consume the free oxygen in the interstitial waters creating an anaerobic environment in which the anaerobes become active and attack the sulfate ion which is the second most important anion in sea water. The sulfate is reduced by the bacteria to sulfide which is liberated as hydrogen sulfide (marsh gas). Thus the oilfield waters, or brines, are quite different from the average composition of sea water (Table 2.3). With the exception of sulfate, all of the ions in the Smackover formation (carbonate) brine are enriched with respect to sea water. Several mechanisms of enrichment are possible: (1) the original sea water may have evaporated if it was trapped in a closed basin, (2) movement of the waters through beds of clay may have concentrated cations by acting like a semipermeable membrane allowing water to pass through, but excluding or retarding the passage of the dissolved salts, and (3) mixing with other geologic waters containing high salt concentrations may have occurred. The content of alkali cations is many times greater in oilfield brines than the water that owes its salinity to salts from the Earth or to filtration of high-salinity waters from other sources.

There are many reactions between ions that can occur as the environmental conditions change with respect to burial. Consequently the composition of oilfield waters varies greatly from one reservoir to another. Commonly, the salinity (total amount of dissolved salts, or TDS) of petroleum-associated waters increases with depth (there are a few exceptions to this). The principal anions change in a

Table 2.3 Average Composition of Sea Water Compared to Smackover, Arkansas Oilfield Brine (After Collins) [21]

Constituent	Sea Water (mg/1)	Smackover Brine (mg/1)
Lithium	0.2	174
Sodium	10,600	67,000
Potassium	380	2800
Calcium	400	35,000
Magnesium	1300	3500
Strontium	8	1900
Barium	0.03	23
Boron	5	130
Copper	0.003	1
Iron	0.01	41
Manganese	0.002	30
Chloride	19,000	172,000
Bromide	65	3100
Iodide	0.05	25
Sulfate	2690	45

characteristic manner as depth increases: (1) sulfate is the major anion in near-surface waters; (2) below about 500 m, bicarbonate may become the principal anion; and (3) in brines from deeper formations, chloride is the principal anion. The ratios of the cations also change with respect to depth. The Ca/Na ratio increases and the Mg/Na ratio decreases [21].

The concentrations of salts in formation waters are expressed as weight percent (wt%), milligrams per liter (mg/l), or parts per million (ppm). The density quantities are related as follows: $1\% = 10,000$ ppm and 1 mg/L = 1 ppm.

Where ionic reactions are involved, the quantities of each ion are expressed as milliequivalents per liter (meq/L). One milliequivalent of a cation reacts quantitatively with exactly one milliequivalent of an anion:

$$\text{meq/L} = (\text{mg/L}) \times \left(\frac{\text{valence}}{\text{molecular weight}}\right) \tag{2.10}$$

The calcium and magnesium cation concentrations of subsurface waters are probably functions of the origin of the specific oilfield water as well as its history of contact with infiltrating waters. These salts undergo reactions forming dolomite and enter into ion exchange reactions; consequently, they are normally found in lower concentrations than sodium. Other cations are present in concentrations less than 100 mg/liter [13].

Oilfield waters are frequently referred to as connate or interstitial water which is water found in small pores and between fine grains in the rocks. As defined by Collins the two terms are synonymous and, indeed, they are indistinguishable as used in the petroleum literature [28]. Connate water implies that it is the original fossil water present in the rocks from the time of original deposition. One cannot be certain of this since the original water may have been displaced or mixed with other water during the
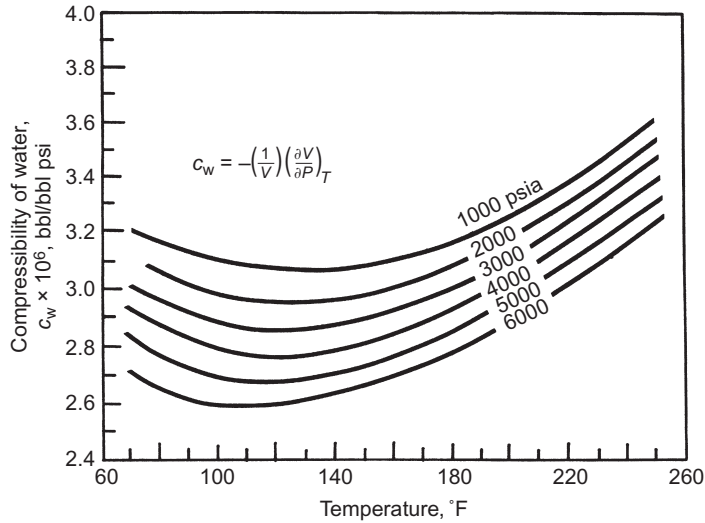
FIGURE 2.13

Compressibility of water as a function of temperature and pressure [27].

geologic history of the sedimentary formation. Collins considers connate water as fossil water that has not been in contact with water from other sources for a large part of its geologic history.

Compressibility

Compressibility of water is a function of the environmental pressure and temperature as shown in Figure 2.13. At any given pressure, the compressibility decreases as the temperature is increased from ambient reaching a minimum compressibility at about 55°C (131°F); then the compressibility increases continually as the temperature is increased [29]. At any given temperature, the compressibility decreases as the pressure in increased. The isothermal compressibility (c_w) is expressed as follows:

$$c_w = -\frac{1}{V_1}\left(\frac{dV}{dp}\right)_T = \left(1 - \frac{V_2}{V_1}\right)\left(\frac{1}{p_2 - p_1}\right) \qquad (2.11)$$

where: V_1 and V_2 are the volumes at pressure p_1 and p_2

The ratio V_2/V_1 is equivalent to the amount of water expansion as the pressure drops from p_2 to p_1.

