

The tungstic acid was filtered off, dissolved from silica by ammonia, the solution evaporated, and tungsten determined as WO_3 . The filtrate containing chromium was brought to boiling and chromium hydroxide thrown down by ammonia. Alloy II, as obtained in original sample, contained iron 0.0423, chromium 0.0317, tungsten 0.0102. The analytical results gave :

TABLE IV. FERROTUNGSTENCHROMIUM CARBIDE.

	Alloy II.	Atomic ratio.	Alloy II B.	Atomic ratio.
Iron.....	0.4724	0.843	0.4723	0.843
Chromium.....	0.3542	0.676	0.3682	0.702
Tungsten.....	0.1139	0.060	0.1007	0.054
Carbon.....	0.0595	0.496	0.0599	0.494

No manganese, silicon, or phosphorus was present in II B. These results give the ratios :

Alloy II. Fe : CrW : C :: 1.69 : 1.49 : 1, or formulated $Fe_3(CrW)_2C_4$.

Alloy II B. Fe : CrW : C :: 1.73 : 1.53 : 1, or formulated $Fe_3(CrW)_2C_4$.

Carbon in both cases was determined by direct combustion of the crystals. To the compound I give the name Garrisonite, from Professor F. Lynwood Garrison, a valued contributor to the study of the microstructure of iron and to its metallurgy. Alloy II B contained, chromium 0.1070, tungsten 0.0871.

ON THE POSSIBILITY OF THE OCCURRENCE OF HYDROGEN AND METHANE IN THE ATMOSPHERE.¹

Received September 9, 1895.

BY FRANCIS C. PHILLIPS.

WHATEVER may have been the process by which organic remains have in the course of time been caused to yield gas and petroleum, a considerable portion of the gas evolved in the early stages of decay must have escaped into the atmosphere before the burial of such remains under sedimentary deposits, and the consequent imprisonment of the more volatile products could have occurred. This would have been the case if, as in the view of the older geologists, the source of gas and oil is to be looked for in the slow decomposition, at low temperatures, of

¹ Read at the Springfield meeting.

masses of seaweeds as they were gradually buried under accumulating sediments. It would have occurred likewise if, according to Engler's hypothesis, gas and oil have come from the distillation of animal remains under pressure of overlying sediments and at a gentle heat.

For a long interval of time must have elapsed between the commencement of decay and the final burial of such remains under marine deposits, of sufficient thickness and compactness, as to cause the retention of the hydrocarbons until the sediments became consolidated into rock.

In a paper upon the origin of natural gas¹ I have called attention to the great difference in the nature of the changes which may occur in organic remains submerged under water and protected from atmospheric influences. The early stages of the decay are rapid, and much hydrogen may be produced. The later stages are more gradual, and methane may be a chief product of the decay. At the beginning of the process the cell contents are chiefly concerned in the change. Even if buried under deep sediments the tumultuous nature of the gas evolution must cause the gas bubbles to break through and escape from dense masses of clay and sand.

The following experiment was described in the paper cited: A quantity of a seaweed was allowed to decay under water in an apparatus so constructed that any gas produced could be collected over mercury. Rapid decomposition soon set in and continued for ten days, when the evolution of gas apparently ceased, having become much retarded towards the end. In all 803 cc. of gas were collected. Analyses were made of the first portion of 300 cc., of a second portion of 300 cc., and of a third portion of 203 cc. The results are tabulated below:

	First portion.	Second portion.	Third portion.
Carbon dioxide.....	18.23 per cent.	32.47 per cent.	53.44 per cent.
Carbon monoxide..	0 "	0 "	0 "
Ethylene.....	0 "	0 "	0 "
Methane.....	0.30 "	0.28 "	0.08 "
Hydrogen.....	62.24 "	48.97 "	42.02 "
Nitrogen.....	19.23 "	18.28 "	4.46 "
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

The temperature during the experiment did not exceed 20° C.

