124. *The Preparation of Pure Ethane, Methane, and Hydrogen, and the Analysis of Their Mixtures.*

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In connexion with other work, it was necessary to find a rapid and accurate method for the analysis of mixtures of ethane, methane, and hydrogen. In this paper an account is given of the methods used for the preparation of the gases in the pure state, and also of the analysis of small or large samples of their mixtures.

The explosion of a mixture of ethane, methane, and hydrogen does not give sufficient data to allow us to calculate the proportions in which the gases are present. It is therefore necessary to remove one of the components by a chemical or physical method, leaving the other two for determination by explosion or slow combustion. The principles of fractional condensation, or of condensation followed by fractional distillation, as a method for the analysis of mixtures of this type have been applied by many investigators.

Tropsch and Dittrich (*Brennstoff-Chem.*, 1925, **6**, 169) passed the gas mixture through a series of glass bulbs cooled to different temperatures. Burrell and Seibert alone (*J. Amer. Chem. Soc.*, 1914, **36**, 1537) and with Robertson (*Bur. Mines. Tech. Paper No.* 104, 1915) used an apparatus in which the principle of fractionation was employed. Shepherd and Porter (*Ind. Eng. Chem.*, 1923, **15**, 1143) used a modified form of this apparatus, incorporating a fractionation column. Davis (*Ind. Eng. Chem. Anal.*, 1929, **1**, 61) and Podbielniak (*Oil and Gas J.*, 1929, **38**, 161) both used some type of fractionation column, and carried out the analysis by plotting the volume distilled against the boiling points of the components. Such a method as this is useful where the sample is large and contains several hydrocarbons. Fractionation in a column similar to that described by Podbielniak has been used successfully in this laboratory for the past 18 months, both as a method of analysis where samples of 2 or 3 litres are available and as a method of purification of supplies of ethane and methane.

Moulders and Schaffer (*Rec. trav. chim.*, 1930, **49**, 1057) have described a method for the analysis of ethane–methane–hydrogen mixtures which consists in the separation of the mixture into two fractions by condensation with liquid air, each fraction then being determined by combustion over copper oxide. King and Edgcombe (*Fuel Research Tech. Paper No.* 33) have carried out exhaustive experiments on the oxidation of hydrogen and carbon monoxide in the presence of saturated hydrocarbons. The oxidation was carried out over freshly prepared copper oxide at 280°, at which no oxidation of the methane occurred, but ethane, propane, and butane were slowly oxidised, a small error thus being introduced into the analysis. More recently, Walker and Shukla (*Trans. Faraday Soc.*, 1931, **27**, 35) used a similar method for the analysis of mixtures of ethane and methane, which could not be analysed satisfactorily by explosion. Later (J., 1931, 368) they modified this method to include mixtures containing hydrogen, freezing out the ethane with liquid air and adsorbing the hydrogen from the remaining hydrogen–methane mixture with palladium-black, the ethane and the methane portion being pumped off with a Toepler pump, transferred to a Bone and Wheeler apparatus, and analysed.

Owing to the difficulty of obtaining complete separation of the components by freezing out one of them, an attempt has been made to find a method which avoided the use of low temperatures. The method now described consists in the oxidation of the hydrogen in the mixture by palladium-black, followed by the explosion of the two remaining components. This explosion has been found to be perfectly satisfactory provided that the right conditions be observed.

EXPERIMENTAL.

Explosion of Ethane–Methane Mixtures.—In view of the fact that explosions of hydrocarbon gas mixtures with excess of oxygen are considered to give rise to inaccuracies, it was originally decided to carry out the analysis by combustion over copper oxide. For this purpose an ordinary silica micro-combustion tube was used; it was packed with copper oxide and heated in an electric furnace to 900°. This rather high temperature for combustion was found to be necessary whenever methane was contained in the gas. The gas sample was contained over mercury in a sampling pipette, which had a three-way tap at the top. This tap was connected into the flow of oxygen to the combustion tube and was used to admit small portions of a measured quantity of the gas mixture into the oxygen stream from time to time. The products of combustion were collected in two micro-absorption tubes filled with phosphoric oxide and "Sofnolite." The method was capable of giving very accurate results, for it enabled each component to be estimated to within 0·1%; it also constituted a useful check on the purity of the gases prepared by fractionation, but it was too lengthy for the present purpose, and the explosion method was therefore examined more closely.

