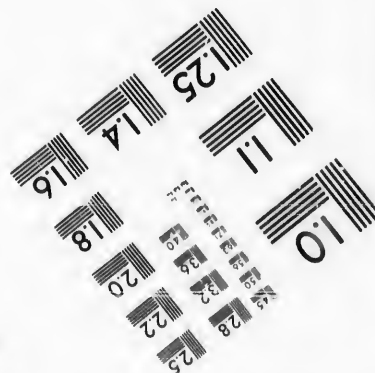
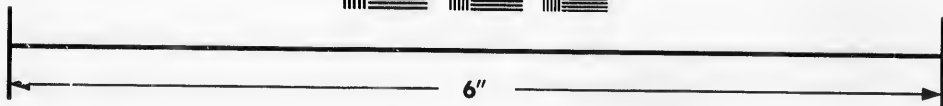
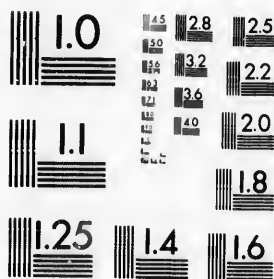


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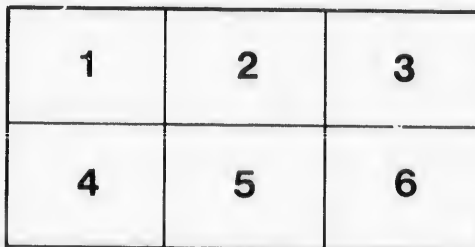
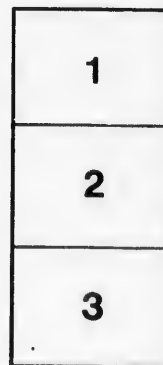
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NOTES ON THE HISTORY  
OF  
PETROLEUM OR ROCK OIL.

BY  
T. STERRY HUNT, M.A., F.R.S.,  
*Of the Geological Survey of Canada.*

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*(From the Canadian Naturalist, July, 1861.)*

Public attention has lately been drawn to the petroleum furnished by the oil wells in Canada and the United States, and we have therefore thought it well to bring together some few facts which may serve to explain the origin of this and of similar substances, including naphtha, petroleum or rock oil, and asphalt or mineral pitch, all of which are forms of bitumen, the one being solid and the others fluid at ordinary temperatures. These differences are, in many cases at least, due to subsequent alterations; the more liquid of these substances are mixtures of oils differing in volatility, and by exposure to the air become less fluid, and partly by evaporation, partly by oxydation from the air, eventually become solid and are changed into mineral pitch. These substances, which are doubtless of organic origin, occur in rocks of all ages, from the Lower Silurian to the tertiary period inclusive, and are generally found impregnating limestones, and more rarely, sandstones and shales. Their presence in the lower palæozoic rocks, which contain no traces of land plants, shows that they have not been in all cases derived from terrestrial vegetation, but may have been formed from marine plants or animals: the latter

is not surprising when we consider that a considerable portion of the tissues of the lower marine animals is destitute of nitrogen, and very similar in chemical composition to the woody fibre of plants. Besides the rocks which contain true bitumen we have what are called bituminous shales, which when heated burn with flame, and by distillation at a high temperature yield, besides inflammable gases, a portion of oil not unlike in its characters to petroleum. These are in fact argillaceous rocks intermixed with a portion of organic matter allied to peat or lignite, which by heat is decomposed and gives rise to oily hydrocarbons. These inflammable or lignitic shales, which may be conveniently distinguished by the name of *pyroschists*, (the *brandschiefer* of the Germans) are to be carefully distinguished from rocks containing ready-formed bitumen; this being easily soluble in benzole or sulphure of carbon can be readily dissolved from the rocks in which it occurs, while the pyroschists in question yield, like coal and lignite, little or nothing to these liquids.

