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III.—*The Direct Union of Carbon and Hydrogen.*

By WILLIAM ARTHUR BONE and DAVID SMILES JERDAN.

INTRODUCTION.

ABOUT thirty years ago, Berthelot investigated the action of hydrogen on carbon at high temperatures, and, as is well known, obtained acetylene by the direct union of its elements at the temperature of the electric arc. His experiments may be briefly summarised as follows.

(1) He heated retort carbon, contained in a porcelain tube, in a current of hydrogen to such a temperature that the tube softened; (2) he passed a series of electric sparks between carbon poles in an atmosphere of hydrogen; and (3) he formed the electric arc in an atmosphere of hydrogen between carbon terminals.

The first two experiments, according to Berthelot, gave no positive result, whilst in the third experiment acetylene was formed.

Berthelot, however, seems only to have examined the products of the action of hydrogen on carbon in the foregoing experiments *qualitatively*; moreover, he did not look for any other hydrocarbon except acetylene, for a reason which he himself expresses as follows:—"Quant à l'hydrogène, toutes ses combinaisons avec le carbon, extraites jusque là de produits organiques se detruisaient précisément sous l'influence d'une temperature rouge; il semblait dès lors chimérique de chercher à les former directement" (*Ann. Chim. Phys.*, 1863, [3], 67, 52). During the past two years, the authors have reinvestigated the whole question, and at an early period in their work satisfied themselves that Berthelot's brilliant, pioneering researches leave much to be still worked out.

The authors' experiments may be conveniently divided into two series, as follows:—(1) In which a current of hydrogen was passed over carefully purified sugar-charcoal contained in a porcelain tube heated to about 1200° in a Fletcher furnace, in such a way that it was completely protected from the furnace gases. An examination of the exit gas showed that whereas it contained no acetylene or other un-

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saturated hydrocarbon, about 1 per cent. of a saturated hydrocarbon, most probably methane, was invariably present. (2) In which the electric arc was passed between terminals of purified carbon in an atmosphere of hydrogen, the apparatus being so arranged that samples of the gas could be drawn off for analysis at regular intervals. The products were found to contain both methane and acetylene. Experiments in which the arc was active for about two hours, and in which samples of the gas were drawn off from time to time and analysed, indicated a somewhat rapid formation of methane and acetylene during the first half hour, after which, however, the amounts of the gases seemed gradually to approach a limit, which was found to vary slightly with the voltage at the terminals, and possibly with other conditions.

The establishment of this equilibrium between hydrogen, acetylene and methane is of considerable interest, and the authors were led to form the arc under similar conditions in an atmosphere of methane or acetylene. It was expected, from the results obtained with hydrogen, that the greater part of the methane or acetylene would be readily resolved into its elements, but that, on the continued passage of the arc, an equilibrium between hydrogen, methane, and acetylene, similar to that obtained in the experiment with hydrogen, would be established; this expectation was fully borne out by the experimental results.

Berthelot (*Compt. rend.*, 1868, 67) does indeed mention the establishment of a similar equilibrium when electric sparks are passed through methane, but he calls it an equilibrium between acetylene, hydrogen, and carbon vapour, and expressly states that no other hydrocarbon, except perhaps the polymerides of acetylene, takes part in the equilibrium.

The results of the present investigation may be briefly stated as follows.

1. At a temperature of 1200°, or thereabouts, carbon unites directly with hydrogen to form methane, no acetylene or other unsaturated hydrocarbon being formed at this temperature.
2. When the electric arc is passed between carbon terminals in an atmosphere of hydrogen, methane and acetylene are both formed; on continuing the passage of the arc, a state of equilibrium between hydrogen, methane, and acetylene is finally established.
3. The same state of equilibrium is produced when the electric arc is passed in an atmosphere of either methane or acetylene under similar conditions.

It may be stated that all gas analyses in connection with this work were carried out by means of a modified form of McLeod's gas-analysis apparatus, kindly placed at our disposal by Professor Dixon.

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PART I.

EXPERIMENTS ON THE COMBINATION OF CARBON AND HYDROGEN AT A TEMPERATURE OF ABOUT 1200°.

In the first series of their experiments, the authors passed a current of hydrogen over purified carbon enclosed in a porcelain tube, and heated to bright redness in a Fletcher injector furnace by means of a coal-gas air blowpipe.

Experiments on the Diffusion of Gases through Porcelain at high Temperature.

Before making the actual experiments with carbon, the authors thought it necessary to find to what extent the porcelain tubes to be used were permeable to the furnace gases at the high temperatures of the subsequent experiments. This was done as follows.

A tube of the best Berlin porcelain, glazed within and without, having an internal diameter of 12 mm. and an external diameter of 16 mm., was placed in the Fletcher furnace in a manner to be described later. A glass tap was fitted into each end of the tube by means of a rubber stopper, the tube itself being of such a length that it projected a sufficient distance on either side of the furnace to prevent the rubber stopper being appreciably heated during the course of an experiment.

Experiment I.—A slow current of air which had been passed through a concentrated solution of potassium hydroxide and afterwards through sulphuric acid, in order to remove carbon dioxide and water vapour respectively, was sent through the porcelain tube heated to bright redness in the Fletcher furnace, and samples of the issuing gases were collected over mercury. Since any carbon compound diffusing through the walls of the tube would be converted into carbon dioxide under the conditions of experiment, if indeed it had not entered as such, it was only necessary to estimate the contraction which occurred when a measured volume of the exit gases was treated with a solution of potassium hydroxide in the McLeod apparatus, in order to determine the amount of such diffusion in terms of carbon dioxide; in this way it was found that 334 volumes of the issuing gases underwent a contraction of 0·3 volume.

