

isting professors. We think the conditions of a professor's employment are a matter which must be left to the university to determine; but in our opinion it is not necessary or advisable to prohibit private practise altogether.

Thus the duties of the clinical teachers in a medical school are defined. They certainly do correspond well with the opinions of some of our leading educators. Enough has been said to show the trend of the report, the full meaning of which can not be had without studying all of the pages of this excellent document. At any rate it is clear that there are far-sighted reformers on both sides of the Atlantic.

Whether or not a great hospital should conduct pay wards is not discussed. However, it is stated that in a hospital which has no end in view but medical education and the advancement of medical science, the public interest must be considered, and the question of the privilege of access to the great London hospitals can not be treated as a matter of private right or decided as if it were the private property of the existing medical schools.

FRANKLIN P. MALL

*THE OPTICAL ACTIVITY OF PETROLEUM
AND ITS SIGNIFICANCE*¹

THE wide distribution of deposits of bitumen, in its various forms, is attested in the very earliest writings, both sacred and profane. In the book of Genesis we learn that slime was used for mortar, and in the second book of the Maccabees we are told that

Neemias commanded the priests to sprinkle the sacrifices with the thick water . . . and when this was done . . . there was a great fire kindled, so that every man marvelled.

¹ Address of the retiring president of the Kansas Academy of Science. Read December 23, 1912, at Topeka, Kansas.

Herodotus gives us the following description of the manner of its collection:

At Ardericca is a well which produces three different substances, for asphalt, salt and oil are drawn up from it in the following manner: It is pumped up by means of a swipe, and, instead of a bucket, half a wine skin is attached to it. Having dipped down with this, a man draws it up, and then pours the contents into a reservoir, and, being poured from this into another, it assumes these different forms: the asphalt and the salt immediately become solid, but the oil they collect, and the Persians call it rhadinance. It is black and emits a strong odor.²

For more than 2,500 years the disciples of Zoroaster have worshiped the "eternal fires" in the neighborhood of Baku, Russia, and not until recently have their temples been replaced by oil reservoirs and refineries.

Within the last half century a new shrine has been set up in oildom, and our modern devotees have shown such zeal and activity that it may again well be said "that every man marveled." But the marvelous development of the petroleum industry has been rendered possible only by reason of the gigantic strides which have been made in the fields of natural science and technology. We may look for even greater things in the future, for science is still in its infancy. I have chosen for my subject to-night what I consider to be one of the infant industries of science.

In the year 1835 Jean Baptiste Biot published his memoir on the circular polarization of light and its application to organic chemistry,³ which contains a table giving polarimetric data regarding essential oils. This includes a sample of "naphte" rectified by distillation, which, examined by red light gave a rotation to the left equivalent

² "Petroleum and its Products," S. F. Peckham, 1882, p. 1.

³ *Mem. de l'Acad. de Sciences*, 13: 39, 1835. See also "Die Polarimetrie der Erdöle," M. A. Rakusin, Berlin, Wien, p. 6, 1910.

to 15.21° for a tube length of 200 mm. It is, however, very unfortunate that we have no information as to the source of this very remarkable sample.

Nearly fifty years later, in connection with their researches upon the petroleum of the Caucasus,⁴ Markownikow and Ogloblin examined the natural "white naphtha" as well as some petroleum distillates, and, finding these samples inactive, they did not continue this subject any farther. In 1885, however, Demski and Morawski⁵ examined some of the more important mineral oils of commerce, among which one rotated the plane of polarization 1.2° to the right. In 1898, Soltsien⁶ found that the commercial paraffin oils are dextrorotatory, and that the amount of rotation increases with their specific gravity. Since that time general interest has been awakened in this subject and petroleum from all parts of the world have been examined polarimetrically. In general, it has been found that the lightest and least colored oils (including the so-called white naphthas) manifest little or no optical activity, while the heavier, dark and viscous oils yield active products.⁷

In a typical Kansas oil, examined in connection with the work of the University Geological Survey, slight optical activity was detected in the upper kerosene fraction which distilled between 250° and 300° under ordinary atmospheric pressure. The higher boiling portions of this oil after fractional distillation under diminished pressure were dextrorotatory, the amount of rotation gradually increasing with the rise in boiling point until, in the neighbor-

hood of 280° at 27 mm., it reached almost one degree of arc.⁸

In some oils a maximum activity has been observed in the vacuum distillates collected at about 275° , and in the case of a German oil a second maximum was reached at a temperature of 310° . Javanese petroleum yields vacuum fractions boiling about $150\text{--}180^\circ$ which are laevorotatory, but the higher boiling fractions are dextrorotatory.⁹ A sample of petroleum from Borneo yielded a distillate collected between 260° and 340° under atmospheric pressure which was laevorotatory.¹⁰ A laevorotatory activity has also been reported in an oil from Argentine Republic.¹¹