EXAMPLE

The bottom hole temperature of a gas reservoir is 140°F; calculate the amount of water expansion, per unit volume, that will occur when the pressure is decreased from 4000 psi to 3270 psi. From Figure 2.13, the estimated compressibility of water at the given reservoir conditions is 2.8×10^{-6} psi^{-1}.

$$V_2/V_1 = \left[1 - \left(2.8 \times 10^{-6}\right)(3270 - 4000)\right] = 1.02$$

Water compressibility decreases when the water contains hydrocarbon gases in solution according the following empirical equation [30,31].

$$c_{sw} = c_w\left(1.0 + 0.0088 \times R_{sw}\right)$$

where:
c_{sw} = compressibility of water containing solution gas (1/kPa or 1/psi)
c_w = compressibility of water
R_{sw} = solubility of gas in water m^3 gas/m^3 water (ft^3/bbl).

Gas Solubility

The solubility of hydrocarbon gases in water at any given pressure does not change very much as the temperature is increased. The behavior is similar to compressibility since the solubility decreases slightly as the temperature is increased from ambient temperature reaching a minimum solubility at about 66°C (150°F) and then increasing continuously as the temperature is increased (Figure 2.14). On the other hand, pressure has a large influence. According to Figure 2.14, the solubility of natural gas in water at 500 psi and 150°F is about 4.1 ft^3/bbl and at 2000 psi and 150°F the solubility increases to about 11.9 ft^3/bbl (2.1 m^3 gas/m^3). The solubility of gas in water also is influenced by the amount of dissolved salts. Increasing salinity decreases the solubility of hydrocarbon gases in water according to the following empirical relationship:

$$R_B = R_{wp}\left[1 - X_c \times (\text{salts, ppm})\left(10^{-7}\right)\right] \tag{2.12}$$
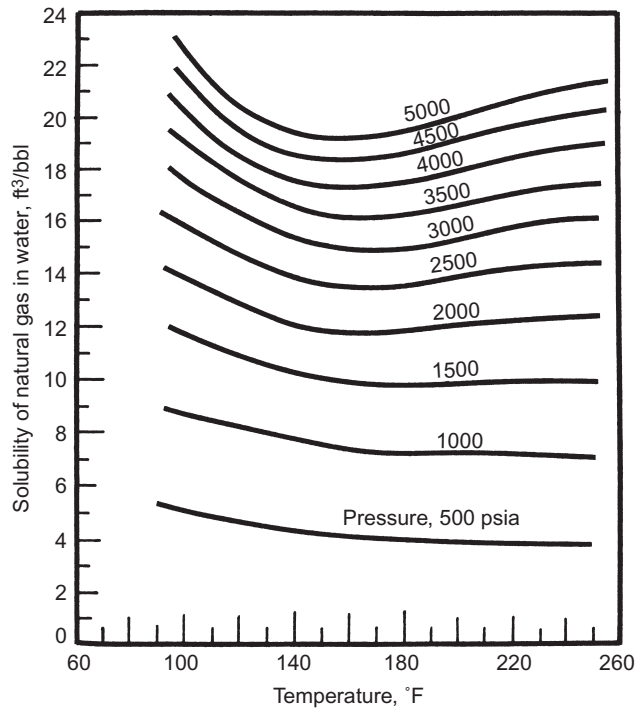

FIGURE 2.14

Solubility of natural gas in water as a function of temperature and pressure [27].

Table 2.4 Salinity Correction Factor for Estimation of the Solubility of Hydrocarbon Gases in Brine [24]	
X_c (Salinity Correction Factor)	$T°$F
75	100
50	150
44	200
33	250

where:

R_{wp} = solubility of gas in pure water, m^3/m^3 (SCF/bbl)
R_B = solubility of gas in brine, m^3/m^3 (SCF/bbl)
X_c = salinity correction factor (Table 2.4)

EXAMPLE

Brine from a 7000 feet deep reservoir in Kansas where the mean annual surface temperature is 70°F contains 80,000 ppm of total dissolved salts (TDS). If the reservoir pressure is 3300 psi, estimate the solubility of hydrocarbon gas in the oilfield brine at reservoir conditions. Assume a geothermal gradient of 1°F/100 feet of depth and use Equation (2.11) to estimate the reservoir temperature (T_f):

Solution

$$T_f = 70 + 1.0(7000/100) = 140°F$$

Use Figure 2.14 to obtain the solubility of gas in pure water ($R_{wp} = 16$ ft^3/bbl). Then, extrapolate the salinity correction factor (X) to 140°F using Table 2.5.2 ($X = 55$).

$$R_B = 16\left[1 - 55\left(80,000 \times 10^{-7}\right)\right] = 8.96 \text{ SCF/bbl}$$

Viscosity

All fluids resist a change of form, and many solids exhibit gradual yield in response to an applied force. The force acting on a fluid between two surfaces is called a shearing force because it tends to deform the fluid. The shearing force per unit area is the shear stress (τ). Consider two layers of fluid with area, A, separated by a distance, y. The upper layer is in motion with velocity, v, resulting from action of a force, F; and, the lower area is at rest (velocity = 0) A. Newtonian fluid (shear rate is a linear function of the applied shear force between the two layers) will develop a constant shear velocity (dv/dy) between the two layers, which is opposed by the friction between the fluid molecules, and the absolute viscosity is defined by:

$$\tau = F/A = -\mu(dv/dy) \tag{2.13}$$

where:

τ = shear stress
μ = absolute viscosity
v = fluid velocity = distance between the plates.