This result pointed to a slight diffusion of furnace gases through the heated porcelain. In order to confirm this conclusion, the authors repeated the experiment with the difference that the air was enclosed and heated in the porcelain tube for an hour, and was then expelled and collected over mercury. 703 volumes of this air gave an absorption of 3·5 volumes.

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Experiment II.—A slow current of hydrogen, free from all gaseous carbon compounds, was dried by sulphuric acid and was then passed through the porcelain tube. After the air in the tube had been expelled, the furnace was gradually heated to bright redness, and as soon as the maximum temperature was attained the tap at each end of the tube was shut, and the hydrogen thus enclosed was kept at a bright red heat for $5\frac{1}{2}$ hours. The gas was finally expelled by a current of the same hydrogen, and collected over mercury.

102·1 volumes of this gas were mixed in the McLeod apparatus with 385·2 volumes of air free from carbon dioxide, and exploded; when 336·8 volumes of gas remained, which on treatment with potassium hydroxide solution were further reduced to 336·5 volumes. Thus after explosion 0·3 volume of carbon dioxide was found in the residual gas. Since the original hydrogen on being exploded with a large excess of air free from carbon dioxide was not reduced in volume after treatment with potassium hydroxide solution, it is evident that carbon compounds had diffused through the walls of the tube during the heating.

Experiment III.—A supply of nitrogen was made by Harcourt's ammonia-air method and stored over water in a gas-holder. A slow current of this gas was passed successively through concentrated potassium hydroxide solution, over a heated copper spiral, through sulphuric acid, and finally through the porcelain tube heated to redness; by these means, any carbon dioxide, oxygen, or water vapour present in the gas would be removed before it entered the tube. After the current had been passed long enough to expel all the air from the tube, the taps were shut and the enclosed nitrogen was heated for an hour; finally the gas was expelled by a current of nitrogen and collected over mercury.

380·0 volumes of this nitrogen on standing in the McLeod apparatus over potassium hydroxide solution were reduced to 379·4 volumes. The residual gas was further treated with a solution of cuprous chloride in hydrochloric acid to absorb carbon monoxide, and was then washed with potassium hydroxide solution, but no further reduction in volume was observed.

This result confirms those of the previous experiments, and further shows that the gaseous carbon compounds diffusing through the tube consist chiefly of carbon dioxide.

Experiment IV.—The amount of water vapour from the furnace gases diffusing through the porcelain tube was estimated as follows.

A slow current of air was passed successively through potassium hydroxide solution and sulphuric acid, and over a layer of calcium chloride, so as to remove carbon dioxide and water, and then through the porcelain tube heated to bright redness. The issuing gases were

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passed through a weighed calcium chloride tube, protected from the outer atmosphere by a wash-bottle containing sulphuric acid. The current of air was passed through the heated tube at a constant rate of 2 litres per hour, and at the end of 1½ hours the calcium chloride tube had increased in weight by 7 milligrams. The calcium chloride tube was again attached, and after 3 hours, during which 5 litres of air were passed through the apparatus, it had increased in weight by 10·5 milligrams. The authors have calculated from the above results that the percentage of water vapour in the issuing air was 0·30 per cent. in the first case, and 0·26 per cent. in the second.

As it was thus evident that the porcelain tubes to be used in the experiments were to a certain extent porous to the furnace gases at a bright red heat, it was decided to avoid heating the tubes in direct contact with the furnace gases. This was accomplished, as will be more fully described later, by surrounding the tube containing the carbon by a wide porcelain tube, and passing a current of dry hydrogen through the annular space thus formed between the two tubes, an arrangement which proved to be thoroughly satisfactory.

Preparation and Purification of the Carbon.

Pure cane sugar was carbonised by heating it it in a nickel crucible over a Bunsen flame. The residue was transferred to a platinum crucible and strongly ignited over a blowpipe, the charcoal thus obtained being then placed in a combustion tube and heated to redness in a furnace, while a current of dry chlorine was passed over it for 7 hours. The charcoal was next washed with hot distilled water to remove the greater part of the chlorine, drained by means of the filter pump, and dried at 100°. It was then heated in a combustion tube in a current of dry hydrogen for about 40 hours, until no more hydrogen chloride was evolved, and was afterwards transferred to a short hard glass tube, one end of which had been sealed off. The other end of this tube was drawn out, and attached to a Sprengel pump, the air thoroughly exhausted, and the tube then strongly heated in a small furnace for several hours, the exhaustion being continued meanwhile. The carbon thus prepared was kept in an exhausted desiccator over phosphoric anhydride for several months, and was afterwards used as required.

Preparation of the Hydrogen.

The hydrogen used in these experiments was prepared by the action of pure dilute sulphuric acid on redistilled zinc free from arsenic. The gas evolved, after being passed first through a solution of lead acetate, and then through two Erlenmeyer flasks containing a strongly

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alkaline solution of potassium permanganate maintained at a temperature of 60°, in order to oxidise and remove hydrocarbons, was collected in large glass gas-holders over water. Before being passed over the heated carbon in subsequent experiments, the gas in the holders was sent through potassium hydroxide solution, sulphuric acid, then over a heated copper spiral, and finally through wash-bottles containing potassium hydroxide solution, and sulphuric acid, respectively. The hydrogen thus purified from carbon dioxide, and traces of oxygen and moisture, was found on analysis to be practically free from carbon compounds.