But the fractions obtained in the distillation of petroleum do not represent distinct chemical individuals, but consist of more or less complex mixtures. Hence it is necessary for us to make use of other processes before we can isolate the optically active constituents. The fact that the distillation products of petroleum have found such a ready market without the necessity of chemically transforming them has, no doubt, greatly hindered the development of chemical methods for their utilization. But in recent years competition in the refining of illuminating oils is beginning to force the refiners to look to the utilization of their waste products. In Russian refineries the alkaline sludges are now treated so as to recover the so-called naphthenic acids which find a ready market for the manufacture of cheap soaps.

The fact that the naphthenic acids derived from kerosene show greater optical

⁴ *Annales de chim. et de phys.* (6), t. II., 387, 1884.

⁵ *Dingler's Polytech. Jr.*, 258: 82, 1885.

⁶ *Chemisches Centralblatt*, I., 869; II., 455, 1898.

⁷ Zaloziecki and Klarfeld, *Chemiker Zeitung*, 1170, 1907.

⁸ Univer. Geol. Survey of Kansas, Vol. IX., p. 317, 1908.

⁹ "Die neueren Ansichten über die Entstehung des Erdöls," C. Engler, Berlin, p. 55, 1907.

¹⁰ Jones and Wootton, *Jr. Chem. Soc.*, 91: 1146, 1907.

¹¹ Longobardi, "Petroleum," VI., 552, 1911. *Jr. Russ. Phys.-Chem. Soc.*, 43: 792, 1911.

rotation than the kerosene was first observed by Rakusin.¹² The naphthenic acids derived from lubricating oils were found by Marcusson¹³ to be much more strongly active than those derived from kerosene.

A study of isomeric naphthenic acids¹⁴ has recently been made in the laboratory of industrial research of the University of Kansas. Commercial naphthenic acids, after being freed from hydrocarbons, were converted into esters, which were repeatedly fractionally distilled. The lowest boiling fractions were strongly laevorotatory. The succeeding fractions showed a gradual decrease until in the intermediate fractions a neutral or inactive point was reached. Above this there was a gradual increase in dextrorotatory activity. A portion of free naphthenic acids, which were similarly purified, were separately fractionated and gave results exactly parallel to those of their esters, the only difference being that the boiling points of the free acids were uniformly about 50° higher than the boiling points of their methyl esters. In other words each and every optically active constituent boiled 50° higher in the one case than in the other. This shows that these optically active constituents are acids which are esterifiable, and marks the first distinct step toward their isolation. The simplest interpretation of these facts is that the cause of the optical activity resides within the naphthenic acids themselves.

It does not necessarily follow, however, that the optically active constituents pres-

ent in the commercial naphthenic acids are identical with those originally present in the petroleum. There seems to be good evidence that this is not the case, for it has been shown by Albrecht¹⁵ that the optical activity of lubricating oils is not appreciably reduced by thorough refining by means of alkali. This result has also been confirmed by experiments with the Kansas oil distillates already mentioned, which retained most of their optical activity after being boiled with alcoholic potash. On the other hand, these experiments do not prove that no optically active acids are removed by the treatment with alkali, for it is quite possible that both laevorotatory and dextrorotatory acids may be removed in approximately equal quantities. To satisfactorily settle this question an experiment should be carried out at a refinery upon a large quantity of oil.

The naphthenic acids are generally believed to be the oxidation products of the naphthenes, or saturated cyclic hydrocarbons of the series C_nH_{2n} , which are present in most of the petroleum, but particularly in those of Russia. It is to be expected, therefore, that active acids should result from the oxidation of certain active hydrocarbons. The determination of the constitution of any of the active acids to be found in petroleum products would thus shed light upon the constitution of the active hydrocarbons from which they were formed.

The crucial test as to the correctness of our knowledge of the constitution and structure of organic compounds depends upon the methods for their synthesis. But chemical synthesis is a species of architecture, and just as the architect before beginning the erection of his structure must

¹² "Die Untersuchung des Erdöls und seiner Produkte," p. 178, 1906.

¹³ *Chemiker-Zeitung*, No. 33, p. 421, 1907.