Table 2.5 Physical Properties of Various Hydrocarbons and Associated Compounds [32]

| Constituent | Molecular Weight | Normal Boiling Point | | Liquid Density (lb_m/cu ft) | Gas Density at 60°F, 1 atm (lb_m/cu ft) | Critical Temperature (°R) | Critical Pressure (psia) |
		°F	°R				
Methane, CH_4	16.04	−258.7	201	18.72[a]	0.04235	344	673
Ethane, C_1H_6	30.07	−127.5	332	23.34[a]	0.07986	550	712
Propane, C_3H_8	44.09	−43.8	416	31.68[b]	0.1180	666	617
Iso-butane, C_4H_{10}	58.12	10.9	471	35.14[b]	0.1577	735	528
n-Butane, C_4H_{10}	58.12	31.1	491	36.47[b]	0.1581	766	551
Iso-Pentane, C_3H_{10}	72.15	82.1	542	38.99	—	830	483
n-Pentane, C_3H_{12}	72.15	96.9	557	39.39	—	847	485
n-Hexane, C_3H_{14}	86.17	155.7	615	41.43	—	914	435
n-Heptane, C_7H_{16}	100.20	209.2	669	42.94	—	972	397
n-Octane, C_8H_{18}	114.22	258.1	718	44.10	—	1025	362
n-Nonane, C_9H_{20}	128.25	303.3	763	45.03	—	1073	335
n-Decane, $C_{10}H_{22}$	142.28	345.2	805	45.81	—	1115	313
Nitrogen, N_2	28.02	−320.4	140	—	0.0739	227	492
Air (O_2+N_2)	29	−317.7	142	—	0.0764	239	547
Carbon dioxide, CO_2	44.01	−109.3	351	68.70	0.117	548	1073
Hydrogen sulfide, H_2S	34.08	−76.5	383	87.73	0.0904	673	1306
Water	18.02	212	672	62.40	—	1365	3206

[a]*Apparent density in liquid phase.*
[b]*Density at saturation pressure.*

Hydrocarbon fluids deviate from Newtonian fluid behavior in many ways that depend of their chemical composition; hence, the viscosity is defined at a specific temperature and pressure and is most often correlated to the API gravity.

The viscosity of gases increases as temperature (T) is increased at constant pressure (P) and also increases as P increases at constant T. Liquids, however, exhibit a decrease of viscosity as T is increased, and an increase of viscosity as P is increased.

Viscosity is reported in terms of several different units: Poise (CGS unit of absolute viscosity) = g/cm s = 14.88 lbm/ft s; Centipoise = 0.0 1 poise; stoke (CGS of kinematic viscosity) = g/cm s g/cm³); Centistoke = 0.0 1 Stoke; and Pascal-seconds (SI units) = 0.1 Poise [33,34].

Figure 2.15 may be used to estimate the viscosity of oilfield waters as a function of salinity, temperature and pressure. A separate chart (inset on Figure 2.15) is used to obtain a factor relating the viscosity to pressure.
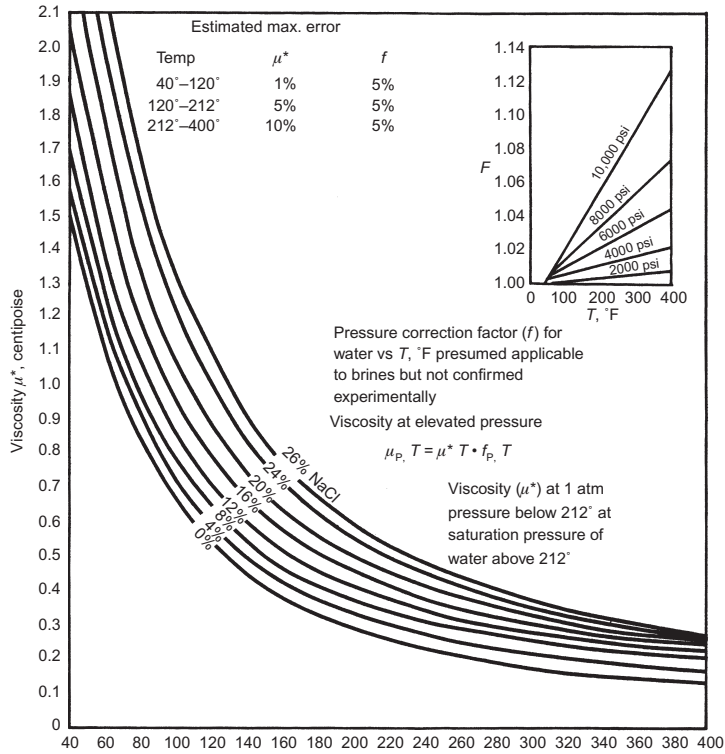
FIGURE 2.15

Viscosity of water as a function of temperature, salinity, and pressure [22].

EXAMPLE

Estimate the viscosity of a brine containing 12% salts which was obtained from a reservoir with a fluid pressure of 6000 psi and temperature of 180°F.

