that at least some of it escaped the various destructive forces that prevail between the areas of erosion and the sea and became reincorporated in sediments.

objectives

TRANSFORMATION OF ORGANIC MATTER INTO PETROLEUM

In addition to the hydrocarbons in living organisms, there are hydrocarbon compounds that are petroleum-like in their composition and could readily and easily be transformed into petroleum hydrocarbons. Transformation of some of these petroleum-like hydrocarbons probably accounts for a part of the petroleum supply, and such transformation most likely occurs early, or by the time diagenesis of the sediments is complete, for we find petroleum widely disseminated through the nonreservoir sediments. These various hydrocarbons and hydrocarbon compounds occur in minute quantities per acre-foot of nonreservoir sediments, but the volume of such sediments is so vast that the escape of but a fraction of them would be adequate to supply the petroleum of the world many times over.

The transformation of a primary petroleum-like organic material into petroleum begins with its deposition in the sediments in a reducing environment. The transformation process requires energy, and several possible sources of energy are available. These include: (1) bacterial action, (2) heat and pressure, (3) catalytic reactions, and (4) radioactive bombardment.

Bacterial Action

The well-known, everyday decomposition of organic matter of all kinds by bacterial fermentation, and the evolution of methane as one of the products of such decay, are good reasons for considering bacterial action as an agency in the formation of other petroleum hydrocarbons as well. Many organic chemical reactions are brought about as readily by bacteria in nature as by chemists in the laboratory. Some bacteria require free oxygen (aerobic bacteria); others use combined oxygen and cannot live in the presence of free oxygen (anaerobic bacteria); and still others can live either in the presence or in the absence of free oxygen (facultative bacteria). Bacteria grow readily under a wide variety of temperatures and pressures, in fresh water and in brines, in soils, streams, lakes, and swamps. The rapid decay that takes place in an oxidizing environment, as in contact with the atmosphere, is largely due to the rapid growth of aerobic bacteria. The slow decay or absence of decay in a reducing environment is largely due to the low bacterial population resulting from the low oxygen supply. Available oxygen is supplied through air and carbonic acid dissolved in water. The supply of free oxygen diminishes rapidly below the surface of the sea floor, and anaerobic bacteria become important reducing agents during the diagenesis of the sediments, and possibly long

ing its viscosity. (3) The carbon dioxide produced by bacteria *in situ* develops an internal gas pressure, which tends to drive oil from dead-end pockets and through interstitial spaces. (4) Some bacteria are thought to have a greater affinity for solid surfaces than oil does, so that they crowd it off. They are called *thigmotactic bacteria*. Some bacteria produce detergents, or surface-active substances, that liberate oil from solid surfaces, presumably by changing the interfacial tensions.

Bacterial Release of Oil from Plants. Some plants synthesize appreciable amounts of hydrocarbons, and selective decomposition of the plant material by bacteria may release these hydrocarbons for eventual accumulation in the sediments.

Bacterial Oxidation. Most kinds of petroleum hydrocarbons are susceptible to oxidation by bacteria under certain conditions. Many microorganisms that are known to utilize hydrocarbons are commonly found in marine sediments, and they are particularly abundant in the soil around storage tanks, oil wells, and oil and gas seepages. Oil spread on the ground may be completely destroyed in a few months, whereas under water it may retain its physical characteristics for years. Long-chain aliphatic and paraffinic compounds are oxidized more readily than corresponding aromatic and naphthenic compounds.

