

alkaloids, those of Gladstone on refraction equivalents, or those of Baeyer upon the phthaleins, become well reduced to practice in the operations of analytical work. The simple volumetric estimations of acid and alkali are expanded in ten-fold application in thousands of analytical laboratories by means of varied indicators from the color discoveries of coal tar chemists such as Otto Witt. Analysis bows its acknowledgment of indebtedness to synthetic research. The interests of the section of analytical chemistry are all interwoven with the interests of all the sections of this congress. The analytical chemist will be a good listener to all the papers in the rich and varied repertory of the week before us.

ON THE ARTIFICIAL PRODUCTION OF PETROLEUM.

BY DR. C. ENGLER.

SCIENTISTS have discussed very often in the last few years the question in which way petroleum, this source of wealth, with its special scientific interest for this country, was formed by nature. According to one theory it is generated from inorganic materials. Sokoloff thinks, that petroleum was produced during the period of the formation of our planet out of cosmical hydrocarbons, which in the beginning dissolved in the soft mass, separated from it later on. Mendelejeff assumes that water entering by fissures and chasms the interior of the earth came in contact with melting carbide of iron and produced so in a simple manner oxide of iron and the hydrocarbons of petroleum. Strong objection cannot be made to these two theories from the chemical standpoint; but the composition of the different kinds of petroleum is against them, and geology considers them not free from objections.

For a series of years the idea that petroleum was produced from the remains of plants by a kind of a distillation process, was most generally adopted, especially by chemists. Chemical and geological reasons are against this theory. From the chemical standpoint it seems quite impossible that the substance of the plants could be split up by distillation into petroleum without

¹ Read before the World's Congress of Chemists, August 23, 1893.

leaving charcoal or coke. There would also be a genetic connection between coal and petroleum: but in occurrences of the ordinary kind, coal is nearly always absent. If this were really the case, then there ought to be with every oil occurrence in close connection a coal bank, which really seldom happens.

By a third theory the remains of animals form the raw materials from which petroleum is formed in nature. There are many facts proving the decay of masses of animals which we find now in banks in the crust of the earth in the form of the remains of shells, fishes, saurians, etc. Prominent scientists, amongst them the Americans, Wrigley, Whitney, Hunt, and others, and in Europe Höfer and Ochsenius especially, defend this idea on geological grounds. But I will not enter into the geological discussion preferring to try to give an answer to the question: How can the transmutation of animal remains into oil be imagined?

In order to answer this some thousands of salt water fishes and also shells have been distilled under strong pressure. The result was a liquid, containing mostly nitrogenous bases, such as pyridin, which was little or not at all similar to petroleum. I then recalled some experiments of Wetherill and Gregory, who found that the wax found in cadavers, the so-called "Adipocere," was nothing else but the fatty residue, which remains after the putrefaction of all the other animal matter, especially of the nitrogenous constituents of the cadaver. It is also well known that even fossil bones frequently contain fat. The question now raised was this: Could not the process in nature have been a similar one; should not first of all the nitrogenated animal substance have been destroyed leaving the fat, which was then transformed into oil. In order to prove chemically this possibility, I submitted animal fat (train-oil) to distillation—first in a sealed glass tube, later on in a large iron vessel—under a pressure of twenty-five atmospheres at a moderate heat (300–400° C.) and to my great delight found that under favorable conditions seventy per cent. of the train oil was transformed into petroleum. This equals ninety per cent. of the theoretical output. Besides the oil some water and some combustible gas was

always formed. The same behavior has been shown by other fats like butter, the fat of hogs, artificial fats, also the chemically pure glycerids of the fats like tri-olein, tri-stearin and the free fatty acids. All could be transformed into petroleum by distillation under pressure, when managed in the proper way.

This liquid, which you see here, is the distillate of the fish oil, and I have isolated from it almost all the hydrocarbons which have been discovered in the petroleum of Pennsylvania. The other products—the oil burning in this small lamp, too—are oils obtained from the crude material by purification.

But not only illuminating oils are produced. I separated also by distillation those lighter hydrocarbons which compose the gasoline, the ligroin, the benzine, etc. Recently I have succeeded in finding and separating paraffin wax and lubricating oils from those parts of the crude oil which show a high boiling point. This removes the objection of O. Ross to my theory of the formation of petroleum from animal remains. As a matter of fact I have found in the distillate obtained by decomposition of train oil, nearly all the constituents which have been separated from the natural crude petroleum, and even the gases, which, like natural gas, consist essentially of marsh gas.

Very recently I have made close investigations on the mechanism or on the chemism of the formation of the hydrocarbons of the petroleum produced by distillation of fat under pressure. This paper is published in a recent number of the *Berichte der deutschen chemischen Gesellschaft*, 1893, **26**, 1436. These experiments prove that the simpler organic acids split up in the same way, yielding almost the theoretical quantity of the respective hydrocarbon. Thus phenylacetic acid yields toluene. For further details I am obliged to refer to the paper itself. I need only remark, that we have to assume that the acids with high molecular weights are decomposed with the production of a number of hydrocarbons.

To recapitulate, it is a geological fact that we find in nature the remains of antediluvian animals as shells, fishes, saurians accumulated in masses. Whether these animals have been piled up in consequence of a natural super-production in special places in the ocean, or by currents, or in consequence of great

revolutions of the earth, this must be decided by geology: but the remains exist.

Now in which manner do the organic substances of these animals become decomposed?

The animal substance consists essentially of nitrogenated material and fat. The former is easily decomposed, the latter is very stable, a fact which has been very well known for a long time and has been shown again by exact investigations. Therefore we find the wax of cadavers in old graves, therefore the fat in the bones of mammals thousands of years old, therefore the fat on the bottom of the ocean recently found.

Whether and how far the fat was decomposed in this long period by the water splitting up glycerol and forming the free acid, for instance the fat in the bones of mammals, cannot be answered. Both, fat as well as the fatty acids form petroleum, when distilled under pressure.

We can imagine, that such remains wrapped in mud and transported by the currents in the ocean, easily accumulate and later on, under the pressure of sedimentary layers or strata, perhaps under the influence of heat too, are transformed into petroleum. This is only one of the many possibilities by which the mechanical process of the transmutation of fat into petroleum may have happened.

Under any circumstances I think I have proven that from the chemical standpoint, the formation of petroleum from animal remains has the greatest probability, as we are able now to transform every animal fat into petroleum.

THE DETERMINATION OF PHOSPHORIC ACID BY THE TITRATION OF THE YELLOW PRECIPITATE WITH STANDARD ALKALI.¹

BY HENRY PEMBERTON, JR.

I N the year 1882, I described a process for determining phosphoric acid, volumetrically, by ammonium molybdate, on the principle of Wildenstein's sulphuric acid determination, or of Gay Lussac's silver method. An *aqueous* solution of am-

¹ Read at the stated meeting of the Chemical Section of the Franklin Institute, held September 19, 1893. Communicated by the author.