The procedure adopted for the explosion was as follows. The gas sample was passed into the burette of the Bone and Wheeler apparatus, and the volume measured. The burette was kept at constant temperature by circulating, by means of a pump, water from a thermostat through the water jacket. The sample was mixed with 12 times its volume of oxygen and the volume again measured. The mixture was then passed into the explosion pipette and fired. After a few minutes had elapsed, in order to allow the gas to cool, the products of combustion were passed back into the absorption vessel, *via* the burette, where they were washed with 10% sulphuric acid. Before each measurement the gas was similarly washed. The contraction in volume due to the water formed by the combustion was then measured and the carbon dioxide formed was measured by absorption with 20% caustic potash.

In calculating the results of the earlier experiments, it was found that the figure due to the amount of water formed was in every case too high, and that due to the absorption of carbon dioxide always too low. This seemed to indicate that the error might be due to the absorption of some of the dioxide by the 10% sulphuric acid. This error is well known, and a correction is often applied for it in gas analysis. Complete elimination of the washing at this stage was not desirable, as it is necessary to remove any traces of water vapour before measuring the gas volume. It was therefore decided to reduce the time of washing to a few seconds instead of 2 or 3 minutes as in the initial experiments. After this it was found that very accurate results could be obtained, and that explosion as a method of analysis of a mixture of methane and ethane was very satisfactory. It is, however, necessary to observe several precautions. The explosion pipette must be kept absolutely free from grease, which is easily carried over from the taps when the gas is expelled with mercury. The surface of the mercury in the burette should be kept just moist with 10% sulphuric acid, but any excess of acid should be carefully avoided. The washing of the gas with acid before the measurement of the contraction should be limited to 4 or 5 seconds.

In order to check the method, gas mixtures of known composition were prepared with the aid of a small volumenometer from supplies of pure ethane and pure methane. The figures obtained are given below :

	C_2H_6.	CH_4.	C_2H_6.	CH_4.	C_2H_6.	CH_4.	C_2H_6.	CH_4.
As made up, % ...	54·7	45·3	78·9	21·1	38·4	61·6	54·9	45·1
Found, %	54·0	46·0	78·3	22·3	37·2	63·0	54·0	46·4
Check, %	54·1	46·4	78·1	22·4	37·3	62·9	53·5	47·0

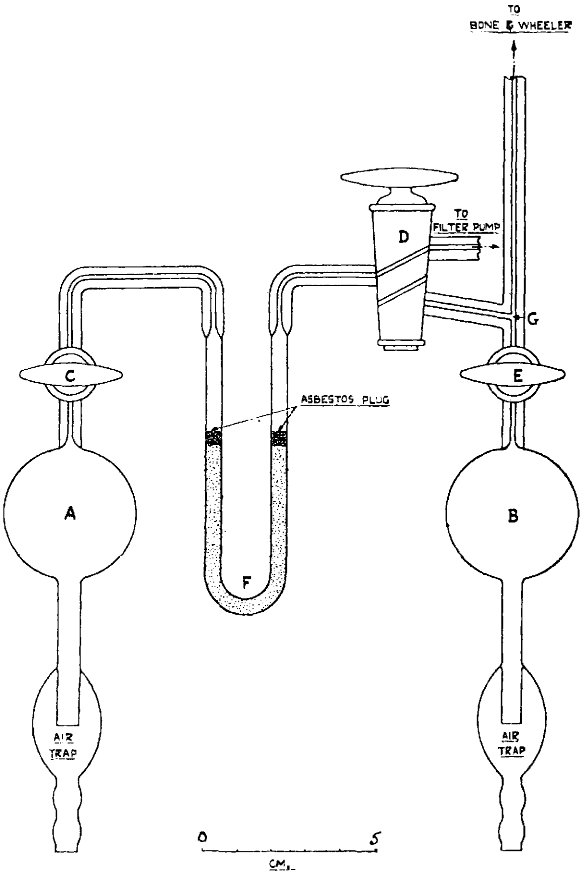
Analysis of Ethane–Methane–Hydrogen Mixtures.—When dealing with mixtures containing hydrogen, the method adopted was to remove the hydrogen first by oxidation over palladium-black and then determine the remaining mixture of ethane and methane by explosion.