Heat and Pressure

Heat combined with pressure, or pressure alone, has been advanced as a means of transforming organic matter into petroleum. The reaction may or may not be aided by the presence of catalysts. (See pp. 524–526.) Heat and pressure occur together in rocks in varying degrees; if it could be shown that they were able to accomplish the transformation, they would offer a simple and ready agency. Rich early decided that "the oil was distilled from the carbonaceous rocks in what was, virtually, a giant high-pressure cracking still, and that it found easiest escape laterally along the bedding, being driven out to cooler zones by the gases generated during the distillation." [64] Experiments by Seyer led him to conclude: "The transformation of the waxy substance can then be regarded as a sort of low-temperature, high-pressure cracking process in which production favors cyclic hydrocarbons." [65]

Solid organic matter, such as that found in kerogen shales and "source rocks," is a pyrobitumen; that is, heat is required—a temperature of 350–400°C (662–752°F)—to break it down into gaseous and liquid substances. Doubt has been raised about the generally accepted conclusion that the presence of porphyrins in petroleum is evidence that the temperature of petroleum has never exceeded 200°C (392°F).[66] Time may replace temperature; but even so, if there is any validity to the porphyrin thermometer, 200°C is the maximum allowable temperature. Reservoir temperatures up to 235°F

content of marine sapropel, which supports the aerobic bacteria, and a loss of oxygen with burial, which suggests that, as the source of air and free oxygen is shut off, there is a change from aerobic to anaerobic bacteria.

TABLE 11-2   Effects of Oxidation in Various Zones (in percent)

Type of Material	Carbon	Hydrogen	Oxygen	Nitrogen	Phosphorus
Marine sapropel	52	6	30	11	0.8
Recent sediments	58	7	24	9	0.6
Ancient sediments	73	9	14	0.3	0.3
Crude oil	85	13	0.5	0.4	0.1

Bacteria not only may have a direct part in the origin of organic matter and its transformation into petroleum hydrocarbons, but may promote its development in many other ways. Some of these are as follows:

Evolution of Hydrogen.   Fermentation of organic matter in the absence of free oxygen may result in the liberation of appreciable quantities of hydrogen, according to ZoBell.[43] The liberation of hydrogen has been accomplished experimentally. In anaerobic bacterial fermentation that produces no free hydrogen, the reason for the absence of free hydrogen may be (1) that hydrogen is activated and united with carbon dioxide to produce methane, as in the equation

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$
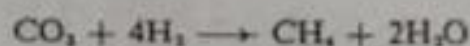
or (2) that certain bacteria cause hydrogen to reduce some sulfate to hydrogen sulfide, as in the equation

$$SO_4 + 5H_2 \longrightarrow H_2S + 4H_2O$$

or (3) that bacteria activate the hydrogenation of unsaturated organic compounds.

All these reactions are known to be carried out by anaerobic bacteria that occur in marine sediments. In marine sediments, therefore, one would expect to find the reduction products (methane, hydrogen sulfide, or saturated hydrocarbons) rather than free hydrogen. It may be significant in this regard that unsaturated compounds are not found in petroleum.

Release of Oil from Sedimentary Rocks.   There are several mechanisms by which bacteria might liberate the oil held in oil-bearing sediments. (1) One mechanism is the solution of carbonates by H_2CO_3 and organic acids produced by bacteria; the oil contained in limestones and dolomites is liberated when channels and pores are formed by solution of the carbonates. (2) Carbon dioxide produced by bacteria tends to promote the movement of oil by decreas-

after burial. The presence of sulfate-reducing anaerobic bacteria in wells[58] is indicative of continuing reduction after burial.

Bacteria are thought to function in several ways in aiding the final transformation of organic decay products into petroleum. The evidence for this view is derived in part from results in the laboratory and in part from natural phenomena observed in the field. Investigators differ in regard to the efficiency of bacterial action; some believe that it can completely transform organic matter into petroleum, while others give it credit only for slight changes that merely make the original organic material more petroleum-like. Bacteria, for example, are able to deoxygenate certain kinds of organic matter (decarboxylation), to increase its nitrogen content (ammonification), and to remove the sulfur in producing hydrogen sulfide. Laboratory experiments to date have shown that bacteria are able to produce only methane from organic matter; various investigations are still in progress to determine if bacteria can produce higher hydrocarbons.

Most of the recent work on the relation of bacteria to the origin of petroleum has been done by ZoBell and his associates at the Scripps Institution of Oceanography, at La Jolla, California.[60] ZoBell finds large populations of living bacteria in ocean bottom deposits. Thousands of viable bacteria per gram of bottom sediments were recovered from material more than twenty feet below the sea floor. These bacteria or their enzymes (which act as organic catalysts) are capable of producing many chemical changes in organic material.