The authors have analysed many such samples of hydrogen, prepared at different times during the course of their work, by exploding a measured volume of the gas with an excess of air in the McLeod apparatus, and measuring (1) the contraction, C, on explosion, and (2) the absorption, A, caused by potassium hydroxide solution in the residual gas. The following results are selected at random from a large number of such analyses, and will serve to show the average percentage composition of the hydrogen employed in the experiments.

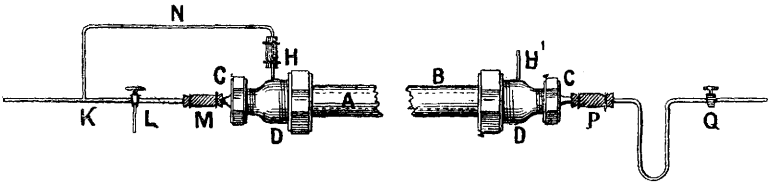
Hydrogen, $C \times \frac{2}{3}$	98·6	99·2	98·8	98·9	99·4	99·7	98·5	98·7	99·1	98·9	99·4	99·5
Absorption by KOH, A.	0·2	nil.	nil.	nil.	0·1	nil.	nil.	0·2	nil.	nil.	0·2	0·1
Nitrogen (by difference)*	—	0·8	1·2	1·1	—	0·3	1·5	—	0·9	1·1	—	—

It will thus be seen that the hydrogen often contained no appreciable amount of carbon compounds, although in some cases traces were noticeable, but in no instance was hydrogen used in an experiment which, after explosion, gave an absorption, A, exceeding 0·2 per cent.

Description of Apparatus.

The arrangement of the furnace and the porcelain tubes in which the carbon was heated in a current of hydrogen, is shown in the accompanying diagrams, Figs. 1, 2, and 4, and may be described as follows. The inner porcelain tube, A, Figs. 1 and 2, was of Berlin

Fig. 1.



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* Nitrogen is only taken by difference when no carbon compounds are present.

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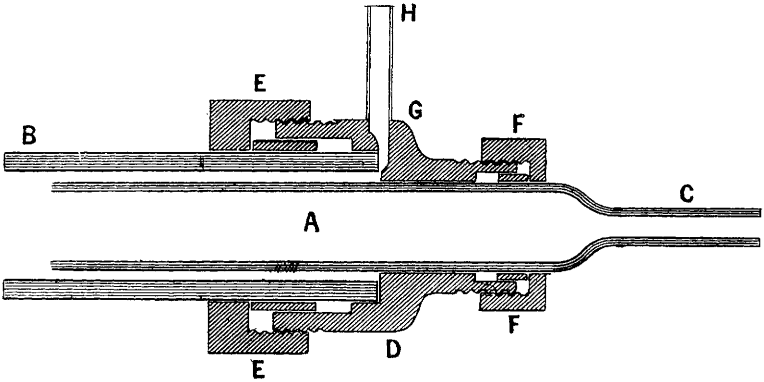
porcelain, glazed within and without, and was drawn out at either end as shown at C. The total length of A was 60 cm., its internal diameter was 12 mm., and its external diameter 16 mm. This tube was fitted within a wider tube, B, also of glazed porcelain. The total length of B was 48 cm., its internal diameter 20 mm., and its external diameter 26 mm. The tubes were kept in position by two brass joints, one of which is shown in section in Fig. 2, in such a way that the two tubes had a common axis. D is a brass ferrule provided with two stuffing-boxes, EE and FF, Fig. 2, corresponding in diameter to the tubes B and A respectively. The stuffing-boxes were packed with a composition of asbestos and lime moistened with a strong solution of sodium silicate, which, when the collars were placed in position and the caps screwed down, gradually became solid, and made a good gas-tight joint. The ferrule, D, was bored at the point G, so as to admit of the insertion of the brass side piece, H, which served for the passage of the hydrogen through the jacket.

Fig. 2.



The furnace, Fig. 4 (next page), employed for heating the porcelain tubes was rectangular in shape, and was made of fire-clay. Its length was 30·5 cm., breadth 24 cm., and depth 7 cm. The furnace was bored at each side for the insertion of the porcelain tubes, and also in front for the introduction of the blowpipe. The furnace had a circular fire-clay cover, bored obliquely so as to allow the furnace gases to escape.

In setting up the apparatus, the inner porcelain tube, A, was wrapped round spirally with asbestos string, so that each turn of the string was about 2 cm. apart from the previous turn, and was then inserted into the wider tube, B. In this way the two tubes could be accurately centred, and kept apart when subsequently heated, while at the same

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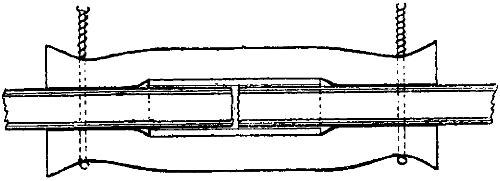
time a current of gas could be passed without difficulty through the annular space between them. The two tubes were then placed in position in the furnace, after which the brass joints were fitted on and packed with the composition of asbestos, lime, and sodium silicate as already described. A current of dry air was then passed through the jacket between the tubes for about two days, in order that the joints might be thoroughly dried. In this way a perfectly gas-tight joint was obtained.