The same apparatus was kept in position for two and one-half years after the above experiment was made. During this time a continuous production of gas was observed, but it was so slow that at the end of this period only about 30 cc. of gas had collected. This was found to consist of methane.

Frankland & Jordan¹ found that grease left to decay under water, air being excluded, evolved gas of the following composition :

	In 3 days.	In 3 days.	In 4 days.
Carbon dioxide.....	84.63	87.66	84.41
Oxygen.....	0.13
Hydrogen.....	6.90	8.75	9.17
Other combustible gases	2.51	0.71	0.27
Nitrogen.....	5.83	2.88	2.15

I have examined gas collected from swamps in many localities. Gas samples have been taken from streams having muddy bottoms and in which vegetable remains had accumulated. Carbon dioxide, nitrogen and methane are usually found in shallow swamps. In deeper swamp waters, where masses of vegetable debris of greater thickness occur, hydrogen is often found in small quantities mixed with carbon dioxide, nitrogen and methane.

According to the hypothesis of Mendeleeff natural gas and petroleum have been produced by the action of steam at high temperatures upon the metallic compounds of carbon.² The general result of experiments upon the action of steam upon the heated carbides of iron, manganese and other metals, has been to show that in all such cases there is produced mainly hydrogen mixed with relatively small quantities of hydrocarbons. It is found, however, that the natural gas which flows from the wells of Pennsylvania, New York, West Virginia, Ohio, and Indiana, consists mainly of methane with small quantities of other hydrocarbons, but does not contain free hydrogen. Hence if we accept the hypothesis of Mendeleeff we must suppose that the natural gas, now flowing from the earth in such vast quantities, represents the diminished residue of a much larger volume

¹ J. Chem. Soc. (Lond.) 1883, p. 295.

² Mendeleeff: Principles of Chemistry, I, 365.

of gas from which the free hydrogen has escaped through the overlying rocks. Whatever view is adopted as to the origin of natural gas there seems to be good reason to believe that considerable volumes of hydrogen and of gaseous paraffins have found their way into the atmosphere, and that the process has been continuous since early geological times.

Evolution of carbon dioxide from organic remains is merely one stage in a cycle of changes. The carbon dioxide present in the atmosphere parts with its carbon to growing plants. They, in their turn, yield back carbon dioxide as they die and decay. On the other hand each bubble of hydrogen and of methane, once set free at the earth's surface, probably escapes unoxidized and unabsorbed to ascend into the higher strata of the atmosphere.

Of all the forms which hydrogen and carbon can assume in nature, free hydrogen and methane are among the most stable and unalterable as regards all influences at the earth's surface. Their slight solubility in water protects them still further from oxidation.

In the natural gas regions gas bubbles are easily produced by stirring up the sediments at the bottom in streams, ponds and rivers. This is not only the case where decaying vegetation occurs, but in streams flowing over gravel and pebbles where no decay is in progress. The loose gravel appears merely to arrest temporarily the gas on its way out from the earth and renders it visible as it escapes in bubbles through the water. If the gas accumulated under gravel and sand in streams be dislodged by stirring it is usual to find that, in a day or two, or even after a few hours, it has again collected in considerable quantity. Constant agitation of the gravel seems not to diminish the amount of the gas flow.

Such emanations of gas are common in Western Pennsylvania and Western New York, in regions where the occurrence of hard rock directly below the gravel bed of a stream precludes the supposition that the gas has resulted from the decay of recently buried tissues. It is probable that the gas which is continually accumulating in such situations is derived from great depths, that its presence is the result of a slow process of diffusion from

below, which only terminates as the gas enters the atmosphere, and that it constitutes a considerable portion of the natural gas which was stored originally in the rocks.

The feebly luminous flame produced by this gas distinguishes it from the nitrogen, which so frequently collects in the sands of river beaches in regions of constant fluctuations of water level due to tides, and where organic remains are abundant.