Geographic and geologic conditions have an effect on the distribution and type of microorganism[61] and determine the kind of bacteria found, the kind of organic matter that becomes the food for the organisms, and the kind of microbiological activity that occurs. At 3 to 4 feet below the surface, for example, deltaic clayey muds have a much higher bacterial population than carbonate material.

Numerous bacteria have also become recovered from ancient sediments and from petroleum found at depths of several thousands of feet. There is always a question, however, whether these bacteria may have been introduced either during the drilling of the well or afterward. Bacteria have been found, however, in petroleum produced from a well many years after it was drilled, which indicates that they are growing, at present at least, within oil-bearing formations. ZoBell concludes from the observations he has made on these bacteria that neither salinity, hydrostatic pressures of 150,000 pounds per square inch, nor temperatures of 85°C can prevent bacterial activity in a petroliferous environment. Most of these bacteria are facultative.

In a highly reducing environment bacteria tend to convert the organic remains of plants and animals into substances that are more petroleum-like. They do this by splitting oxygen, nitrogen, sulfur, and phosphorus from various organic compounds. The trend of these reactions[62] is illustrated in Table 11-2. The table shows the effect of the oxidizing zone in the high oxygen
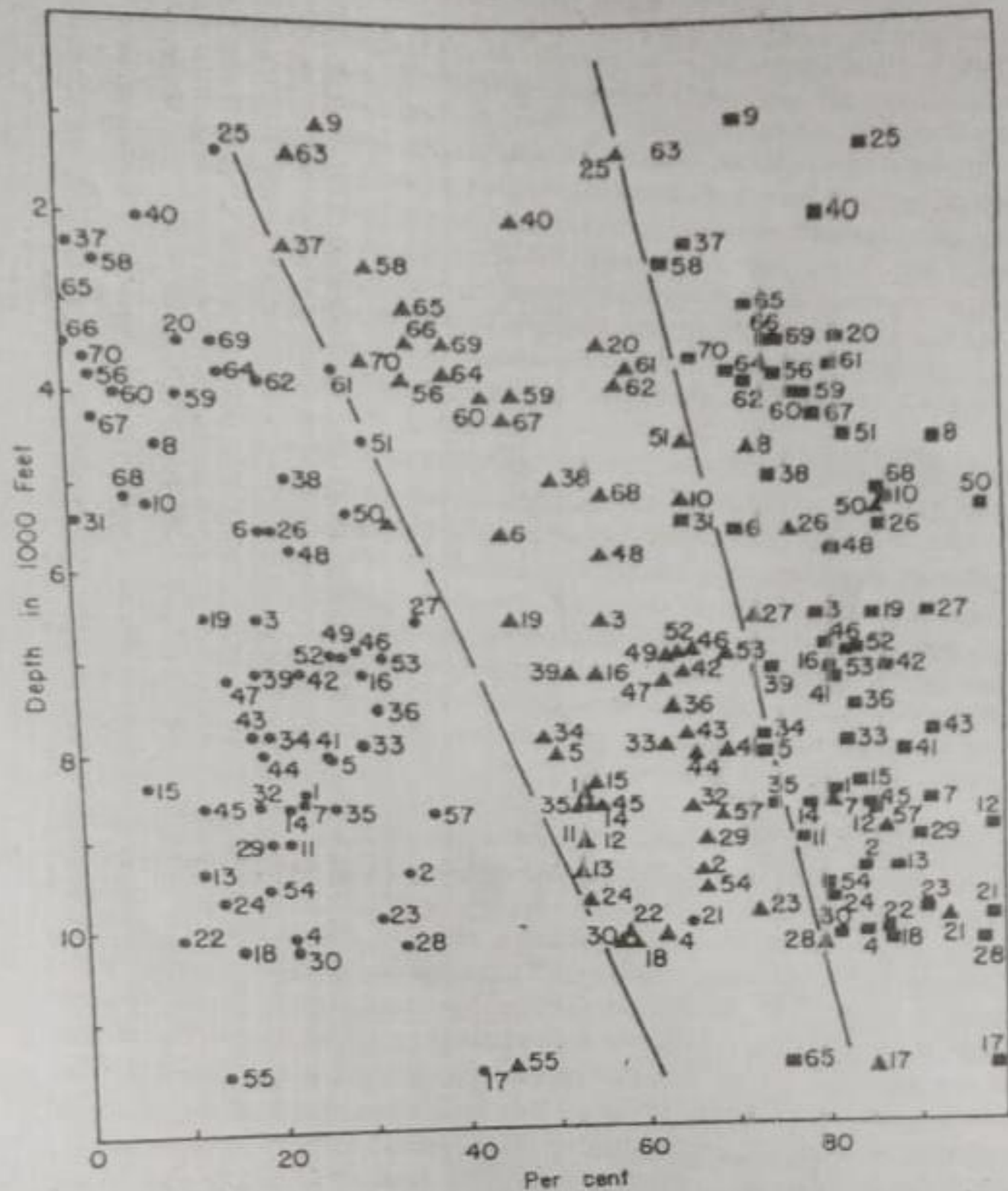
FIGURE 11-1 *Changes that occur with depth in seventy different crude oils of Miocene age from Louisiana. The small circles represent gasoline and naphtha, the distance from the left line being their percentage; the distance from the circles to the triangles represents the percentage of kerosene and gas oil; the distance from the triangles to the squares represents the percentage of lubricating oil distillates; the distance from the squares to the right line represents the percentage of heavy residue. Note the progressive increase in naphthas and gasolines and the decrease in heavier fractions as the oils become deeper. [Redrawn from Brooks, Bull. Amer. Assoc. Petrol. Geol., Vol. 33 (1949), p. 1604, Fig. 3.]*