Apparatus.—The apparatus consists of a Bone and Wheeler apparatus fitted with an explosion pipette and a tube filled with palladium-black. The rest of the Bone and Wheeler apparatus is of standard pattern in every way except that all the taps are slightly larger than is usual and are hand-made. The explosion pipette is 1″ in diameter and 10″ long. Two platinum contacts are provided for firing at a point 2½″ from the top. The design of the palladium absorption tube is shown in Fig. 1. It consists of a small **U**-tube *F*, which is filled with activated palladium-black held in position with two small plugs of asbestos wool. At either end of the **U**-tube there are two bulbs *A* and *B*, which are fitted with mercury reservoirs. These bulbs are used to force the gas backwards and forwards over the palladium. They can also be used as small Toepler pumps in order to withdraw all the gas from the palladium.

Method of Analysis.—The tube *F* was surrounded with a beaker of boiling water, evacuated with a good filter pump for ½ hour, and then completely evacuated by means of the bulb *B*, which was used as a Toepler pump : 6 or 7 strokes were necessary for this operation. The gas mixture was then introduced into the apparatus, measured, and diluted with 8 times its own volume of oxygen. Both the bulbs *A* and *B* had been previously flooded with mercury, the mercury being brought up to above the tap in the case of *A* and to the mark *G* in the case of *B*. The mixture was then passed from the measuring burette into the bulb *B*, and from there passed four times slowly backwards and forwards over the palladium, which was kept at 80—90° in a beaker of water. The gas was then transferred back to the burette, the bulb *B* being again used as a Toepler pump in order to remove the last traces of gas from the palladium. The contraction due to the combustion of the hydrogen was measured, and the mixture passed over palladium again, in order to ensure that all the hydrogen had been burnt. The percentage of hydrogen in the mixture was then calculated from the contraction and the rest of mixture analysed by explosion.

The temperature at which the palladium is maintained during the combustion is very important. In the first experiments, carried out with pure hydrogen, it was found that a temperature of 70° was high enough for the combustion to be carried to completion.

Fig. 1.



Too high a temperature or too rapid passage of the mixture over the palladium resulted in an explosion. When the mixture is diluted with ethane and methane, a higher temperature can be used without risk of an explosion. If there is less than 20% of hydrogen present the temperature can be raised to 90°, but as the percentage of hydrogen increases the temperature must be lowered to 80° for mixtures containing 80—90% of hydrogen.

This method of analysis was checked in the same way as for the explosion method described above, mixtures of known composition being made up in a volumenometer capable of measuring the volume to 0·01%. The figures obtained are shown below.

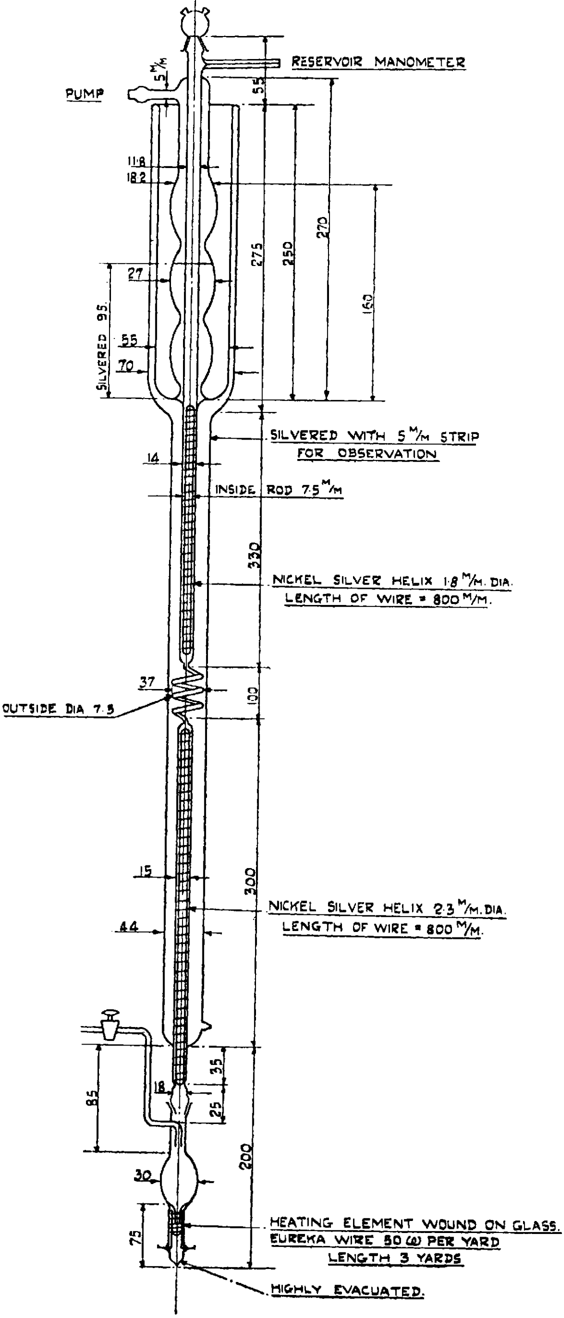
	As made up, %.	Found, %.	Check, %.		As made up, %.	Found, %.	Check, %.
C_2H_6	36·7	36·9	36·6	C_2H_6	34·0	35·6	34·5
CH_4	48·0	47·3	47·8	CH_4	32·4	29·9	31·6
H_2	15·3	15·8	16·2	H_2	33·6	34·8	35·2
C_2H_6	17·0	17·9	17·3	C_2H_6	8·7	8·6	
CH_4	15·8	14·4	14·9	CH_4	47·3	47·3	
H_2	67·3	67·1	66·2	H_2	44·0	44·8	