In the latter case the air penetrating the sand at low tide parts with its oxygen to the decaying matter, and as the tide rises again the residual nitrogen is expelled in bubbles under the pressure of the advancing water, while the carbon dioxide formed is retained in solution.

Gas collected from the gravel bottom of a stream flowing into the Ohio river near Sewickley, Pa., was found to have the following composition :

	Per cent.
Methane	93.06
Nitrogen	6.70
Carbon dioxide	0.24
	100.00

There is no reason to suppose that the diffusion of gas from the earth into the atmosphere is confined to surfaces covered by water, although it can only be made visible by the formation of bubbles in water.

It is no doubt continually in progress in regions of Devonian and carboniferous rocks.

This slow diffusion of gas from the earth into the atmosphere has occurred since early geological times and in regions where erosion has finally carried away whole systems of sedimentary rocks, liberating the imprisoned hydrocarbons by slow degrees. The gas thus escaping from within the earth's crust is added to that which is derived from recent decay on the surface, and probably forms no inconsiderable part of the total quantity carried continually into the atmosphere.

Hydrogen in a limited volume of air follows the well-known law of diffusion, mixing completely with the air.

Should a large mass of hydrogen enter the earth's atmosphere, the case would be different. Hydrogen, while it would diffuse

laterally with the air, would tend to accumulate in the upper strata on account of the great difference between its specific gravity and that of the constituents of the air. Ferrel,¹ has fully discussed the hypothetical case of the occurrence and arrangement of a very light constituent in the atmosphere, "Where the relative densities of the constituents regarded as independent atmospheres, would be nearly the same at the different altitudes, as in the case of oxygen and nitrogen, a constant agitation of the whole may keep them so mixed up that the proportions are nearly the same at all altitudes; but, in the case of a very rare constituent, the tendency would be for it to rise up so far above all the others that it could not become mixed up with them except in the lower strata, and at a considerable altitude it would be the only sensible constituent unaffected by the agitation of the comparatively much denser constituents which would exist, only sensibly lower down, near the earth's surface."

If the presence of hydrogen is ever positively detected in the atmosphere, it must be looked for in air samples collected as far away from the earth's surface as possible.

An experimental demonstration of the presence or absence of hydrogen in air, would be of great interest if the method to be employed were certain as regards its results. Existing methods for the detection or determination of hydrogen when present in traces, are not satisfactory.

After many trials, I have devised a method for the detection of traces of free hydrogen in a gas mixture. The method consists, briefly, in passing the gas over anhydrous palladium chloride contained in a glass tube. Free hydrogen reduces this salt at once, and in the cold, being converted into hydrochloric acid, which is recognized by passage through a silver nitrate solution.

Having in palladium chloride a reagent of extreme delicacy for free hydrogen, it seemed to be of interest to attempt a test for hydrogen in air, and in order to avoid as far as possible, all danger of impurities from local conditions at the earth's surface, some experiments were tried on Mount Washington, New Hampshire, during August, 1892.

¹ Annual Report of the Chief Signal Officer of the Army for 1888, pt. 2, p. 41.

The elevation of Mount Washington, nearly 7000 feet, did not justify the belief that upon its summit strata of air materially different from those at sea level could be reached, but there was the undoubted advantage of greater purity and freedom from local contamination.

By permission of Mr. Mark Harrington of the U. S. Agricultural Department, a room in the Weather Observer's building on the mountain, was used for the purpose.

I desire here to express my appreciation of the courtesy shown by Mr. Harrington and also by Mr. Mitchell in charge of the station, in affording facilities for the work.

Details of the work are omitted, as the results of two very carefully conducted experiments were negative, and therefore did not lead to a definite conclusion.

It may be suggested that ozone, by reason of its great oxidizing power, would tend to prevent the accumulation of combustible gases in the upper atmosphere. Oxygen is well known to derive its active properties from the influence of the electric discharge.