with age, in the direction of more petroleum-like material.[16] In the top 3–4 feet of sediment, for example, hydrocarbons made up only 7.5 percent of the organic matter extracted, of which 92.5 percent was in the form of asphaltic and complex organic matter, whereas in the samples at 102–103 feet the proportion of hydrocarbons had increased to 30.9 percent and that of asphaltic and complex organic matter had decreased to 69.1 percent.

Hunt[18] has shown that in Wyoming, where only Mesozoic and Paleozoic oils were analyzed, the API gravity increased with depth. In the Tensleep oils, for example, where all of the geologic factors have been comparatively constant except the depth of burial, the deeper oils contained more gasoline and the shallower oils contained more of the heavy residuum.

Changes in Gravity. If the carbon-ratio theory, as originally proposed by David White and later further amplified by him,[17] is correct, and only the application is at fault, then there is reason to believe that low degrees of heat and pressure, as evidenced by the carbon ratios of the affected coals, determine the state of decomposition of the petroleums of any area. The carbon-ratio theory points to the progressive transformation of organic matter into petroleum by low temperatures and pressures, the end point being the formation of the low-boiling hydrocarbons found in natural gas. A more complete discussion of the carbon-ratio theory is deferred to Chapter 14, for its chief importance is its influence on exploration.

Catalytic Reactions. Catalysts are substances that aid or accelerate a chemical reaction but take no part in the reaction; they remain the same in composition at the completion of the reaction as at the beginning. Organic catalysts are called *enzymes*. Catalysis is a complex and essentially a free-surface-energy phenomenon. One method of increasing catalytic action, therefore, is to increase the surface area, either by using a more finely divided catalyst or by increasing the pore surface of the material catalyzed. The atoms that are adsorbed on the surface layers of a catalyst are stimulated into unusual activity by the atoms of the catalyst, and, when atoms of two or more substances are adsorbed by the catalyst, they interact to form new combinations. This is why, the greater the catalytic surface exposed, the more rapidly the reaction goes forward. The large surface areas of fine particles in reservoir rocks, together with the complex chemical substances found there, suggest catalytic effects as an aid in the transformation of organic matter into petroleum, or at least into petroleum-like materials. A stronger reason, however, is that catalysts, at the low temperatures found in the reservoir rocks, may promote reactions that would not otherwise go forward except at high temperatures. In refinery operations, catalysts are exceedingly useful and work in many ways. They should be considered as possible tools in the natural transformations and alterations of organic matter into petroleum.