It is the more necessary to insist upon the distinction between lignitic and bituminous rocks, inasmuch as some have been disposed to regard the former as the source of the bitumen found in nature, which they conceive to have originated from a slow distillation of these matters. The result of a careful examination of the question has however led us to the conclusion that the formation of the one excludes more or less completely that of the other, and that bitumen has been generated under conditions different from those which have transformed organic matters into coal and lignite, and probably in deep water deposits, from which atmospheric oxygen was excluded. Thus in the palæozoic strata of North America we find in the Utica and Hamilton formations, highly inflammable pyroschists which contain no soluble bitumen, and the same is true to a certain extent of some limestones, while the Trenton and Corniferous limestones of the same series are impregnated with petroleum or mineral pitch, and as we shall show, give rise to petroleum springs. The fact that intermediate porous strata of similar mineral characters are destitute of bitumen, shows that this material cannot have been derived from overlying or underlying beds, but has been generated by the transformation of organic matters in the strata in which it is met with. This conclusion is accordance with that arrived at by Mr. S. P. Wall in his recent investigations in Trinidad. He has shown that the asphalt of that island and of Venezuela belongs to strata of the

tertiary formation (of upper miocene or lower pliocene age,) which consist of limestones, sandstones and shales, associated with beds of lignite. The bitumen is found not only in the famous pitch lake, but *in situ*, where it is confined to particular strata which were originally shales containing vegetable remains; these have undergone "a special mineralization producing a bituminous matter instead of coal or lignite. This operation is not attributable to heat, nor of the nature of a distillation, but is due to chemical reactions at the ordinary temperature, and under the normal conditions of climate." He also describes wood partially converted into bitumen, which last when removed by solution leaves a portion of woody tissue. (Proc. Geol. Soc. London, May, 1860.)

The sources of petroleum and mineral pitch in Europe and in Asia, are for the most part, like those just named, confined to rocks of newer secondary and tertiary age, though they are not wanting in the palæozoic strata, which in Canada and the United States furnish such abundant supplies of petroleum. In the great palæozoic basin of North America bitumen, either in a liquid or solid state, is found in the strata at several different horizons. The forms in which it now occurs depend in great measure upon the presence or absence of atmospheric oxygen, since by oxidation and volatilization the naphtha or petroleum, as we have already explained, becomes slowly changed into asphalt or mineral pitch, which is solid at ordinary temperature. It would even appear that by a continuance of the same action the bitumen may lose its fusibility and solubility, and become converted into a coal-like matter. Thus in the Calciferous sandrock in New York a black substance, which has been called anthracite, occurs in cavities with crystals of bitter spar and quartz. It sometimes coats these crystals or the walls of the cavities, and at other times appears in the form of buttons or drops, evidently according to Mr. Vanuxem, having been introduced into these cavities in a liquid state, and subsequently hardened as a layer above the crystals, which have conformed to them, showing that this coal-like matter was once in a plastic state. It is very pulverulent, brittle, of a shining black, and according to Vanuxem yielded but little ash, and  $11\frac{1}{2}$  per cent of volatile matter, which he regarded as water, (Vanuxem, Geology of New York, iii. 33). A similar material occurs in the Quebec group in Canada, the equivalent of the Calciferous sand-rock, and fills cavities and fissures in the limestones, sandstones, and even in the accom-

panying trap rocks, as at Quebec, Orleans Island, Point Levis, and at Acton, presenting mamillary surfaces as noticed by Vanuxem, which evidently show that it has once been semi-fluid. This matter from the first two localities is completely infusible, and insoluble in benzole; it readily crumbles between the fingers and gives a very black powder. When exposed to a high temperature it gives off abundance of inflammable strong smelling vapors, which condense into a tarry oil, and leaves a black residue, which when heated slowly burns away, leaving only a trace of ash. The volatile portion is equal to from 19.5 to 21.0 per cent. The mineral from the Acton copper mine is much harder and less friable, and approaches to anthracite in its characters. When heated it gives off watery vapor without any bituminous odor. Its loss by heat was 6.9 per cent, and the residue of ash was equal to 2.2 per cent.