¹⁴ Orig. Com. Eighth Internat. Cong. Appl. Chem., VI., 57-67, 1912. The same isomeric naphthenic acids have since been independently isolated, by the method of repeated fractional crystallization of their amides, by Gadaskin and Zaverschinsky, Jr. *Russ. Phys.-Chem. Soc.*, 45: 377, 1913.

¹⁵ *Chemische Revue*, 18: 189, 1911. See also "Die Polarimetrie der Erdöle," M. A. Rakusin, p. 39.

lay down his plans and draw his designs so that each and every part shall be fitly adapted to its specific use, so the chemist must first in his imagination plan the order and arrangement of the various elements and groupings which are to be combined in such a manner as to produce the desired specific results.

The distinguishing characteristic in the structure of the optically active organic substances is that they contain at least one carbon atom which is combined with four different atoms or groups. If we consider the space distribution of the four different atoms or groups about the central carbon atom, we shall find that two arrangements are possible. The two resulting forms are related to each other in the same manner as an asymmetric object and its mirror image. Such a carbon atom is called an asymmetric carbon atom. We have for each substance containing such an asymmetric carbon atom the possibility of a right-handed structure and a left-handed structure. Corresponding to these theoretical structures we find that nature has furnished us with dextrorotatory and lævorotatory isomeric substances, which are closely identical in all of their physical and chemical properties, but differing chiefly in that the one rotates the plane of polarized light as far to the right as the other does to the left. When these two so-called stereoisomeric substances are mixed in equal quantities the resulting product is inactive. So also, when two asymmetric carbon atoms occur within the same molecule inactivity may result from internal compensation. It is thus found that among substances of asymmetric structure there are two classes which are optically inactive. The members of the one class—said to be inactive by internal compensation—are not separable into active components, while the members of the other

class—said to be inactive by external compensation—are separable into dextrorotatory and lævorotatory components.

We have three methods for the separation of the optically active components, all of which are due to the researches of Pasteur.¹⁶

1. In some instances enantiomorphic crystals may be formed which may be mechanically separated.

2. By the aid of suitable active substances compounds may be formed which differ in their solubility, thus permitting the two optical isomers to be separated by fractional crystallization.

3. Through the action of certain micro-organisms one of the optical isomers may be destroyed by fermentation while the other remains unaffected.

The direct synthesis of optically active substances from inactive material has not been effected, because both of the stereoisomeric forms are simultaneously produced by synthetic processes, but the same result is accomplished indirectly by first synthesizing the inactive mixture, or compound, and then separating the components by one of the methods already mentioned.

When, however, we find in nature substances which show optical activity we know that they must contain constituents which are asymmetric in structure. In endeavoring to determine their constitution, the chemist, therefore, gains the distinct advantage of leaving out of consideration all that vast array of substances which are symmetrically built, and of being permitted to concentrate his attention and efforts upon the relatively few possibilities of asymmetric structure.

But the chemist is not alone in the ad-

¹⁶ "Researches on the Molecular Asymmetry of Natural Organic Products," by Louis Pasteur (1860), Alembic Club Reprint No. 14.

vantage thus gained. From what has been said regarding synthesis from inactive material it follows that all theories accounting for the formation of petroleum from inorganic material, and excluding the action of optically active organic substances, must be rejected.

But still another factor which must be considered by the geologist with reference to the origin of petroleum and other optically active bitumens is that of temperature. All theories involving violently energetic chemical reactions and the production of high temperatures must likewise be rejected.

Having thus limited the possibilities of petroleum formation, it is well to inquire what sources remain which are capable, under the conditions imposed, of supplying a sufficient amount of material for the accumulation of the vast stores which are being unearthed, and also whether the study of the polarimetric data gives promise of furnishing positive specific evidence as to the kind of material from which petroleum has been derived.

In answer to the first of these questions I quote from the report of Professor Haworth.¹⁷

Few people realize the vast amount of organic matter annually carried down to the ocean by surface drainage. Vegetation covers practically the entire dry land area of the earth and has done so throughout all geologic time. Varying climatic conditions and other influences doubtless have made a corresponding variation in the richness of organic materials in different rock masses. But when all allowances are made for such variations, it remains that the amount of organic matter thus entombed is and has been enormously great. And such matter need not be confined to vegetation, for our ocean-water is teeming with animal life. Speaking broadly, it is well known that animals subsist on vegetation, and that the constant addition of food matter to the ocean-water for the ocean fauna comes from vegetation, as plants are

¹⁷ The University Geological Survey of Kansas, Vol. IX., 194-195.

the great agents for changing inorganic matter into organic matter. . . . If one will put himself into a position which makes it necessary to give a reasonable account for the whereabouts of all this vast quantity of organic matter, animal and vegetable, which has been engulfed in the masses of stratified rock, one will find that the quantity of oil and gas now available is all too small, rather than too large, for such accounting.