Thermal cracking in refinery operations—without catalysts—involves the

treatment of petroleum stocks at temperatures in the range 850–1,150°F (454–620°C) and at pressures from atmospheric pressure up to 1,600 psi. But with catalysts the reactions are accelerated, the temperatures are reduced to 750–1,000°F (399–538°C), and pressures are reduced to 100 psi and less. Reactions that take place to various degrees in refinery catalytic processing include cracking, polymerization, alkylation, aromatization, isomerization, hydrogenation, dehydrogenation, and cyclization.[78] Such reactions occur quite rapidly and are complex. The catalysts used are clays, synthetic pellets or beads, and synthetic "fluid" catalysts.

Some catalysts may occur as compounds within the petroleum. For example, vanadium, molybdenum, and nickel are common elements in the ash from crude oils, and certain salts of these elements are effective catalysts for the laboratory synthesis of hydrocarbons. Presumably these elements were extracted from sea water by organisms, and would be available for catalytic action during the entire decomposition period of the organic matter.

The organic matter associated with clay sediments may occur as discrete particles mechanically mixed with the clay particles, or it may occur as molecules adsorbed on the lattice planes of the clay minerals, especially the basal cleavage surfaces.[79] The effect of the clay minerals on the organic matter is thought to be catalytic and due to the close molecular structural similarity between some of the clay minerals and some of the organic compounds. Adsorption of organic matter by the clays, and replacements within the lattice structure, provide a possible means of changing organic matter in the direction of petroleum. This phenomenon may have wide significance as a mechanism whereby buried organic material is transformed into petroleum or petroleum-like substances.

A common application of catalytic adsorption is found in the use of Fuller's earth to change the character of many oils. Fuller's earth is a highly siliceous clay consisting essentially of hydrous aluminum silicates. It has the property of selectively adsorbing certain organic coloring matters from vegetable and mineral oils, and is used in many petroleum refinery operations. Its selective adsorptive action is thought to be largely due to the surface activity of its particles, which are of colloidal size.[80] Other commercial adsorptive materials are acid-treated bentonites, dehydrated silica gels, and bauxite. Gayer[81] has pointed out that laboratory experiments with rock samples from many geologic formations, such as the Sylvan shale (Silurian) of Oklahoma, the "green sands" (Cretaceous) of New Jersey and Texas, the Stanley shale (Mississippian) of Oklahoma, the Reagan sandstone (Cambrian) of Texas, and the Calvin sandstone (Pennsylvanian) of Oklahoma, showed that they all aided materially in the polymerization of propylene (C_3H_6) at a temperature of 35°C, which is well below the ordinary cracking temperatures. A number of naturally occurring substances, therefore, are known to have catalytic adsorptive properties.

Two points especially suggest that catalytic action is an important agent

(113°C) have been measured in oil pools, and a high recorded underground temperature—found in the Frontier sand (Cretaceous) of Wyoming at a depth of 20,521 feet, in a test well * that was not productive of oil or gas— is 325°F (163°C). Most oil-producing reservoirs have temperatures less than 200°F (93.2°C), and in many reservoirs this temperature has probably never been exceeded.

The explanation offered by Treibs[87] and others,[88] for example, is that time may replace temperature—that some reactions, if given a geologically long period of time, will occur at temperatures lower than those that are necessary in the laboratory. Maier and Zimmerly found that the conversion of the kerogen in a kerogen shale into a bitumen soluble in carbon tetrachloride behaved as a chemical reaction of the first order, which means that it was dependent, not solely on temperature, but also on time. In other words, the reaction would take place at any temperature, but the lower the temperature the longer the time required; an extremely slow but finite reaction may have produced a lot of product in the course of geologic time. If time has not accounted for a complete transformation at the low temperatures of the sediments, the transformation of only a minute percentage of the organic matter available could add a vast amount of petroleum hydrocarbons to those already available; time is the imponderable, as it is in many geologic problems.