An evidence of the presence of unaltered petroleum in almost all the Lower Silurian limestones is furnished by the bituminous odor which they generally exhibit when heated, struck or dissolved in acids. In some cases petroleum is found filling cavities in these limestones, as at Rivière à la Rose (Montmorenci,) where it flows in drops from a fossil coral of the Birdseye limestone, and at Pakenham, where it fills the cavities of large orthoceratites in the Trenton; from some specimens nearly a pint of petroleum has been obtained; it is also said to occur in the township of Lancaster in the same formation. The presence of petroleum in the Lower Silurian rocks of New York is shown in the township of Guilderland near Albany, where according to Beck, considerable quantities of petroleum are collected upon the surface of a spring which rises through the Hudson River or Loraine shales. On the Great Manitoulin Island also according to Mr. Murray, a petroleum spring issues from the Utica state, and he has described another at Albion Mills near Hamilton rising through the red shales of the Medina group; these have probably their origin in the Lower Silurian limestones, which may in some localities prove to be valuable sources of petroleum.

In the Upper Silurian and Devonian rocks bitumen is much more abundant; Eaton long since described petroleum as exuding from the Niagara limestone, and this formation throughout Monroe county in western New York is described by Mr. Hall as a granular crystalline dolomite including small laminæ of bitumen, which give it a resinous lustre. When the stone is burned for



lime the bitumen is sometimes so abundant as to flow like tar from the kiln. In the Corniferous limestone, at Black Rock on the Niagara River, petroleum is described as occurring in cavities, generally in the cells of fossil corals, from which, when broken, it flows in considerable quantities. It also occurs in similar conditions in the Cliff limestone (Devonian) of Ohio.

Higher still in the series, at the base of the Hamilton group, occur what in New York have been called the Marcellus shales; these enclose septaria or concretionary nodules which contain petroleum, while at the summit of the same group similar concretions holding petroleum are again met with. The sandstones of the Portage and Chemung group in New York are in many places highly bituminous to the smell, and often contain cavities filled with petroleum, and in some places seams of indurated bitumen. A calcareous sandstone from this formation at Laona near Fredonia in Chatauque county contains more than two per cent of bituminous matter. At Rockville in Alleghany county, according to Mr. Hall, the same sandstones are highly bituminous and give out a strong odor when handled, and in the counties of Erie, Seneca and Cataaugus abundant oil springs rise from the sandstones and have been known to the Seneca Indians from ancient times. In the northern part of Ohio, according to Dr. Newberry, petroleum is found to exude in greater or less quantity from these sandstones wherever they are exposed, and the oil wells of Pennsylvania and Ohio are sunk in these Devonian sandstones, often through the overlying carboniferous conglomerate, and in some cases apparently, according to Newberry, through the sandstones themselves, which are supposed by him to be only reservoirs in which the oil accumulates as it rises through fissures from a deeper source, in proof of which he mentions that in boring wells near to each other, the most abundant flow of oil is met with at variable depths. In some instances the petroleum appears to filter slowly into the wells from the porous strata around, which are saturated with it, while at other times the bore seems to strike upon a fissure communicating with a reservoir which furnishes at once great volumes of oil. An interesting fact is mentioned in this connection by Mr. Hall. In the town of Freedom, Catarragus Co., New York, is a spring which had long been known to furnish considerable quantities of petroleum. On making an excavation about six yards distant, to the depth of fourteen feet, a copious spring of petroleum arose, and for some time afforded large

quantities of oil, after which the supply diminished in both the old and new springs, so that it is now less than at the first settlement of the country. Notwithstanding its general distribution throughout a considerable region in the adjacent portions of New York, Pennsylvania and Ohio, it is only in a few districts that it has been found in quantities sufficient to be wrought with profit. The wells of Mecca in Trumbull Co., Ohio, have been sunk from 30 to 200 feet in a sandstone which is saturated with oil; of 200 wells which have been bored, according to Dr. Newberry, a dozen or more are successfully wrought, and yield from five to twenty barrels a day. The wells of Titusville on Oil Creek, Pennsylvania, vary in depth from 70 to 300 feet, and the petroleum is met with throughout. The oil from different localities varies considerably in color and thickness, and in its specific gravity, which ranges from 28° to 40° Baumé, (from .890 to .830.)