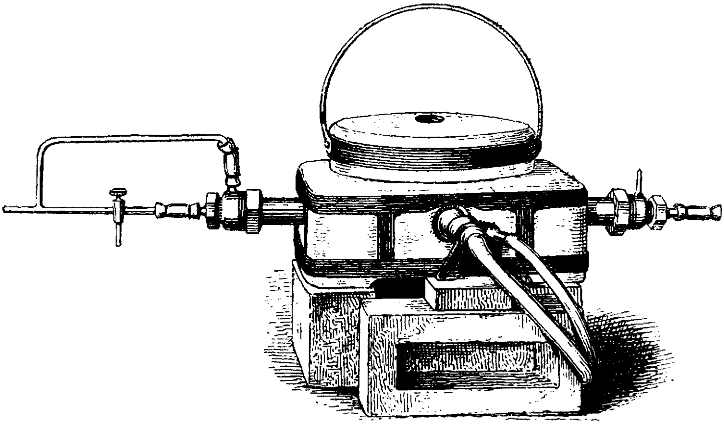
This arrangement of two concentric porcelain tubes was adopted in order to avoid heating the tube containing the carbon, in direct contact with the furnace gases, by surrounding it with a jacket of hydrogen.

Fig. 3.



To this intent the current of hydrogen, purified as already described (p. 45), was divided into two at K, Fig. 1, one part passing through the tap L, and the other joint M into the inner tube, A, and the other part passing by the branch N, through the jacket between the tubes,

Fig. 4.



and making its exit through H′ whence, after passing through a wash-bottle containing sulphuric acid, it escaped into the atmosphere. The

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other end of the inner tube was connected by means of a joint, P, with a U-tube terminating in a tap, Q, by means of which connection could be made with a Schiff's nitrometer containing mercury, which served to collect the gases from the inner tube.

The tap, L, was a three-way tail-tap, so that samples of the hydrogen entering the inner tube could be conveniently drawn off during the course of an experiment. The connections, M and P, were made by sliding a short length of wider glass tubing over the ends of the porcelain and glass tubes to be connected, and securing the joint by means of thick rubber pump-tubing, Fig. 3. In this way, the hydrogen was prevented from coming in contact with a rubber surface in the near neighbourhood of the furnace.

The complete arrangement of furnace and tubes is shown in Fig. 4.

Description of the Experiments.

Blank Experiment.—The first experiment performed with the apparatus just described was intended to test whether or not any diffusion into the inner tube was now possible.

A current of purified dry hydrogen was passed through the tubes for 6 hours in order to displace all the air. The furnace was then lighted, and the tubes gradually raised to a bright red heat. The taps, L and Q, were closed and the hydrogen thus shut up in the inner tube, A, was maintained at this temperature for about 3 hours, during which time a current of the same hydrogen was passed through the jacket between A and B. The hydrogen in the inner tube was then drawn off and collected in the nitrometer for analysis. In the meantime, a sample of the hydrogen entering the tube had been collected through the tail-tap, L, and the two samples were then analysed by the method described on page 46.

The gas which was drawn off at L, after explosion in the eudiometer with excess of air free from carbon dioxide, gave an absorption of 0·10 per cent on treatment with potassium hydroxide solution; whilst the gas which had been heated for three hours in the inner tube, when treated in the same way, gave an absorption of 0·15 per cent.

On repeating this experiment a similar result was obtained. Thus the arrangement of the tubes prevents any appreciable diffusion of furnace gases into the inner tube even on prolonged heating.

Actual Experiments.—Many experiments in which the purified carbon was heated in the tube A in a current of hydrogen were performed, the method of procedure being as follows.

The purified carbon, which had been kept in a desiccator in a vacuum over phosphoric anhydride, was as rapidly as possible trans-

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ferred to the inner tube, A. The apparatus was then put together and a current of dry hydrogen passed through the whole for several days in order to sweep out all the air; the tubes were then gradually heated to bright redness, the current of hydrogen through A and through the jacket between A and B being maintained meanwhile. The heating was continued for 6 to 8 hours, after which samples of the exit gas from A were collected for analysis; samples of the gas entering the tube were also collected at L. The same carbon was used for several experiments, and was not changed until it became necessary to take the apparatus to pieces and refit it.

The authors generally found that the gases which had passed over the heated carbon contained small amounts of carbon monoxide. At first they were inclined to attribute this to a small inleakage of air; but on investigating the matter they found the suspicion to be groundless, because the gas entering the tube was found to be free from oxygen, and contained practically the same proportion of nitrogen as the exit gas. The authors finally concluded that the carbon monoxide was due in part to small amounts of oxygen or moisture occluded in the pores of the carbon used, and in part also to a possible slight reduction of the glaze of the inner porcelain tube in the presence of hydrogen and carbon at a high temperature. The latter supposition was based on the appearance of the inner tube after it had been used for a long series of experiments; although the outer surface of that part of the inner tube which had been strongly heated was coloured black the glaze appeared intact, whilst on the inner surface of the tube the glaze appeared to have been considerably disintegrated.