Although kerogen may not be broken down into petroleum hydrocarbons, there are many liquid hydrocarbons and petroleum-like hydrocarbon compounds mixed with and attached to the solid matter that may be transformed into petroleum, and heat and pressure may either make or help make such transformation possible. The kerogen, then, is chiefly a nonpetroleum material left behind as a residue.

When folding or rock deformation occurs in sedimentary rocks, the constituent particles of the rock transmit the pressures through their contacts with one another. According to the character of the rock (its clay content, its soluble material, the character of its particles, etc.), its porosity may be increased (dilatancy) or decreased (compaction and cementation). At the points of particle contact, however, the pressures are momentarily great, and the particles glide over one another, so that shearing may occur and the temperature may rise. Fash[89] has called this last effect "skin frictional heat" and suggests it as the source of heat that may bring about the transformation of minute amounts of organic matter into more petroleum-like substances or even into petroleums.

Alteration of Petroleum by Heat and Pressure

There is empirical evidence suggesting that once crude oil has been formed, various changes in its composition and gravity occur along with changes in

* Superior Oil Company, Pacific Creek No. 1. Sec. 27 T. 27 N. R. 10W Sublette County, Wyoming.

pressure and temperature. These observable alterations suggest that at least part of the original transformation of organic matter was into asphaltic and naphthenic compounds, which were later further altered by pressure and heat. How the original transformation may have occurred, however, is not known. The evidence for these changes in petroleum character is of two kinds: (1) the changes in composition occurring with increasing depth of burial, presumably as a result of increasing pressure and rising temperature, and first studied by Barton[70] and later by Hunt; (2) changes in gravity and character as a result of regional metamorphism, presumably also a result of increased pressure and higher temperature, and first proposed by David White as the carbon-ratio theory.[71] (See also pp. 630–634.)

Changes in Composition. The progressive change in the character of petroleum that occurs with the increase in pressure and rise in temperature accompanying burial has been studied by Barton,[70] Brooks,[72] Pratt,[14] and Hlauscheck,[73] who all believed that the first crude oil formed—the protopetroleum —was naphthenic and asphaltic in character and heavier than the final oil evolved from it. A chart showing the changes in composition with depth of a group of Gulf Coast Tertiary crude oils is given in Figure 11-1; it suggests that the shallow crudes are closer to the composition of organic matter than are the deeper crudes with their increasing paraffin content. The chart also suggests that, if progressive changes such as these could occur with an increase in pressure and a rise in temperature, and if we extrapolated upward to near the surface of deposition, we might find that even the lower temperatures and pressures prevailing there might have initiated the transformation of at least some of the fresh organic material into petroleum or petroleum-like substances. The change in composition that accompanies the rise in pressure and temperature resulting from increasing depth of burial has been termed "maturing" of the oil.[14] While this chart and others like it suggest that the changes in the character of oil are a function of the increasing depth of burial, the same changes may also be correlated with facies, the higher gravities accompanying a change from continental, shallow-water, and sandy facies to marine, deeper-water, and shaly facies.[73]

There are many exceptions to the progressive and regular increase in lower boiling-point fractions with depth (see also p. 197) but in most of those cases the geologic section is broken by unconformities, hiatuses, and other disturbances, or by abrupt changes in facies with depth, that could account for the difference. For the studied examples of Gulf Coast oils, the geologic column is nearly complete and represents almost continuous deposition down to the Recent. For that reason the over-all changes are significant, for they indicate the normal undisturbed effects of increasing pressure and temperature, even though facies changes may cause some irregularities in the orderly arrangement. Even the Recent sediments near the surface of the water-sediment contact in the Gulf of Mexico suggest an early change, with depth or possibly

activity, while black organic shales contain high concentrations of the three principal radioactive elements. Russell,[92] who examined the radioactive content of 510 samples of sedimentary rocks, found that marine shales are highly radioactive as compared with other sediments, that the Paleozoic shales average higher in radioactivity than the Cenozoic shales, and that there is more contrast between the different strata in the older formations than in the younger.