The valley of the Little Kenawha in Virginia, which is to be looked upon as an extension of the same oil-bearing region, contains petroleum springs, which so long ago as 1836, according to Dr. Hildreth, yielded from fifty to a hundred barrels yearly. It here rises through the carboniferous strata, and as elsewhere is accompanied by great quantities of inflammable gas.

The black inflammable shales of the Devonian series in western Canada which were formerly referred to the Hamilton group, and are now considered to belong to the base of the overlying Portage and Chemung, appear at Kettle Point on Lake Huron and in portions of the region southward to Lake Erie, but the oil wells sunk in Enniskillen show that the source of the oil is really below the horizon of these shales, inasmuch as the underlying argillaceous shales and limestones of the Hamilton group are there found near the surface, and have been penetrated 120 feet, at which depth oil is still met with, leaving but little doubt that it is derived from the limestones beneath, which both in New York, and in Canada are impregnated with petroleum. A somewhat slaty brownish-black bituminous dolomite belonging to the Corniferous limestone from ~~Pine Creek near Alma, in~~ Kincardine, gave me not less than 12.8 per cent. of bitumen, fusible and readily soluble in benzole, and another from the Grand Manitoulin Island, which was a brown crystalline dolomite, yielded from 7.4 to 8.8 per cent. of similar bitumen. The solid form of this bitumen at the outcrop of the rocks, is probably due to the action of the air.

The existence of liquid bitumen in the Corniferous limestone in western Canada was pointed out as long ago as 1844 by Mr. Murray, who tells us that this rock is generally bituminous, and that cavities in it are often filled with petroleum; the quarries near Gravelly Bay in Wainfleet are cited as an example, (Report of Geol. Survey, 1846, p. 87). In the Report for 1850 we find a notice of what are called oil springs, in which petroleum rises to the surface of the water near the right bank of the Thames in Mosa, and in two places on Bear Creek in Enniskillen. Subsequently Mr. Murray described a considerable deposit of solid bitumen or mineral tar, which occurs in the same township, extending over about half an acre, and in some places two feet in thickness, doubtless formed by the drying-up of petroleum springs (Report for 1851, p. 90.) I had already in the Report for 1849, p. 99, described this bitumen from specimens in the Museum of the Geological Survey, and called attention to its economic applications, remarking that "the consumption of this material in England and on the continent for the construction of pavements, for paying the bottoms of ships, and for the manufacture of illuminating gas is such that the existence of these deposits in the country is a matter of considerable importance." At this time solid bitumen was thus employed, but in the liquid form of petroleum its use was chiefly confined in Europe to medicinal purposes. Under the names of Seneca oil and Barbadoes tar it had long been known and employed medicinally by the native tribes of America. Its use for burning, as a source of light or heat, in modern times has been chiefly confined to Persia and other parts of Asia, although in former ages the wells of the island of Zante described by Herodotus furnished large quantities of it to the Grecian Archipelago, and Pliny and Dioscorides describe the petroleum of Agrigentum in Sicily, which was used in lamps under the name of Sicilian oil. The value of the naphtha annually obtained from the springs at Bakoum in Persia on the Caspian sea was some years since estimated by Abich at about 600,000 dollars, and the petroleum wells of Rangoon in Burmah are said to furnish not less than 400,000 hogsheds yearly. In the last century the petroleum or naphtha obtained from springs in the Duchy of Parma was employed for lighting the streets of Genoa and Amiano. But the thickness, coarseness and unpleasant odor of the petroleum from most sources were such that it had long fallen into disuse in Europe, when in 1847, the attention of Mr. Young, a manufacturing