Even though the study of the chemical constituents of petroleum is in its infancy, attempts have already been made to detect among them specific optically active substances which may definitely and with certainty reveal their origin. The substance which has received the greatest consideration from this standpoint is cholesterin, the optically active constituent of many animal fats, or phytosterin, its vegetable equivalent. Cholesterin when distilled yields products which closely resemble the distillation products of petroleum. Furthermore, the optically active petroleum distillates usually give the same color reactions as are given by cholesterin products. Chemists are inclined, however, to view color reactions with suspicion, and demand more positive methods of proof of identity than the supporters of the cholesterin hypothesis have been able to furnish. On the other hand, the amino-acids and numerous other decomposition products of albuminous material as well as the remains of balsams, resins, terpenes, tannins, etc., must all be looked upon as contributing to the optical activity of the organic remains which may retain them. The time is ripe for the study and solution of problems of this nature.

The knowledge of the nature of the substances contained in petroleum which is to be revealed through the instrumentality of their optical properties may be put to practical use in the development of methods for extracting them and utilizing them for industrial purposes. The output of petro-

leum refineries in the past, even though enormous in quantity, has been restricted almost entirely to the extraction and clarification of products which exist ready-made in the crude oil. The various grades of gasoline and naphtha, illuminating oil, lubricating oil, paraffin, fuel oil and road oil are all marketed in a low-developed stage in the art of manufacture. The coal-tar industry, on the other hand, which utilizes a crude material closely resembling petroleum, and not a bit more inviting, has reached a high stage of development in that its products are completely transformed into an almost infinite variety of costly dye-stuffs, flavoring matters, medicinal preparations and other articles which have contributed to our wealth, our comfort and to the advance of our civilization. This utilization of what was formerly a waste product which could be disposed of only at considerable expense is a splendid example of what chemical industrial research has accomplished. The fact that petroleum products are not similarly utilized simply demonstrates that we lack the requisite knowledge.

F. W. BUSHONG

*AN ASCENT OF THE SNOW MOUNTAINS
OF NEW GUINEA*

DR. A. F. R. WOLLASTON has recently returned from his second expedition to Netherlands, New Guinea. Last year he published an official account of the unlucky expedition of the British Ornithological Union to the "Snow Mountains" of New Guinea. Those who have read his "Pygmies and Papuans" (London, Smith, Elder & Co., 1912) will gain some idea of the extreme difficulty of traveling in the unknown districts of that island. That expedition did not attain its main objects, but, determined not to be beaten, Dr. Wollaston has made another attempt, which has proved successful. On the present occasion Mr. C. B. Kloss, curator of the Kuala Lumpur Museum, Federated

Malay States, accompanied Dr. Wollaston, and, in addition to an engineer and five native collectors, they took with them seventy-five Dyaks, and a large escort was provided by the Netherlands government. It took four and a half months to reach the mountains from the coast. The mountains, as approached from the south, are a steep escarpment of limestone rock rising abruptly from broken foothills, through which many large torrents flow in excessively steep gorges. The heavy forest of the low country extends up to between 6,000 and 7,000 feet, beyond which height it becomes less dense, and more herbaceous plants appear. Geraniums, gentians, daisies and many other palaearctic forms, besides numerous terrestrial orchids, are found in the higher regions. The limit of perpetual snow on the Inkipulu Mountains (Nassau range) was found to be at a height of about 14,200 feet.

Unlike the Mimika River, visited by the former expedition, the Utkwa is uninhabited, probably on account of the absence of sago. The expedition was frequently visited by natives from other rivers, some of whom came from great distances. Unfortunately, they did not provide themselves with supplies for the return journey, and as the expedition proceeded on its way it encountered the dead bodies of some 30 or 40 natives, mostly women and children, whose curiosity had led them down to the low country, and who had perished from exhaustion as they were going home. The meeting with these bodies was the most terrible experience of the expedition. A hitherto unknown tribe of a rather short people of Papuan type were met with at an elevation of some 4,000-6,000 feet. Despite the very cold nights they wear no clothing. They are mainly collectors and hunters, but also grow sweet-potatoes, tobacco and sugar cane. They carry bows and arrows and shoulder bags containing apparatus for making fire, tobacco, knives, spoons and other small belongings in true Papuan style. Their knives are made of a hard, slaty stone that can be brought to so keen an edge that bamboos can be cut with them. The people are said to be extremely attractive, most friendly and in some respects