Bombardment of saturated fatty acids having the formula RCOOH [an example is palmitic acid ($C_{15}H_{31}COOH$)] by alpha particles produced paraffin hydrocarbons.[97] Subsequently bombardment of a naphthenic acid (cyclohexanecarboxylic acid) by alpha particles produced a cyclic hydrocarbon (cyclohexane).[98] These results are significant, for certain fatty acids have been recognized in the organic matter of sediments. The efficiency of the process is low, however, and the rate of conversion is small, which indicates that it would require an even geologically long time to produce important amounts of hydrocarbon in this way. Alpha-particle bombardment of methane and other gaseous hydrocarbons in the laboratory has yielded large percentages of hydrogen and unsaturated hydrocarbons.[99] Bombardment of liquid hydrocarbons gives similar high percentages of hydrogen and perhaps a higher yield of unsaturated hydrocarbons, but these are not present in crude oil except possibly in very minor quantities.

Lind [100] points out that, in general, the thermodynamic relations between the saturated hydrocarbons involve only small amounts of free chemical energy. This means that under ordinary conditions these hydrocarbons are quite inactive toward one another because there is no driving force to cause interaction. It likewise means that there is no large opposing force to overcome in any reaction, and that heats of reaction are low. If, therefore, suitable energies are available, one may expect these reactions to proceed by successive steps in all directions. Lind reasons that a complex product may thus be formed from a relatively simple one, and that, at the pressures and temperatures of the upper part of the earth's crust, any member of the paraffin series might be transformed into the complex hydrocarbons found in petroleums. He suggests that other energies might operate also, such as electrical discharge, alpha radiation, and ultraviolet radiation. All of these have been found effective in causing hydrocarbons to interact. Lind points out the further interesting fact that all of these energies exhibit the striking ability to condense hydrocarbons of low boiling point into liquids and solids, with only such elimination of gaseous compounds as is necessary to avoid chemical supersaturation. Since electrical discharge and ultraviolet radiation do not occur in the earth's crust, they may be eliminated as possible sources of energy in the transformation of simple hydrocarbons to complex hydrocarbons. Alpha radiation, however, is everywhere present, even though of low intensity.

Objections to Radioactive Transformation Processes. The chief objection to ascribing the transformation of organic matter into petroleum to alpha

out the earth might have a direct influence on the formation of petroleum, and their idea has received increasing attention from a number of investigators. Much of the material that follows is taken from articles by Bell, Goodman, and Whitehead,[88] Beers,[90] Lind,[91] Russell,[92] Shepard,[93] and Beers and Goodman.[94]

The atomic nuclei of naturally radioactive elements, such as uranium, thorium, and potassium, are unstable; they decay by spontaneous disintegration through several transformations until the final, stable end-product is reached. During the decay, some atoms always emit high-velocity electrons known as *beta particles*, while other atoms emit high-velocity helium nuclei known as *alpha particles*. Alpha particles account for more than 75 percent of the energy released by the terrestrial radioactive elements.[95] *Gamma rays* are emitted after the emission of alpha and beta particles; they are high-penetration, electromagnetic waves similar to but shorter than x-rays. Gamma-ray well logging measures the natural gamma-ray emissions of the formations drilled. (See also pp. 81–83.)