Solution

Obtain the pressure correction factor from the chart (Pressure Correction Factor = 1.018)

Viscosity of 12% brine at 180°F and 14.7 psia = 0.48 cP

Viscosity at 180°F and 6000 psia = (0.48)(1.018) = 0.49 cP

PETROLEUM

Petroleum is a complex mixture containing thousands of different compounds, most of which are composed exclusively of hydrogen and carbon (hydrocarbons). Included in the mixture are compounds containing nitrogen, sulfur, oxygen, and metals (heterogeneous compounds) (Table 2.5). In 1927, the

American Petroleum Institute (API) initiated Research Project 6 "The Separation, Identification, and Determination of the Chemical Constituents of Commercial Petroleum Fractions," which was designed to elucidate the structure of compounds in crude oil from the Ponca City oilfield, Oklahoma. By 1953, 130 hydrocarbons had been identified. The number of compounds clearly identified has increased greatly since then after introduction of gas chromatography and mass spectroscopy [13].

The density and viscosity of hydrocarbon gases and liquids are very important physical quantities. They are used to characterize pure and mixed hydrocarbons and to evaluate their fluid flow behavior in the reservoir.

Gas Density

The density of gases may be calculated from the equation of state for real gases (Equation (2.15)), which is corrected for non-ideal behavior by a compressibility factor Z. The factor Z is the ratio of the actual volume occupied by a real gas to the volume it would occupy if it behaved like an ideal gas where $Z = 1.0$ [30,33].

$$pV = ZmRT/M \qquad (2.14)$$

or

$$\rho = m/V = PM/ZRT \qquad (2.15)$$

where:

p = pressure, psi
V = volume, ft^3
Z = real gas deviation factor
m = mass of gas, lbs
R = gas constant (10.73 psi-ft^3/lbmole-°R)
T = temperature, °R
M = molecular weight of the gas

Gravitational units are used because, to date, engineering charts in the United States have not been converted to SI units.

The compressibility factor, or real-gas deviation factor, is obtained from the reduced temperatures and pressures and the compressibility charts for pure and mixed gases (Figure 2.16). The reduced temperature and pressure are calculated from the gas pseudo critical temperatures and pressures as follows:

$$T_{pr} = T/T_{pc} \quad T_{pr} = p/p_{pc} \qquad (2.16)$$

where:

T_{pr} and p_{pr} = pseudo reduced temperature and pressure
T_{pc} and p_{pc} = critical temperature and pressure.

Viscosity of Gases

Gas viscosity varies with respect to temperature, pressure, and molecular weight. The exact mathematical relationships have not been developed; however, Carr *et al.* developed two charts that may be used to estimate gas viscosities at various temperatures and pressures (Figures 2.17 and 2.18) [30].
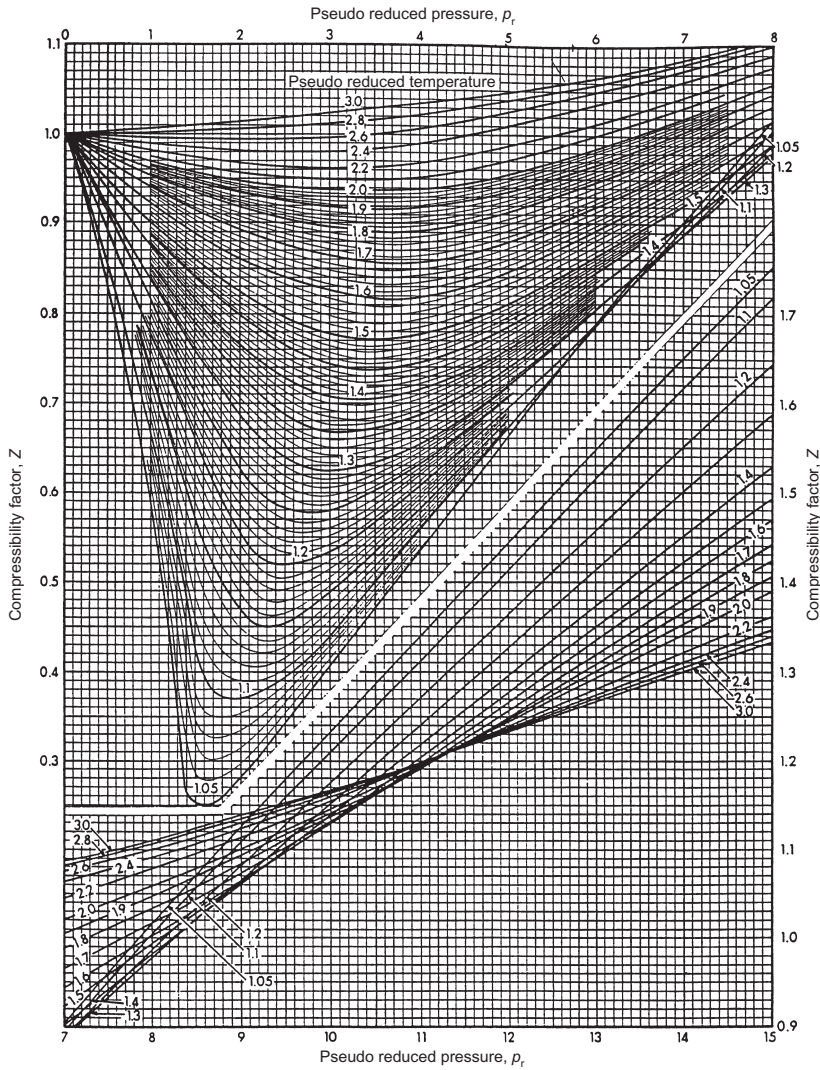
FIGURE 2.16

Real-gas deviation factor as a function of P_{pr} and T_{pr}.