Preparation of Pure Ethane and Methane.—In order to carry out the work on ethane and methane it was necessary to prepare reasonably large quantities of these gases in the pure state. Originally the preparation was carried out by the method outlined by Verschoyle (*Proc. Roy. Soc.*, 1931, *A*, **130**, 453). The apparatus consisted essentially of two glass bulbs of about 100-c.c. capacity. The gas was condensed in one of these bulbs and then distilled backwards and forwards from one to the other. In each distillation the first and the last portion of the gas were rejected. The degree of purity of the liquid was estimated by means of a glass bell enclosed in one of the bulbs. This bell could be raised magnetically and lowered into the liquid entrapping some of the vapour phase. If the entrapped vapour phase collapsed completely without the application of excess pressure the liquid was regarded as pure. The liquid was finally distilled into a small steel bomb of 50-c.c. capacity, and allowed to expand from there into a steel storage cylinder of 1 litre capacity.

Both ethane and methane were purified in this manner. The methane used initially was a sample of natural gas from Heathfield, Sussex, and contained about 95% of methane. The ethane was prepared from a Grignard compound made from freshly distilled ethyl iodide. This compound was placed in a flask which was connected to the distillation apparatus through a train of wash-bottles containing fuming sulphuric acid, concentrated sulphuric acid, 20% caustic potash, and finally solid caustic potash. The apparatus, washing train, and flask containing the Grignard compound were evacuated and the ethane generated by dropping distilled water on to the ethylmagnesium iodide. The ethane was condensed in the purification apparatus and distilled in the same manner as for the methane. This method was tedious when large quantities of the pure gases were required.

Recently, a more rapid and efficient method of purification has been found by making use of the principle of fractional distillation.

Fig. 2.


RESERVOIR MANOMETER
5 M/M
PUMP
55
11·8
18·2
275
250
270
160
27
SILVERED 95.
55
70
SILVERED WITH 5 M/M STRIP
FOR OBSERVATION
14
INSIDE ROD 7·5 M/M
330
NICKEL SILVER HELIX 1·8 M/M. DIA.
LENGTH OF WIRE = 800 M/M.
37
OUTSIDE DIA 7·5
100
15
300
NICKEL SILVER HELIX 2·3 M/M. DIA.
LENGTH OF WIRE = 800 M/M.
44
35
18
85
25
200
30
75
HEATING ELEMENT WOUND ON GLASS.
EUREKA WIRE 50 ω PER YARD
LENGTH 3 YARDS
HIGHLY EVACUATED.