chemist of Glasgow, was called to the petroleum which had just been obtained in considerable quantities from a coal mine at Riddings in Derbyshire, from which by certain refining processes he succeeded in preparing a good lubricating oil. This source however soon becoming exhausted, he turned his attention to the somewhat similar oils which Reichenbach and Selligie had long before showed might be economically obtained by the distillation of coal, lignite, peat and pyroschists. To this new industry Mr. Young gave a great impetus, and in connection with it attention was again turned to the refining of liquid and solid bitumens, it being found that the latter by distillation gave great quantities of oils identical with those from petroleum. About the year 1853 the attention of speculators was turned to the deposits of bitumen in Enniskillen just described, but it was not till 1857, that Mr. W. M. Williams of Hamilton, with some associates undertook the distillation of this tarry bitumen, when they soon found that by sinking wells in the clay beneath, it was possible to obtain great quantities of the material in a fluid state. Large numbers of wells were subsequently sunk by Mr. Williams and others in the southern part of the township of Enniskillen along the borders of Black Creek, and also about ten miles farther north on Bear Creek. Nearly one hundred wells had been sunk when I visited the place in December last, and many more have since been bored. Of these but a small proportion furnish available quantities of oil, but the whole amount already obtained from the district is perhaps not less than 300,000 or 400,000 gallons. Owing to the difficulties of communication and of procuring casks sufficient for the oil, these wells have not yet been wrought in a continuous manner; large quantities of oil are however taken out at intervals of some days, and it is probable that if continuously worked the supply would be still greater. Here as in Pennsylvania considerable variations are found in the quality of the oil; that from the wells on Black Creek is more liquid and less dense than the oil from Kelly's wells on Bear Creek, and it is said that wells recently sunk to a considerable depth in the rock have yielded an oil still thinner, lighter colored and less dense, which is prized as being more profitable for refining. The present wholesale price of the crude oil from Kelly's wells, delivered at the Wyoming station on the Grand Trunk Railway, is about thirteen cents a gallon. The oil obtained by Mr. Williams is refined in Hamilton, while that from the northern

part of the township has hitherto been sent to Boston, though refining works are now being erected at the wells. The process of refining consists in rectifying by repeated distillations, by which the oil is separated into a heavier part employed for lubricating machinery, and a lighter oil, which after being purified and deodorized by a peculiar treatment with sulphuric acid, is fit for burning in lamps.

These wells occur along the line of a low broad anticlinal axis which runs nearly east and west through the western peninsula of Canada, and brings to the surface in Enniskillen the shales and limestones of the Hamilton group, which are there covered with a few feet of clay. The oil doubtless rises from the Corniferous limestone, which as we have seen contains petroleum; this being lighter than the water which permeates at the same time the porous strata, rises to the higher portion of the formation, which is the crest of the anticlinal axis, where the petroleum of a considerable area accumulates and slowly finds its way to the surface through vertical fissures in the overlying Hamilton shales, giving rise to the oil springs of the region. The oil is met with at various depths; in some cases an abundant supply is obtained at forty feet, while near by it is only met with at three or four times that depth, and sometimes only in small quantities. Everything points to the existence of separate fissures communicating with a deep-seated source. At Kelly's wells however, it would appear that a reservoir has been formed much nearer the surface, where in a bed of gravel and boulders, underlying the superficial clays, the oil rising from the rocks beneath has accumulated. The inflammable gas which issues from the wells is not necessarily connected with the petroleum, inasmuch as it is an almost constant product of the decomposition of organic matters, and is copiously evolved from rocks which are destitute of bitumen. It is similar to the gas of marshes and to the fire damp of coal mines. A curious circumstance is however noticed by Mr. Robb; the gas which accumulates in the oil pits, becomes charged with vapors which produces upon the workmen a sort of intoxication like nitrous oxyd.\* This is not surprising when we remember that volatile hydrocar-

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\* Mr. Charles Robb, C. E., has published in the Canadian Journal for July an interesting paper on the oil wells of Enniskillen, to which, as also to a paper by Prof. E. B. Andrews of Ohio, in Silliman's Journal for July I am indebted for several facts.

bons like amyene, closely related to the hydrocarbons of petroleum, produce similar effects when their vapor is respired.