Within the disintegration series of uranium 238 (atomic weight), which is probably the best-known of the naturally radioactive elements, uranium 234, ionium 230, and radium 226 are produced. The disintegration of radium 226 produces radon 222, one of the inert, stable, noble gases, which is also radioactive, with a half-life of approximately four days. Radon emits alpha rays during its disintegration and is an excellent source of alpha particles for laboratory purposes. Radium 218, radium 214, radium 210, polonium 210, and finally lead 206 are produced. Radon and uranium reach equilibrium after about thirty days, when the rate of decay of uranium is the same as the rate of decay of radon. The amount of radon remains constant because as many radium atoms are breaking down to form radon as are radon atoms breaking down to form radium 218. Radon is more stable in organic liquids, such as petroleum, than it is in water, and crude oils commonly contain radon in excess of the amount to be expected from the disintegration of the quantity of uranium present in the crude oils. The kinetic energy of the alpha particles emitted in the disintegration of radium accounts for approximately 90 percent of the energy liberated. When these particles penetrate matter until they come to rest, the energy appears as heat. The distance an alpha particle penetrates matter, or its range, is a few centimeters in gases and around one-thousandth of that distance in solids and liquids. As the alpha particle passes through matter, ionization of the atoms and chemical changes in the material take place.[96]

The important radioactive elements found in the sedimentary rocks are uranium, thorium, and potassium.[90,94] They occur as follows: (1) associated with the heavy minerals of the sands and sandstones; (2) as the active isotope (K_{40}) of potassium, which is found in evaporites, oil-field brines, clays, shales, and potassium-bearing minerals; (3) in the uranium and thorium content of clays, shales, impure limestones, and organic substances. Beers found that pure limestones and pure quartzites exhibit practically no radio-

at some point in the transformation of organic matter into petroleum, or at least into petroleum-like substances: the general absence of olefins from crude oil, and the general presence of aromatics (benzenes) in crude oil.[82] The olefins that are present in organic matter form paraffins in the presence of catalysts[83] at temperatures below those used in cracking. Because of the absence of olefins from petroleum, it is assumed that they were once present but were hydrogenated to paraffins. Thus, if any hydrogenation occurred, it was catalytic hydrogenation. Clays are usually present and could act as catalysts in reservoir rocks. The benzenes, on the other hand, which do not occur in marine organic matter but are present in humic acid, are formed experimentally from paraffins by active catalysts at temperatures as low as 80°C. Francis[84] has pointed out that, at temperatures below 550°C, reactions without catalysts are of an entirely different kind than reactions with catalysts and would never produce aromatics from paraffins even in geologic time. Erdman[85] concludes that there were many precursors of the aromatic hydrocarbons[86] and that dehydrogenation and a slight change in the arrangement of the bonds, for example, would be sufficient to change terpene into one of the low-molecular-weight aromatic hydrocarbons.

A way in which water-soluble organic matter might be transformed into petroleum hydrocarbons at temperatures below 135°C is suggested by the work of Whitehead and Breger.[86] When a water-soluble fraction of organic matter from Recent muds was collected along the coast of Cuba and was heated up to 135°C, it gave off a complex mixture of gases composed of C_1, C_3, and C_4 hydrocarbons. The mechanism by which this low-temperature pyrolysis of marine organic matter yielded hydrocarbons is unknown, but the presence of catalysts in the mud is suggested as a possibility.

Nutting[87] has described another catalytic effect that may have a bearing on the transformation processes. When vegetable and animal tissues are in intimate contact with finely divided silica and silicates and with some oxides, such as those of aluminum and iron, they are subject to strong disintegrating forces because of the tendency of some of the hydrogen and hydrocarbon radicals to be removed. This makes them oil-wet instead of water-wet, and the products of the reaction, being soluble, tend to hydrolyze. Pressure and shearing increase the rate of disintegration. This process is believed to be active in the breaking down of organic matter for the preparation of plant food by the soils, and it may explain reactions that have sometimes been attributed to bacterial action.

Radioactive Bombardment. The widespread occurrence of radioactive minerals in the earth, together with the known chemical reactions that result from radioactive bombardment, makes it appear possible that some radioactive phenomena, in addition to being a possible source of heat, may also aid or cause the transformation of organic matter into petroleum. Lind and Bardwell[88] first suggested that the small amounts of radioactive material distributed through-