As has already been stated Davis and Podbielniak (*locc. cit.*) used a vacuum-lagged fractionation column for the analysis of hydrocarbon gas mixtures. Such a column, constructed in this laboratory, can be used both for the purification of hydrocarbon gases and for the analysis of mixtures of hydrocarbons. It consists (see Fig. 2) of a vacuum-lagged column filled with a Dufton spiral of nickel-silver wire wound on a glass rod. The vacuum jacket is extended at the top to form a cup in which liquid air is placed to give the necessary cooling for reflux. Between the liquid-air cup and the reflux chamber of the column there is a buffer which can be filled with hydrogen at any desired pressure up to 1 atm. absolute. The top of the column is furnished with a glass cap through which the leads of a copper constantan thermocouple are sealed with de Khótinsky cement. The " hot " junction of the couple is placed at a point just above the top of the Dufton filling. The boiling reservoir at the bottom of the column carries a small heating coil, which is externally wound on an elongation of the reservoir. The heating coil is wound on a glass former, which slips over this elongation, the coil itself being enclosed in a glass bulb which is highly evacuated, thus guarding against the sudden burning out of the coil. This arrangement also has the advantage that the heating coil can be used when the reservoir is immersed in liquid air without excessive loss of heat to the latter. The reservoir is attached to the bottom of the column by means of a ground-glass joint cemented with de Khótinsky cement. This type of joint has been found to be the only satisfactory one at liquid-air temperatures. The apparatus is made with a series of interchangeable reservoirs of different sizes, which are used according to the amount of gas being dealt with.

It should be noted that if, as a result of a fracture occurring, the liquid hydrocarbons and the liquid air become mixed, there is always the danger of explosion. Some experiments were carried out with a view to find out whether the mixture exploded spontaneously. Although such an explosion never occurred, it was shown that the mixture when fired detonated with considerable violence. 1 C.c. of liquid hydrocarbons (33% each of methane, ethane, and propane) was mixed in a cooled test-tube with 1 c.c. of liquid air. The test-tube was shielded with a length of 2½″-diameter seamless-steel tubing with 3/16″ walls. The tube was open at both ends and stood vertically on the ground. When the two components were mixed, no explosion occurred, but when the mixture was fired, it detonated with such violence that the steel tube was split from end to end, and a hole blown in the ground. A fatal explosion was experienced by the Bureau of Standards with liquid air and light petroleum.