The oil wells of the United States are for the most part sunk in the sandstones which form the summit of the Devonian series, but the oils of western Virginia and southern Ohio rise through the coal measures which overlie the Devonian strata, while the wells of Enniskillen are situated much lower, and are sunk in the Hamilton shales, which immediately overlie the Corniferous or Devonian limestone. It is not impossible that in Ohio some of the higher strata, such as the sandstone, were originally impregnated with bitumen, but in Canada from the absence of this substance diffused through the shales in question, we are forced to assign it to a lower horizon, which is doubtless that of the bituminous Devonian limestone. This view I have for some time maintained in opposition to those who conceive the bitumen to be derived from the black pyroschists; see my lecture before the Board of Arts, reported in the Montreal Gazette of March 1, where I asserted that the source of the petroleum was to be sought in the bituminous Devonian and Silurian limestones; besides the Corniferous limestone (Devonian,) we have shown that both the Niagara and the Trenton, (of Upper and Lower Silurian age,) contain petroleum. The question of the extent of the supply of petroleum is not easily answered; the oil now being wrought is the accumulated drainings of ages, concentrated along certain lines of elevation, and the experience of other regions has shown that these sources are sooner or later exhausted; but though the springs of Agrigentum, like those of Derbyshire, have nearly ceased to flow, those of Burmah and Persia still furnish, as they have for ages past, immense quantities of oil; nothing but experience can tell us the richness of the subterranean reservoirs. It is not probable that the Devonian limestone is equally rich in petroleum throughout its whole distribution, but the exposures of it in the west are too few to enable us as yet to say in what portions the petroleum predominates; as however this rock underlies more than one-half of the western peninsula, we may look for petroleum springs much farther east than Enniskillen. A well yielding considerable quantities of petroleum is said to occur in the township of Dereham, about a quarter of a mile S. W. of Tilsonburg, and we may reasonably expect to find others along the line of the anticlinal, or of the folds which are subordinate to it.

It is now many years since Sir William Logan described the occurrence of petroleum springs in Gaspé, and collected specimens of the oil, which are preserved in the Geological Museum. One of these, near Gaspé Bay, is described as occurring on the south side of the St. John's River about a mile and a half above Douglastown, where it may be collected by digging pits in the mud on the beach. Another locality is about 200 yards up a small fork of the Silver Brook, which falls into the Southwest Arm six or seven miles above Gaspé Basin. The oil collects in pools along the stream, and may be gathered in considerable quantities. The cavities in a greenstone dyke on Gaspé Bay were also found to be filled with petroleum, and the odor of it from the rock was perceived at a considerable distance. The dyke, which marks a fold in the stratification, runs in the direction of the petroleum springs, and the evidences of the distribution of petroleum are thus, as Sir William Logan has remarked, visible along a line of twenty miles (Report for 1844, p. 41.) Attention has recently been drawn to these indications, and a company formed with a view of exploring this region for petroleum. Here, as well as in western Canada and the United States, the connection is evident between the springs and undulations of the strata which favor the accumulation of the petroleum.

*Supplementary Note.*

We have stated in the preceding paper that the different mineral combustibles have been derived from the transformations of vegetable matters, or in some cases of animal tissues analogous to these in composition. The composition of woody fibre or cellulose, in its purest state, may be represented by  $C_{24}H_{20}O_{20}$ , or as a compound of the elements of water with carbon: the incrusting matter of vegetable cells, to which the name of lignine has been given, contains however a less proportion of oxygen and more carbon and hydrogen than cellulose, so that the mean composition of recent woods, as deduced from numerous analyses of various kinds, may be represented by  $C_{24}H_{18.4}O_{16.4}$ . We may conceive of four different modes of transformation of woody fibre, all of which probably intervene to a greater or less degree in the production of mineral combustibles; and in considering

these changes we shall for greater simplicity adopt for the composition of woody fibre the first named formula,  $C_{24}H_{20}O_{20}$ .