The analysis of the gases obtained in these experiments was performed as follows.

In a few of the early experiments, the gaseous products were specially tested for carbon dioxide, and unsaturated hydrocarbons generally, by exposing a measured volume of the gas in the McLeod apparatus to the action of potassium hydroxide solution, and fuming sulphuric acid respectively. As in no case did any absorption occur, these gases were not looked for in later experiments.

Acetylene was also specially tested for by passing the gases issuing from the inner tube through an ammoniacal solution of silver chloride, but it was never detected.

In all the experiments, the following method of analysis was adopted.

About 200 volumes of the sample were introduced into the McLeod apparatus and treated for 15 minutes with a hydrochloric acid solution of cuprous chloride (prepared according to instructions given in Hempel's *Gas Analysis*, and then with a dilute solution of

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potassium hydroxide, so as to remove any carbon monoxide. About 100 volumes of the residual gas were mixed with some 400 volumes of air free from carbon dioxide and exploded; after explosion, the gas was treated with potassium hydroxide solution, and the absorption measured. There was always an absorption, and this points to the presence of a saturated hydrocarbon in the gas analysed; most probably this hydrocarbon was methane. The original hydrogen was analysed in the usual manner.

The following table shows the results obtained in six separate experiments.

Analysis of the Gases.

Experiment.	I.	II.	III.*		IV.	V.	VI.
Volume of gas taken	184·9	159·7	251·6	189·4	214·1	207·1	169·8
Volume after treatment with Cu_2Cl_2 and KOH	184·7	159·1	250·8	188·8	212·2	205·1	167·9
Volume of residual gas taken...	107·0	105·5	102·7	105·7	107·7	92·2	96·8
Volume of air added.............	460·1	423·6	421·2	425·1	451·3	389·9	376·5
Volume after explosion	409·5	374·9	370·2	373·2	399·1	345·1	329·3
Volume after treatment with KOH	408·5	374·2	368·8	371·9	397 9	344·3	328·0
Absorption	1·0	0·7	1·4	1·3	1·2	0·8	1·3

Reckoning the saturated hydrocarbon present as methane, the following table gives the percentage composition of the issuing gases.

Percentage Composition of issuing Gases.

Experiment.	I.	II.	III.		IV.	V.	VI.
Carbon monoxide	0·1	0·4	0·3	0·3	0·9	1·0	1·1
Hydrogen	97·2	96·6	97·7	97·5	96·7	97·2	96·2
Methane	0·9	0·7	1·4	1·3	1·1	0·9	1·3
Nitrogen (by difference)	1·8	2·3	0·6	0·9	1·3	0 9	1·3

The composition of the original hydrogen in these experiments is shown in the following table.

Percentage Composition of Original Hydrogen.

Experiment.	I.	II.	III.		IV.	V.	VI.
Hydrogen, $C \times \frac{2}{3}$	98·9	98·9	99·4	99·4	—	98·9	—
Absorption by KOH, A	0·0	0·0	0·2	0·2	0·0	0·0	0·0
Nitrogen (by difference)	1·1	1·1	—	—	—	1·1	—

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* Two separate analyses were made in this experiment.

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Action of Carbon Monoxide on Hydrogen at High Temperatures.

In the experiments just described, the authors had great difficulty in preventing the formation of small quantities of carbon monoxide. Thus, in three of the experiments quoted, nearly ·1 per cent. of carbon monoxide was present in the issuing gases, whilst in the first only of the six experiments was the amount of carbon monoxide inappreciable. Although the amount of methane formed did not seem to depend at all on the percentage of carbon monoxide in the issuing gas, it seemed conceivable that the methane produced in the experiments might be due in part to the action of carbon monoxide on hydrogen at the high temperature employed. To ascertain whether this were so or not, the authors passed a mixture of carbon monoxide and hydrogen, containing 20 per cent. of carbon monoxide, through the porcelain tubes heated to bright redness in the furnace. The inner tube in this experiment was a new one and contained no carbon. The issuing gases were collected and analysed, but no methane was found, so that it appears that the formation of carbon monoxide in the foregoing experiments cannot affect the result so far as the methane is concerned.

PART II.

EXPERIMENTS ON THE COMBINATION OF HYDROGEN AND CARBON AT THE TEMPERATURE OF THE ELECTRIC ARC.

The authors investigated the effect of passing the electric arc between poles of purified gas-carbon in an atmosphere of dry hydrogen enclosed in a glass globe standing over mercury.

Description of the Apparatus.

Figure 5 represents the apparatus used in this series of experiments, and may be described as follows.

A is a glass globe terminating below in a cylindrical portion B, and drawn out conically at the top. This drawn out portion is bent at right angles and sealed on to a three-way tail-tap, C. The dimensions of this part of the apparatus are the following :—Total height, 42 cm. ; diameter of A, 17 cm. ; diameter of B, 6 cm. ; length of B, 12 cm. ; total capacity, 3 litres.