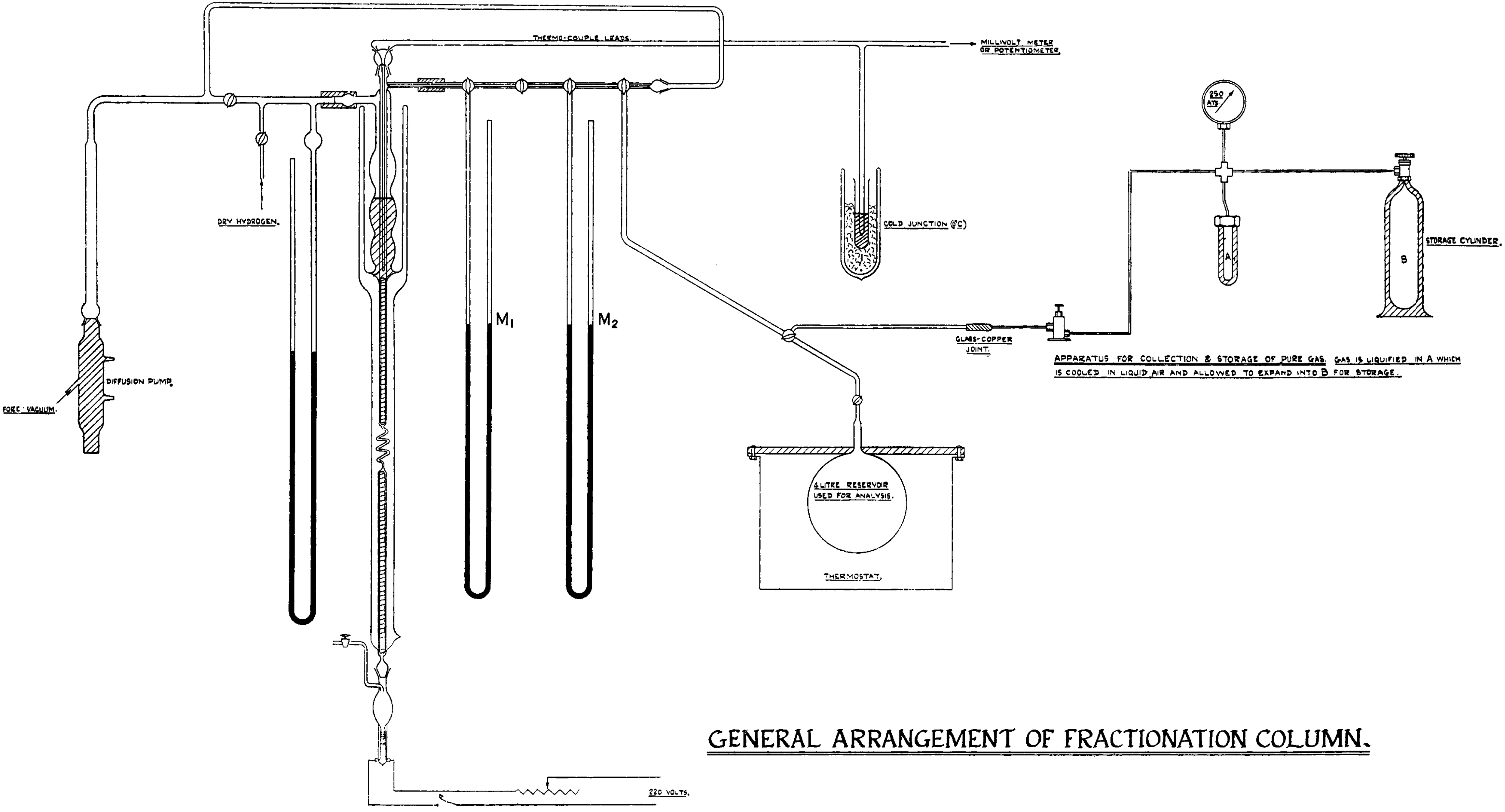

THERMO-COUPLE LEADS.
MILLIVOLT METER OR POTENTIOMETER
DRY HYDROGEN.
COLD JUNCTION (0°C)
250 ATS.
A
B
STORAGE CYLINDER.
M_1
M_2
GLASS-COPPER JOINT.
APPARATUS FOR COLLECTION & STORAGE OF PURE GAS. GAS IS LIQUIFIED IN A WHICH IS COOLED IN LIQUID AIR AND ALLOWED TO EXPAND INTO B FOR STORAGE.
DIFFUSION PUMP.
FORE VACUUM.
4 LITRE RESERVOIR USED FOR ANALYSIS.
THERMOSTAT.
GENERAL ARRANGEMENT OF FRACTIONATION COLUMN.
220 VOLTS.

Fig. 3.

As a result of these experiences it is recommended that liquid nitrogen be used wherever possible, but failing this, the utmost precautions be taken to prevent the accidental mixing of the components which give rise to an extremely dangerous mixture.

Owing to the fact that the column works at a low temperature and that the outside jacket remains at room temperature, it was necessary to provide some type of expansion joint. This was done by making the column in two portions with three turns of a glass helix between them. This helix allows a movement of about 3/16″. An external expansion joint on the outside jacket was tried, but not found to be satisfactory. The whole apparatus has to be carefully annealed at 800°, and a special furnace was designed for this purpose.

The entire apparatus is made of Pyrex glass and the whole of the vacuum jacket and the liquid-air cup are silvered except for two narrow observation slits, which run down the length of the column. The lower half of the hydrogen buffer only is silvered on the inside. The reason for this is that it was not possible to get sufficient control of reflux over the whole range from methane to butane by varying the pressure of hydrogen in the buffer only. By half silvering the surface of the buffer greater cooling can be obtained with a cup full of liquid air. When less cooling is required, liquid air can be withdrawn from the cup until the level stands below that of the silver. At this point, loss of heat from the column by radiation is very small and a smaller heat transfer results.

The fractionation column is connected to the steel bomb used in the previous method of purification. It is also connected to a large glass reservoir, which is used when the apparatus is required for analysis. The whole arrangement is shown in Fig. 3.

Purification by Fractionation.—In this preparation, Heathfield methane was again used. The gas was passed through the usual wash-bottles, and then condensed in the reservoir of the column. Liquid air was poured into the reflux cup, and the hydrogen buffer filled with hydrogen to a pressure of 1 atm. After about 100 c.c. of liquid had been collected in the reservoir, the filling tap was closed and the heating coil switched on. The liquid was allowed to boil, and condense in the reflux chamber, until the whole of the column was wet with the reflux liquid. The rate of boiling was regulated both by means of the heating coil and by raising or lowering the bath of liquid air round the reservoir. The heating coil had a resistance of 150 ohms, and by passing a current of 0·5 amp. at 220 volts and keeping the height of liquid air in the bath such that it surrounded the heating coil but not the reservoir, a steady slow rate of boiling could be maintained. The rate of reflux was adjusted by varying the pressure of hydrogen in the buffer so that the liquid dropped back into the reservoir at the rate of one drop in 5 secs. The rate of boiling was also adjusted so that the pressure on the column was atmospheric.