I. When wood is exposed to the action of moist air, oxygen is absorbed, and carbonic acid and water are evolved in the proportion of one equivalent of the first for two of the last. We may suppose that for  $H_2$  which is oxydised by  $O_2$  from the air, the wood loses  $CO_2$ , so that while the carbon increases in amount the proportions of oxygen and hydrogen are unchanged. In this way an equivalent of cellulose, by absorbing sixteen equivalents of oxygen and losing eight of carbonic acid, ( $8 CO_2$ ) and sixteen of water, ( $16 HO$ ) would leave  $C_{16}H_4O_4$ . Such is the nature of the decay of wood when exposed to the air, and the process, could it be carried out, would leave a residuc of carbon only. If however the wood is deeply buried and excluded from the oxygen of the air two reactions are conceivable.

II. The whole of the oxygen of the wood may be given off in the form of carbonic acid, while the hydrogen remains with the residual carbon. The abstraction of ten equivalents of carbonic acid from one of woody fibre, would leave a hydrocarbon,  $C_{14}H_20$ .

III. Instead of combining exclusively with the carbon, a part of the oxygen of the wood may be set free as water, in combination of the hydrogen. The abstraction from an equivalent of woody fibre of four equivalents of carbonic acid and twelve of water would leave a hydrocarbon  $C_{20}H_8$ .

IV. These decompositions are however never so simple as we have supposed in II and III, for a portion of hydrogen is at the same time evolved in combination with carbon, chiefly as marsh gas,  $C_2H_4$ . The amount of this gas evolved from decaying plants submerged in water, and the immense quantities of it condensed in coal beds and other rocky strata, (forming fire damp,) shew the great extent to which this mode of decomposition prevails.

In nature these various modes of decomposition often go on together, or intervene at different stages in the decomposition of the same mass; they are besides seldom so complete as we have represented them. The first process results in the formation of vegetable mould, which always retains portions of carbon and hydrogen; while the incomplete operation of the processes II, III and IV gives rise to peat, lignite, brown coal, bituminous coal and pyroschists, in all of which the proportion of the oxygen is much less than the hydrogen, so that their composition may be



approximately represented by mixtures of hydrocarbons with vegetable fibre. The following results have been selected from a great number of analyses by various chemists, and are for the most part taken from Bischof's *Chemical Geology*, (Vol. i. cap. XV.) The nitrogen, which in most cases was included with the oxygen in the analysis, has been disregarded, and the oxygen and hydrogen for the sake of comparison, have been calculated for twenty-four equivalents of carbon.

1. Vegetable fibre or cellulose,.....	$C_{24}H_{20}O_{20}$
2. Wood, mean composition,.....	$C_{24}H_{18.4}O_{16.4}$
3. Peat,..... (Vaux,)	$C_2 H_{14.4}O_{10}$
4. do. .... (Regnault,)	$C_{24}H_{14.4}O_{9.6}$
5. Brown coal,..... (Schrötter,)	$C_{24}H_{14.3}O_{10.6}$
6. do. do. .... (Woskresensky,)	$C_{24}H_{13}O_{7.6}$
7. Lignite,..... (Vaux,)	$C_{24}H_{11.3}O_{6.4}$
8. do. passing into mineral resin, (Regnault,)	$C_{24}H_{15}O_{3.3}$
9. Bituminous coal,..... do. ....	$C_{24}H_{10}O_{3.3}$
10. do. do. .... do. ....	$C_{24}H_{10}O_{1.7}$
11. do. do. .... do. ....	$C_{24}H_{8.4}O_{1.2}$
12. do. do. .... do. ....	$C_{24}H_8O_{0.9}$
13. do. do. .... (Kühnert and Gräger,)	$C_{24}H_{7.4}O_{1.3}$
14. do. do. (mean comp.).... (Johnston)....	$C_{24}H_9O_2-O_4$
15. Albert coal,..... (Wetherell,)	$C_{24}H_{15.9}O_{1.6}$
16. Asphalt, Auvergne,.....	$C_{24}H_{17.7}O_{2.2}$
17. do. Naples,.....	$C_{24}H_{14.6}O_2$
18. do. Bastennes,.....	$C_4H_1 O_{0.7}$
19. Elastic bitumen, Derbyshire,..... (Johnston,)	$C_{24}H_{22}O_{0.3}$
20. Bitumen of Idria,.....	$C_{24}H_8$
21. Petroleum and naphtha,.....	$C_{24}H_{24}$