The globe stands in a mercury trough, D, and is supported on two rubber plates, one of which is shown at E. By means of the three-way tap, C, communication is made through a tap, F, with a Schiff's nitrometer, G, filled with mercury, which served for the collection of the products and their transference to sample tubes at L. Each of the carbon terminals, HH, is attached to a stout copper wire which is fixed by a plug of asbestos into a piece of narrow glass tubing, KK,

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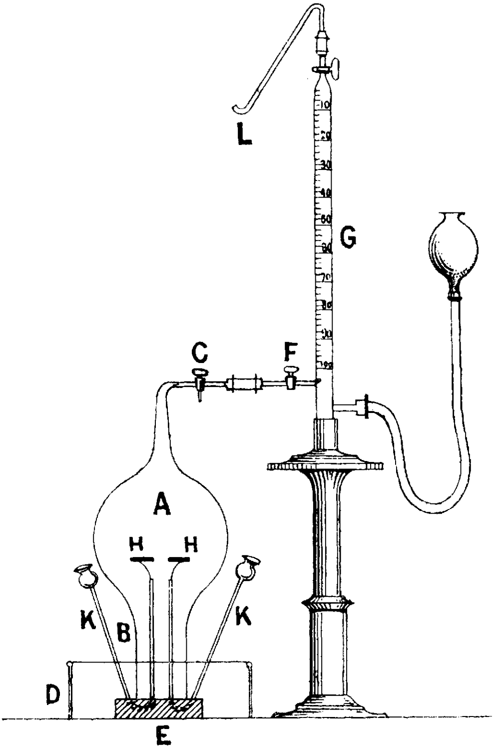
bent as in the figure and filled with mercury. The limb of the tube bearing the carbon is thrust into the globe from below the surface of the mercury in the trough. The other limb of each tube terminates in a thistle funnel, filled with mercury, into which dips a stout copper wire leading from a dynamo. This limb is held in position by a clamp fixed to a retort stand and can be moved backwards and forwards as occasion requires for the making and adjustment of the arc.

FIG. 5.



Preparation of the Carbon Terminals.

The terminals were of gas carbon 3·5 cm. long and 1 cm. in diameter; before being used, they were placed in a combustion tube sealed at one end, and connected at the other end with a Sprengel pump. The tube was thoroughly exhausted, and then strongly heated in a furnace for about 2½ hours, the pump acting the whole time. The tube was allowed to cool, and the carbons were transferred to

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another similar combustion tube and the treatment was repeated. The carbons were afterwards mounted in the apparatus as described.

Description of the Experiments.

The globe was completely filled with mercury by attaching an air-pump to the tap, C, and exhausting the air. Purified dry hydrogen, prepared as described on p. 45, was then introduced either from below the surface of the mercury in the trough or through the tap, C, until the globe was about three-fourths full. The electric arc was then formed between the carbon terminals, and continued for 15 minutes. The globe was again exhausted until the mercury completely filled it. In this way any oxygen occluded in the pores of the carbon terminals would be removed.

The globe was once more filled with the dry hydrogen as before. The arc was again formed and the current passed for a period of time varying from 30 minutes to 2 hours, and at the end of 5, 15, 30, 45, &c., minutes, samples of the gas were drawn off into the nitrometer and transferred to sample tubes for analysis.

Throughout these experiments, an alternating current from a dynamo was employed; the voltage at the terminals of the dynamo in two of the experiments was taken between 40 and 60, whilst in the third it was about 160.

Analysis of the Gases.

The gases obtained on passage of the arc in hydrogen were examined qualitatively, and were found to contain considerable quantities of acetylene. Traces of carbon monoxide might also be present, owing to traces of moisture in the apparatus, and also small amounts of hydrogen cyanide due to the presence of a small percentage of nitrogen in the hydrogen employed. After these constituents, and possible traces of other unsaturated hydrocarbons, had been removed, analysis showed that methane had been formed, to the extent of between 2 and 3 per cent., in the experiments in which the arc had been passed for half an hour or more.

The complete analysis of the gases was carried out as follows. A large volume of the gas was treated, successively, in the McLeod apparatus, with (1) solid potassium hydroxide; (2) fuming sulphuric acid; (3) an acid solution of cuprous chloride, and (4) a dilute solution of potassium hydroxide. The gas was remeasured after absorptions 1 and 4. In this way, the hydrogen cyanide and acetylene (together with traces of unsaturated hydrocarbons and of carbon monoxide) were removed and estimated. In some of the later analyses, the gases were treated with an ammoniacal solution of cuprous chloride in addition to

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the other reagents, but this was not found to affect the final result. A known volume of the residual gas was then mixed with a measured excess of air free from carbon dioxide, and the mixture exploded in the eudiometer; after cooling, the gas was remeasured, allowed to stand over a strong solution of potassium hydroxide in the laboratory vessel, and then the volume was read again. In this way the contraction, C, was determined, and also the absorption by potassium hydroxide solution, A, which corresponds with the amount of methane in the gas.

Experiment I.—(voltage 40 to 60). The hydrogen used in the experiment contained no gaseous carbon compound. The arc was passed for 45 minutes, and samples of the gases were collected at the end of 5, 15, 30, and 45 minutes. The following tables show the results of the analyses of these samples.

	Samples collected at the end of			
	5 mins.	15 mins.	30 mins.	45 mins.
Volume of gas taken	268·2	248·1	244·8	247·7
Volume after treatment with solid KOH	267·9	247·6	244·5	247·1
Volume after treatment with fuming sulphuric acid, acid cuprous chloride, and KOH solution	262·2	235·5	228·8	227·1
Volume of residual gas taken	92·0	82·7	94·9	85·2
Volume of air added	394·2	339·9	373·8	338·5
C	137·3	123·1	140·6	126·6
A	0·6	1·2	2·3	2·1

The above numbers give the following as the percentage compositions of the samples.