Ozone may be produced locally in considerable quantity as a result of violent electrical disturbances in the atmosphere. Much of the ozone thus formed probably expends its power in oxidizing atmospheric nitrogen to nitrous and nitric acid.

Ozone has a specific gravity much greater than oxygen, and would, consequently, tend to descend rather than to rise to the outer limits of the atmosphere. While the production of ozone must occur at points remotely distant and at considerable intervals of time, the evolution of hydrogen and methane at the earth's surface is continuous. Moreover, thunderstorms only occur during a brief portion of the year in temperate climates, and are unusual at all times in far northern latitudes.

In view of these facts it seems improbable that ozone can be considered likely to materially retard an accumulation of the lighter gases, hydrogen and methane, in the upper atmosphere.

Hydrogen and methane are not oxidized by prolonged contact with a two per cent. solution of hydrogen peroxide at 20° C.

It is true that the upper air may contain nitrous acid. Paper coated with potassium iodide and starch was found to be rapidly turned purple when exposed on Mount Washington. Free

hydrogen is, however, not oxidized by fuming nitric acid¹ and it is hardly likely that nitrous acid, in the highly diluted condition in which it must be looked for in air, could cause an oxidation of hydrogen.

Meyer² and Askenasy found that on exposure to bright sunlight, a mixture of oxygen and hydrogen suffered no change. Combination did not occur even on exposure of the gas to a temperature of 600° C.

Meyer and Seubert³ have shown that under highly reduced pressure combination does not occur in a mixture of oxygen and hydrogen under the influence of the electric spark. Experiments with mixtures of various hydrocarbons with oxygen, led to similar results. The minimum pressures at which the electric spark caused an explosion, were about one-tenth of an atmosphere in the case of hydrogen, and one-sixth of an atmosphere in the case of methane. In earlier times Humphrey Davy was led to similar conclusions as regards the explosion of rarified gas mixtures.

Although the minimum pressure at which chemical union would occur, may vary with the character of the discharge, it may be asserted that electrical disturbances are less likely to influence the oxidation of these combustible gases in the higher atmosphere where they must be looked for, if present in the atmosphere at all.

Methane and hydrogen possess under all conditions, great resistance toward oxidizing agents, and, once set free in air, it is questionable whether either gas could undergo any change by which it might be wholly brought back within the sphere of reactions produced by organic life, or by oxygen. Ferrel has suggested that the hydrogen of the sun's atmosphere may form merely an outer layer, resting upon much denser gases below.⁴ It is possible, at least, that such an arrangement exists in the earth's atmosphere.

It seems desirable that tests for hydrogen and methane in air, should be made at still greater altitudes in order that more defi-

¹ Winkler: *Ztschr. anal. Chem.*, 1889, 269.

² *Ann. Chem.* (Liebig), 269, 72.

³ *J. Chem. Soc.* 1884, 587.

⁴ *Loc. cit.*

nite information may be gained upon this interesting subject, although serious difficulties would be encountered in attempting to reach an altitude so high as to render the results of chemical tests positively conclusive.

WESTERN UNIVERSITY LABORATORY,
ALLEGHANY, PA.

A NEW GENERATOR.

BY EDWARD P. HARRIS.

Received May 27, 1895.

A GREAT many forms of automatic generators for the preparation of such gases as hydrogen, hydrogen sulphide, carbon dioxide, etc., have been proposed, that known as the "Kipp apparatus" being probably most widely used.

The chief objection to this and other forms in general use lies in the fact that according to their construction the spent acid at the bottom of the reservoir, containing the metallic salts, is used over and over again until it becomes too weak for further action, while plenty of fresh acid remains in the upper part of the reservoir, unable to enter the inner chamber containing the solid material (zinc, iron sulphide, marble, etc.)

The accompanying figures show how this difficulty is removed by a very simple device. The second figure shows the side