In the above table we see the transition from peat and brown coal to lignite, and thence to bituminous coal. Prof. Johnston from his experiments in various coals, including cannel from Wigan, splint coal from Workington and caking coal from Newcastle, deduced the composition given in 14, in which with  $C_{24}H_9$  the oxygen varies from two to four equivalents. It will be seen from a comparison of the infusible Albert coal with the bitumens 16, 17 and 18, how gradual is the transition to the true petroleums and naphthas, from which oxygen is absent. The asphalts also, as will be observed, differ very much in their composition, and though generally much richer in hydrogen than the bituminous coals, the variety from Naples (17) which is completely fusible at  $140^\circ C$ , contains less hydrogen and more oxy-

gen than the Albert coal analysed by Wetherell; while the idrialine or bitumen found with the mercury ores of Idria, approaches very nearly in composition to the bituminous coals 11, 12 and 13, with which many asphalts may be said to be isomeric. It is however probable that those oxygenized bitumens, unlike the coals, are products of the oxydation of naphtha or petroleum, by a process similar to that by which resins are derived from vegetable hydrocarbons. These formulas must be taken as representing not the true equivalents, but only the proportions of the elements in the bodies in question, which are in most cases mixtures of various substance. This is especially true of naphtha, which may be taken as the representative of pure unoxidised petroleum, and which is separated by distillation into oils of very different boiling points. The late analyses by Uelsmann of the rectified rock oil from Sehnde near Hanover, gave the formula  $C_{15}H_{20}$ , and according to De la Rue and Müller the greater part of the Rangoon petroleum consists of hydrocarbons in which the number of equivalents of hydrogen is a little greater than the carbon; one gave  $C_{26}H_{28}$ . Associated with these are however portions of bodies containing a less proportion of hydrogen, so that we may conceive the mean composition of petroleum to be represented, as in the preceding table, by equal equivalents of hydrogen and carbon; many forms of solid bitumen also, as ozokerite and hatchetine, have the same general composition.

By referring to what has been said above it will be seen that the final result of the third process of decomposition of woody fibre, in which the air being excluded, the oxygen is shared between the carbon and hydrogen, would be  $C_{26}H_{28}$ . A similar result would be obtained, with the simultaneous evolution of marsh gas, if we suppose  $6 CO_2 + 8 HO + 3 CH_4$  to be removed from an equivalent of woody fibre, leaving  $C_{15}H_6 = C_{26}H_{28} = C_{24}H_{28}$ , which approaches the composition of most bituminous coals and of idrialine. A farther elimination of marsh gas would leave a residue of pure carbon, and thus, as Bischof has suggested, vegetable matters may be converted into anthracite without the intervention of a high temperature.

The elimination of the whole of the oxygen in the form of carbonic acid would leave a compound with a large excess of hydrogen, of which it would be necessary to remove a portion in the form of water or marsh gas in order to reduce the residue to the composition of petroleum. We know of no combination

of carbon and hydrogen in which the number of atoms of hydrogen surpasses by more than two, those of ~~hydrogen~~, the general formula being  $C_nH_{n+2}$ , so that oils like  $C_{12}H_{26}$  and  $C_{26}H_{54}$  contain nearly the maximum quantity of hydrogen, and a body like  $C_{14}H_{28}$ , whose formation we have supposed above, could not exist, but must break up into marsh gas and some less hydrogenous oil like petroleum. *carbon*

We do not know the precise conditions which in certain strata favor the production of petroleum rather than of lignite or coal, but in the fermentation of sugar, to which we may compare the transformations of woody fibre, we find that under different conditions it may yield either alcohol and carbonic acid, or butyric and carbonic acids with hydrogen, and even in certain modified fermentations the acetic, lactic and propionic acids, and the higher alcohols, like  $C_{10}H_{12}O_2$ . These analogies furnish suggestions which may lead to a satisfactory explanation of the peculiar transformation by which, in certain sedimentary strata, organic matters have been converted into bitumen.