Oil Density

The most commonly measured physical property of crude oils and its fractions is the API gravity. It is an arbitrary scale which was adopted for simplified measurements by hydrometers, because it enables a linear scale for gravity measurement. The API gravity is directly related to the specific gravity (measured at 60°F) as follows:

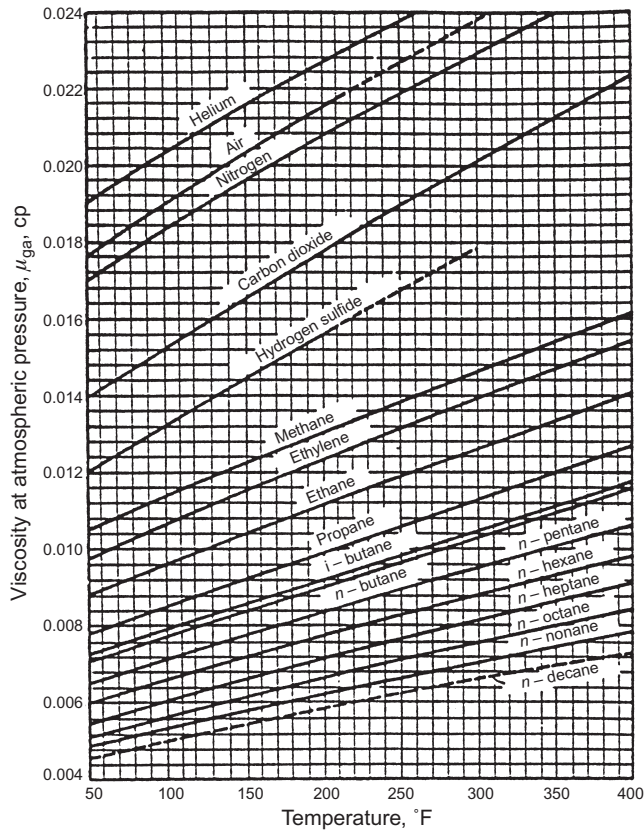$$°API = (141.5/SG_{60°F}) - 131.5 \qquad (2.17)$$

FIGURE 2.17

Viscosity of gases at one atmosphere as a function of temperature [22].

The °API gravity does not have a linear relationship to the physical properties of petroleum, or its fractions, therefore it is not a measure of the quality of the petroleum. The measurements are important, however, because the API gravity is used with other parameters for correlation of physical properties, also the price of petroleum is commonly based on its API gravity.

A comparison of API gravity and specific gravity is shown in Table 2.6. Specific gravity (SG) is the density of the fluid at any temperature and pressure divided by the density of water at 60°F and l4.7 psia (62.34 lbm/ft^3; where lbm = pounds mass). Note that the °API gravity is inversely proportional to the specific gravity and an °API gravity of 10° corresponds to the specific gravity of water at 60°F (SG = 1.0).

Oil Viscosity
Two methods for measuring the viscosity of crude oils and their fractions that have received universal acceptance are: (1) the kinematic viscosity measurement, which is obtained by timing the flow of a measured quantity of oil through a glass capillary, yielding the viscosity in centistokes, and (2) the
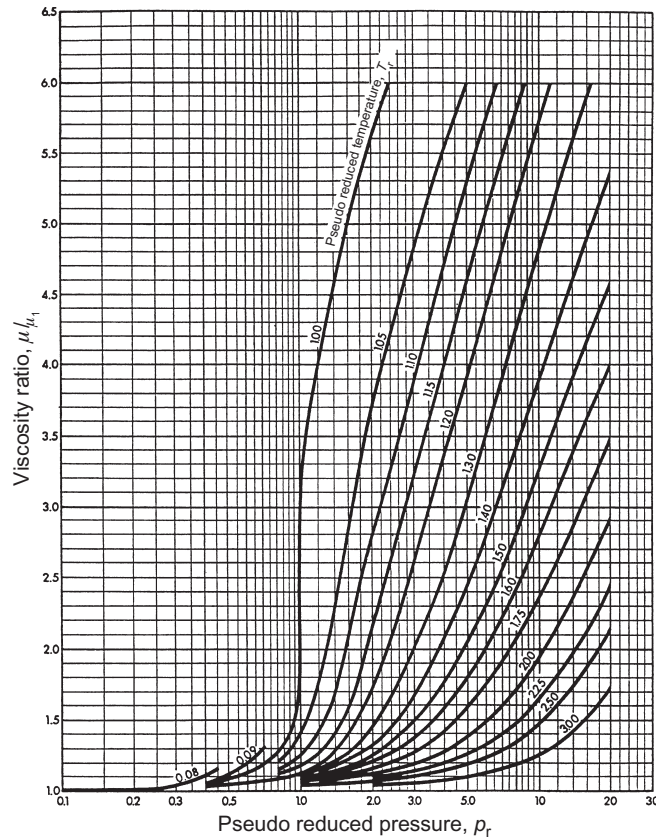
FIGURE 2.18

Viscosity ratio as a function of pseudo reduced pressure [22].