	Samples collected at the end of			
	5 mins.	15 mins.	30 mins.	45 mins.
Hydrogen cyanide	0·1	0·2	0·1	0·2
Acetylene	2·1	5·0	6·4	8·1
Methane	0·6	1·4	2·3	2·3
Hydrogen	96·4	92·0	89·2	87·8
Nitrogen (by difference)	0·8	1·4	2·0	1·6

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Experiment II.—(voltage 40 to 60, rising towards the end of the experiment).—The arc was passed for 2 hours, and samples were collected after 5, 15, 30, 60, 90, and 120 minutes. The following tables show the results of the analyses of these samples.

	Samples collected at the end of					
	5 mins.	15 mins.	30 mins.	60 mins.	90 mins.	100 mins.
Volume of gas taken	312·7	288·4	342·6	300·5	248·9	206·1
Volume after treatment with solid KOH	312·7	288·4	342·3	298·9	246·4	205·3
Volume after treatment with fuming sulphuric acid, acid cuprous chloride, and KOH ...	306·1	274·3	321·3	278·4	230·4	189·7
Volume of residual gas taken ...	89·7	87·7	114·5	95·5	90·5	91·5
Volume of air added............ ..	377·9	379·0	425·1	412·0	365·6	376·3
C	131·8	129·9	169·0	141·1	134·5	136·0
A	0·9	1·5	2·9	2·8	2·1	2·6

The following are the percentage compositions calculated from the above figures.

	Samples collected at the end of					
	5 mins.	15 mins.	30 mins.	60 mins.	90 mins.	120 mins.
Hydrogen cyanide	nil.	nil.	0·1	0·5	1·0	0·4
Acetylene	2·1	4·7	6·2	6·8	6·4	7·6
Methane	1·0	1·6	2·4	2·7	2·1	2·6
Hydrogen	94·3	91·8	89·1	87·7	88·8	87·7
Nitrogen (by difference)	2·6	1·9	2·2	2·3	1·7	1·7

Experiment III.—(voltage—160).—The arc was passed for 1 hour, and samples of the gas were collected at the end of 5, 15, 30, and 60 minutes. The following tables show the results of the analyses.

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	Samples collected at the end of				
	5 mins.*		15 mins.	30 mins.	60 mins.
Volume of gas taken	205·3	146·4	149·7	132·8	335·4
Volume after treatment with solid KOH	205·3	146·4	149·4	131·5	334·2
Volume after treatment with fuming sulphuric acid, ammoniacal cuprous chloride, acid cuprous chloride, and KOH	200·1	142·7	140·3	121·2	308·9
Volume of residual gas taken	90·5	106·1	85·4	99·5	100·4
Volume of air added	365·1	436·8	340·0	408·0	415·2
C	131·3	152·6	125·3	146·8	148·1
A	1·0	0·9	1·9	4·2	4·2

The following are the percentage compositions of the samples calculated from the above figures.

	Samples collected at the end of				
	5 mins.		15 mins.	30 mins.	60 mins.
Hydrogen cyanide	nil.	nil.	0·2	1·0	0·4
Acetylene	2·5	2·5	6·1	7·7	7·5
Methane	1·1	0·8	2·1	3·8	3·8
Hydrogen	92·9	92·5	89·4	84·6	85·5
Nitrogen (by difference)	3·5	4·2	2·2	2·9	2·8

From the foregoing experiments it will be seen that, when the electric arc is passed between carbon terminals in an atmosphere of hydrogen, acetylene and methane are both produced. The nature of the results is best seen from the accompanying diagrams, Fig. 6 (p. 58), in which the abscissæ represent time in minutes, and the ordinates the percentage of acetylene or methane in the products. The curves thus obtained for experiments B and C, in which the arc was continued for an hour or upwards, show how the rate of formation of the gases varies with the voltage employed, the rate being greater with the higher voltage used in experiment C as regards both acetylene and methane. The curves for both gases alike rise rapidly from the origin, but gradually become less steep, and both, after passing the

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* Two analyses were made of this sample.

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ordinate 30, become practically horizontal. In the curves derived from experiment B, the slight deviation from the horizontal is due to a considerable rise in the voltage, which has been already noticed. Thus it appears that for every voltage there exists a certain state of equilibrium between hydrogen, acetylene, and methane, and that the higher the voltage used, the greater the proportion of acetylene and methane present in the final products after the passage of the arc for a sufficient length of time.

Fig. 6.

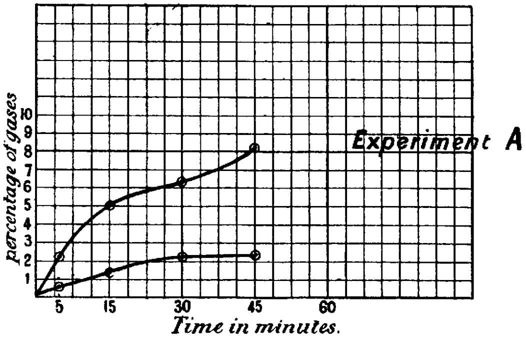
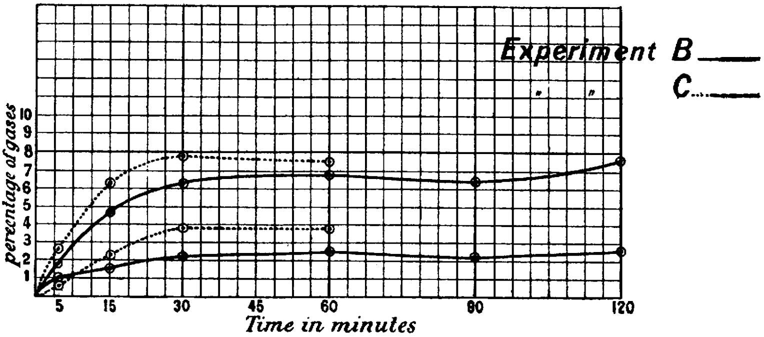


Fig. 7.