Table 2.6 Comparison of API Gravity and Specific Gravity at 60°F and 1 Atmosphere Pressure [13]

API Gravity	Fluid Type	Specific Gravity
−8	Heavy oils and brines	1.1460
−4	Heavy oils and brines	1.1098
0	Heavy oils and brines	1.0760
5	Heavy oils and brines	1.0366
10	Heavy oil and fresh water	1.000
15	Heavy oil	0.9659
20	Heavy oil	0.9340
30	Light oil	0.8762
40	Light oil	0.8251
50	Condensate fluids	0.7796

Saybolt viscosity measurement which is the time (seconds) required for a standard sample of oil to flow through a standard orifice (ASTM Test D-88). The Saybolt Universal viscometer is used for refined oil fractions and lubricating oils and the Saybolt Furol ("fuel and road oil") viscometer is used for high viscosity crude oils and fractions; (the Furol viscometer has a larger diameter orifice). Results of the test are expressed in Saybolt or Furol seconds at a specified temperature.

Tables 2.7 and 2.8 are used to convert from Saybolt seconds to centistokes. Absolute viscosity (centipoises) is obtained by multiplying centistokes by the density of the oil [32].

Table 2.7 Conversion of Viscosity Measured as Saybolt Universal Seconds at Two Temperatures to Centistokes [31]

Centistokes	Saybolt 100°F	Seconds at 210°F	Centistokes	Saybolt 100°F	Seconds at 210°F
2	32.6	32.8	28	132.1	133.0
3	36.0	36.3	30	140.9	141.9
4	39.1	39.4	32	149.7	150.8
5	42.3	42.6	34	158.7	159.8
6	45.5	45.8	36	167.7	168.9
7	48.7	49.0	38	176.7	177.9
8	52.0	52.4	40	185.7	187.0
9	55.4	55.8	42	194.7	196.1
10	58.8	59.2	44	203.8	205.2
12	65.9	66.4	46	213.0	214.5
14	73.4	73.9	48	222.2	223.8
16	81.1	81.7	50	231.4	233.0
18	89.2	89.8	60	277.4	279.3
20	97.5	98.2	70	323.4	325.7
22	106.0	106.7	80	369.6	372.2
24	114.6	115.4	90	415.8	418.7
26	123.3	124.2	100	462.9	465.2

Table 2.8 Conversion of Viscosity Measured as Furol Seconds at 122°F to Centistokes [31]

Centistokes	Furol Seconds at 122°F	Centistokes	Furol Seconds at 122°F
48	25.3	140	67.0
50	26.1	145	69.4
52	27.0	150	71.7
54	27.9	155	74.0
56	28.8	160	76.3
58	29.7	165	78.7
60	30.6	170	81.0
62	31.5	175	83.3

Table 2.8 Conversion of Viscosity Measured as Furol Seconds at 122°F to Centistokes [31]—cont'd

Centistokes	Furol Seconds at 122°F	Centistokes	Furol Seconds at 122°F
64	32.4	180	85.6
66	33.3	185	88.0
68	34.2	190	90.3
70	35.1	195	92.6
72	36.0	200	95.0
74	36.9	210	99.7
76	37.8	220	104.3
78	38.7	230	109.0
80	39.6	240	113.7
82	40.5	250	118.4
84	41.4	260	123.0
86	42.3	270	127.7
88	43.2	280	132.4
90	44.1	290	137.1
92	45.0	300	141.8
94	45.9	310	146.5
96	46.8	320	151.2
98	47.7	330	155.9
100	48.6	340	160.6
105	50.9	350	165.3
110	53.2	360	170.0
115	55.5	370	174.7
120	57.8	380	179.4
125	60.1	390	184.1
130	62.4	400	188.8
135	64.7		

PETROLEUM CHEMISTRY

Petroleums are frequently characterized by the relative amounts of four series of compounds. The members of each series are similar in chemical structure and properties. The four series (or classes of compounds) that are found in petroleums are: (1) the normal and branched alkane series (paraffins), (2) cycloalkanes (naphthenes), (3) the aromatic series, and (4) asphalts, asphaltenes and resins (complex, high-molecular-weight polycyclic compounds containing nitrogen, sulfur and oxygen atoms in their structures—the NSO compounds). The petroleums are generally classified as paraffinic, naphthenic, aromatic, and asphaltic according to the relative amounts of any of the series [14].

Tissot and Welte subdivide this classification further into six groups by adding intermediate types of oils using a ternary diagram (Figure 2.19) [14]. According to this classification, an oil is considered as aromatic if the total content of aromatics, asphaltenes and resins is 50% or greater. Paraffinic oils contain at least 50% of saturated compounds, 40% of which, are paraffins. Likewise, naphthenic oils
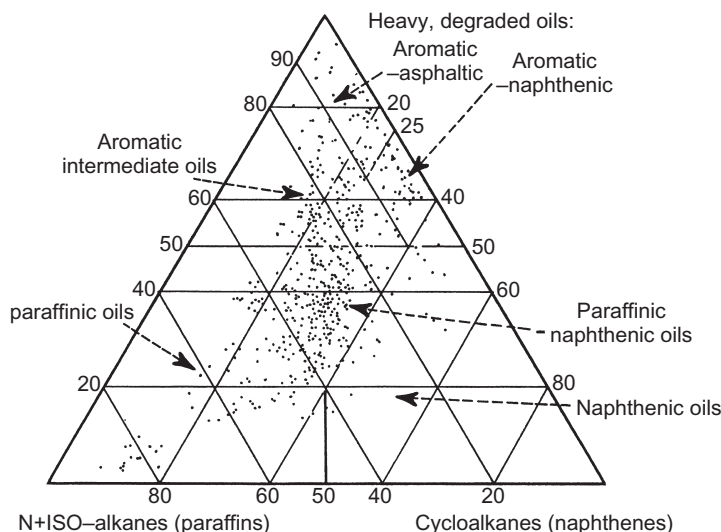
FIGURE 2.19