The authors propose at some future time to investigate more carefully the relations existing between the voltage employed and the corresponding state of equilibrium between the gases.

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PART III.

EXPERIMENTS ON THE ACTION OF THE ELECTRIC ARC ON METHANE AND ACETYLENE.

The experiments described in Part II. show that when the electric arc is passed between carbon poles in an atmosphere of hydrogen, both acetylene and methane are formed, but that these two gases do not accumulate beyond a definite limit, which, however, varies with the conditions of the experiment. It therefore seemed probable that, if methane or acetylene were subjected to the action of the arc, they would be to a large extent resolved into their elements, but that the decomposition products would contain acetylene and methane in approximately the same proportions in which they occurred in the products of the action of the arc on hydrogen. The authors, therefore, decided to study the action of the arc on methane and acetylene respectively, and considering the difficulty of maintaining exactly the same conditions in the three series of experiments, their results bear out in a remarkable way the theoretical conclusions. The experiments which follow show that methane and acetylene are to a great extent easily resolved into their elements by the electric arc, and that the gases drawn off after the arc has been passed for about an hour contain both acetylene and methane in nearly the same proportions as had been obtained in the experiments with hydrogen.

Experiment with Methane.

Methane was prepared by the method of Gladstone and Tribe, that is, by the decomposition of a solution of methylic iodide in methylic alcohol by the zinc-copper couple; the gas was washed with alcoholic potash, and then collected in a gas-holder over water. From the gas-holder, the methane was bubbled through sulphuric acid, and thence into the large globe of the arc apparatus, arranged as described in Part II. When the globe was three-quarters filled with the gas, the arc was formed. It soon became evident that the methane was being decomposed; large flakes of carbon formed in the neighbourhood of the terminals and fell on to the surface of the mercury below; and a hard deposit of carbon adhered to the carbon terminals, closely resembling bunches of iron filings attached to the poles of a magnet, whilst the whole interior surface of the globe was covered with a dense black film. A large increase of the volume of the contained gas also occurred, which could not be accounted for by the mere expansion of the gas by heat. These signs of decomposition continued for about ten minutes, after which the volume of the gas remained fairly constant, and during

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the remainder of the experiment the arc did not differ in appearance from that obtained in the hydrogen experiments. The arc was maintained for an hour, and afterwards samples of the gas were drawn off for analysis. Some of the remaining gas was passed through an ammoniacal solution of silver chloride, when a copious precipitate of silver acetylide was produced. The gas was analysed in the McLeod apparatus in the same way as the gas drawn off from the globe in the experiments with hydrogen, except that after the preliminary absorptions some of the residual gas was exploded with oxygen instead of air. The result of the analysis was as follows.

Volume of gas taken	270·4
Volume after treatment with solid KOH....	268·1
Volume after treatment with ammoniacal cuprous chloride, fuming sulphuric acid, acid cuprous chloride, and KOH	241·5
Volume of residual gas taken	99·4
Volume of oxygen added	396·6
C	148·5
A	2·8

From these numbers, the percentage composition of the samples has been calculated (nitrogen by difference).

HCN.	C_2H_2.	H_2.	CH_4.	N_2.
0·8	9·8	85·6	2·5	1·3

Experiment with Acetylene.

The globe was filled with acetylene prepared by the action of water on the purest obtainable calcium carbide, and dried by exposure to potassium hydroxide. The arc (voltage—160) was made, and at once brought about rapid decomposition ; dense clouds of carbon rose from the terminals, and a large deposit of carbon rapidly formed on them ; a luminous smoky flame rose also for some time from the terminals, and much heat was evolved. After 7 minutes, the action of the arc became quieter, and during the remainder of the experiment, which lasted for an hour, resembled the action of the arc in hydrogen. At the close of the experiment, samples of the gas were collected, and analysed in the McLeod apparatus as before. The following is an account of the analysis.

Volume of gas taken	238·9
Volume after treatment with solid KOH....	238·5
Volume after treatment with ammoniacal cuprous chloride, fuming sulphuric acid, acid cuprous chloride, and KOH	214·9

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Volume of residual gas taken	93·8
Volume of air added	402·9
C	140·2
A	3·4

From these numbers the percentage composition of the gas has been calculated as follows.

HCN.	C_2H_2.	H_2.	CH_4.	N_2.
0·2	9·9	85·3	3·2	1·4

A minute quantity of naphthalene was formed in this experiment, as was apparent from the smell of the products.

An experiment was also made with acetylene prepared by the decomposition of cuprous acetylide by hydrochloric acid. The products contained 2·5 per cent. of methane and approximately 10 per cent. of acetylene.

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