Ternary diagram for classification of crude oils as either paraffinic, naphthenic or aromatic [14].

are those composed of 50% or more saturated compounds of which 40% or more are naphthenes. The gases and low boiling fractions of petroleum contain greater amounts of the low-molecular-weight alkanes. Intermediate boiling fractions contain greater amounts of the cyclic alkanes and aromatics and the higher boiling fractions ($>750°F$-$399°C$) are composed predominantly of the naphthano-aromatics. Hunt presents the composition of a crude oil which is classified as naphthenic according to Figure 2.19 because the oil contains 49% naphthenes and the total amount of saturated hydrocarbons (paraffins and naphthenes) is 79% (Table 2.9) [35]. Also listed in the table are the molecular size ranges (number of carbon atoms per molecule) of average refinery fractions of crude oils and the approximate weight percentage of each fraction that can be obtained from the naphthenic crude oil described above.

The U.S. Bureau of Mines Research Center at Bartlesville, Oklahoma, standardized the classification of crude oils by distillation and has characterized a large number of oils from oilfield around the world. The distillation of a crude oil from the Oklahoma City oilfield is shown in Table 2.10 liter of oil is placed in the flask and the temperature is raised gradually while the volume percent collected at specific temperatures is recorded. After $275°C$ the flask is placed under a vacuum of 40 mm Hg and the distillation is continued as shown in Table 2.10.

Table 2.9 Composition and Refinery Fractions of a Naphthenic Crude Oil [35]			
Molecular Type	**WT%**	**Molecular Size**	**WT%**
Naphthenes	49	Gasoline ($C_4 - C_{10}$)	31
Paraffins	30	Kersone ($C_{11} - C_{12}$)	10
Aromatics	15	Gas oil ($C_{13} - C_{20}$)	15
Asphalts/Resins	6	Lubricating oil ($C_{20} - C_{49}$)	20
		Residium (C_{40+})	

Table 2.10 U.S. Bureau of Mines Distillation Method for Analysis of Crude Oil, Paul-Kune No. 1								
Oklahoma City Field Pure Sand 6511-6646 ft		Sample 38005				Oklahoma Oklahoma County 11 N-3 N-Indian		
General Characteristics								
Specific gravity, 0.844 Sulfur, percent, 0.16 Saybolt Universal viscosity at 77°F, 62 s, at 100°F, 50 s						A.P.I. gravity, 36.2° Color, brownish green		
Distillation, Bureau of Mines Hempel Method								
Distillation at Atmospheric Pressure, 752 mm							First Drop 86°F	
Fraction No.	**at °F**	**Percent**	**Sum Percent**	**SP. Gr. qq0/60°F**	**°API 60°F**	**C.I.**	**S.U. visc. 100°F**	**Cloud Test °F**
1	122	—	—	—	—	—		
2	167	1.7	1.7	0.672	79.1	—		
3	212	3.0	4.7	0.702	70.1	13		
4	257	4.9	9.6	0.734	61.3	19		
5	302	4.7	14.3	0.755	55.9	21		
6	347	4.7	19.0	0.772	51.8	23		
7	392	4.7	23.7	0.787	48.3	23		
8	437	5.0	28.7	0.801	45.2	24		
9	482	5.3	34.0	0.815	42.1	26		
10	527	6.7	40.7	0.829	39.2	28		
Distillation continued at 40 mm								
11	392	3.6	44.3	0.844	36.2	31	41	10
12	437	6.7	51.0	0.851	34.8	30	47	25
13	482	5.9	56.9	0.866	31.9	34	61	45
14	527	6.3	63.2	0.876	30.0	36	87	65
15	572	5.6	68.8	0.884	28.6	37	150	80
Residuum	28.6	97.4	0.925	21.5				
Carbon residue of residuum—4.2%; carbon residue of crude—1.2%								
Approximate Study								

Light Gasoline	**Percent 4.7**	**Sp. Gr. 0.691**	**°A.P.I. 73.3**	**Viscosity**
Total gasoline and naphtha	23.7	0.748	57.7	
Kerosene distillate	10.3	0.808	43.6	
Gas oil	15.0	0.838	37.4	
Nonviscous lubricating distillate	12.4	0.854-0.878	34.2-29.7	50-100
Medium lubricating distillate	7.4	0.878-0.888	29.7-27.9	100-200
Viscous lubricating distillate	—	—	—	+100
Residuum	28.6	0.925	21.5	
Distillation loss	2.6			

Alkanes also are referred to as saturated hydrocarbons because the valence (or bonding capacity) of all of the carbon is satisfied by hydrogen atoms. Each carbon atom is connected to another carbon atom by a single covalent bond, and the remaining bonding capacity is occupied by hydrogen atoms. Isomers are compounds that have the same atomic composition, but differ in molecular structure. There are three structurally different pentanes, although they each have the same number of carbon and hydrogen atoms (n-pentane, iso-pentane and 2,2-dimethyl propane). The structural difference results in slight differences in chemical reactivity and physical properties as indicated by the difference of the boiling points of the three pentanes. As the number of carbon atoms increases in a homologous series, the number of possible isomers also increases, for example there are 18 isomers of octane (eight carbon atoms) and 75 isomers of decane (10 carbon atoms). Thus a single homologous series of compounds exhibits enormous complexity. Even though crude oils from different locations may have the same °API gravity and viscosity, they can vary widely with respect to chemical composition.

The alkanes with 25, or more, carbon atoms are solids at room temperature and are extracted from the crude oils to make industrial paraffin waxes. Crude oils containing these alkanes become cloudy when cooled. The temperature at which this occurs is called the cloud point which is used in refineries as a general indication of the abundance of paraffin waxes. The precipitation of high-molecular-weight alkanes from crude oils in the formation around the producing wellbore and in the production tubing reduces the rate of production and must be periodically cleaned [36].

Crude oils derived principally from terrestrial plant organic material contain high amounts of alkanes, but oil generated from marine organic materials generally contains greater amounts of cyclic saturated and unsaturated compounds. If, after it has migrated from a source rock to an oil trap, paraffinic oil is exposed to the percolation of meteoric water due to diastrophism, aerobic bacteria will remove the paraffins by gradual degradation to carboxylic acids and carbon dioxide [14]. A crude oil that has been exposed to aerobic bacterial degradation will be chiefly composed of aromatics, asphalts and resins.

PROBLEMS

2.1 Convective currents in the mantle are apparently responsible for the movements of continents. Explain the location (accumulation) of continents and basins in response to rising and descending convection currents in the mantle.

2.2 Calculate the seismic velocities through sandstone from the following data and compare them to the velocities in limestone. Why are the velocities different?

$$B = 3.4 \times 10^{10} \text{ Pa}; \ S = 3.1 \times 10^{10} \text{ Pa}; \ \rho = 2.64 \text{ g/cm}^3.$$

2.3 Explain the initial formation of the Appalachian mountain range. What were the geologic periods and estimated time when this began and reached its climax?

2.4 If the relative radiocarbon content of the remains of a plant is 1/7, how long ago did the plant live? What geologic period and epoch was this?

2.5 Explain the meaning of a craton. Where are these located?

2.6 Discuss transgressive and regressive periods of sedimentary deposition. Which leads principally to formation of hydrocarbon source rocks? Why?

2.7 What are the meanings of clastics, granite wash, arkose, and graywacke? Where are some general locations of these types of rocks?

2.8 Well logs of an area show that the temperature at the bottom of a 3140 m deep well is 92°C. If the mean surface temperature is 27°C, what is the geothermal gradient?

2.9 A brine sample from a geopressured zone 2929 m deep had the composition listed below. Compare the brine sample analysis to that of sea water (Table 2.3) and give a reasonable explanation for the differences. What is the TDS of the brine?

Ion	Concentration, PPM
Na	29,400
Ca	2662
Mg	1011
K	172
Ba	5
Cl	46,618
HCO	714
SO	60
Br	40
I	23

2.10 The Saybolt viscosity of oil is 117 s at 100°C. What is the viscosity in centipoises?

2.11 Show the chemical structures of the following compounds: iso-propane, 1-methyl-2-ethyl cyclohexane, para-xylene and anthracene.

2.12 Explain the difference between a structural and stratigraphic hydrocarbon trap.

NOMENCLATURE

B_w water FVF
c_w water compressibility
c_{sw} compressibility of water with solution gas
C_t radioactive decay constant
D depth
F_c salinity correction factor
g_c gravitational constant
G_t geothermal gradient
G_p pressure gradient
G shear modulus
h_o height of oil column
K bulk modulus
m mass of gas, lbm
M molecular weight
N moles
N_o original amount of parent element

N_t	amount of daughter isotope currently present
p	pressure
p_d	displacement pressure
p_f	fluid pressure
p_l	lithostatic pressure
p_{ov}	overburden pressure
p_{pc}	pseudocritical pressure
p_{pr}	pseudoreduced pressure
P_c	capillary pressure
r	radius
r_c	radius of a capillary
R	universal gas constant
R_b	solubility of gas in brine
R_{wp}	solubility of gas in pure water
R_{sw}	solubility of gas in water
SG	specific gravity
SFC	standard cubic feet
t	time
$t_{1/2}$	half-life of parent element
T	temperature
T_f	formation temperature
T_{pc}	pseudo-critical temperature
T_{pr}	pseudo-reduced temperature
T_R	reservoir temperature
T_s	surface temperature
TDS	total dissolved solids
v	velocity
V	volume
x	Cartesian distance coordinate
z	valence
Z	real gas deviation factor
Z_o	height of a column of oil

Greek Symbols

γ	specific gravity
θ	contact angle
μ	viscosity
μ_{ga}	gas viscosity at atmospheric pressure
μ^*_T	viscosity at reservoir temperature and atmospheric pressure
ρ	density
ρ_f	fluid density
ρ_m	rock matrix density
ρ_o	oil density
ρ_w	water density
σ	interfacial tension
τ	shear stress

Subscripts

c   compressional wave
d   displacement
f   fluid
h   horizontal
l   leading pore or edge
o   oil
ob   overburden
s   shear wave
t   trailing pore or edge
v   vertical
w   water
1,2 reservoir zones

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