At this stage the tap between the column and the collecting apparatus was closed and no distillation could take place. The temperature of the liquid condensing at the top of the column was measured by the copper–constantan couple, and when this temperature remained constant, distillation could be commenced. The tap at the top of the column which controls the rate of distillation was then opened slightly, and the gas allowed to distill over slowly. The first portion of the gas to be distilled over was wasted through the pump until the couple registered the correct b. p. In the meantime the steel bomb was cooled in liquid air preparatory to collection of the main volume of the distillate. The gas was then distilled over into the steel bomb at constant temperature and atmospheric pressure. The last portion of the distillate was rejected through the pump. The steel tap was then closed, the liquid air round the steel bomb removed, and the liquid allowed to expand into the storage cylinder.

Ethane was prepared in an exactly similar manner. In this case it was necessary to use a lower pressure of hydrogen in the buffer in order to obtain the same rate of reflux. This ethane was not prepared by a Grignard reaction but by the hydrogenation of ethylene, the excess ethylene being washed out with bromine, followed by the removal of the bromine vapour with caustic soda, and the gas dried over solid caustic soda and condensed.

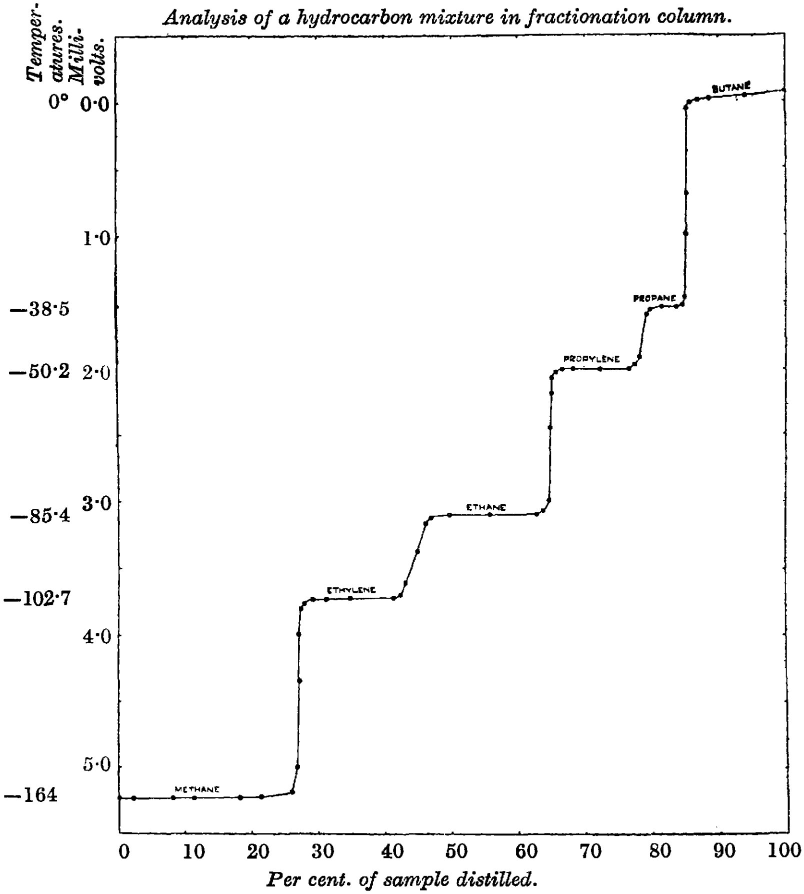
The gases prepared by this method were subjected to only one fractional distillation, after which no impurity could be detected by analysis. A micro-combustion was then carried out on a sample of each gas and the following figures were obtained :

Methane : C/H ratio found, 2·97, 2·96, 3·01 (calc., 2·98).
Ethane : C/H ratio found, 3·95, 3·91, 3·97 (calc., 3·97).

The fractionation column has also been used in this laboratory for the analysis of mixtures of hydrocarbon gases. In this case a smaller reservoir (capable of holding 10—15 c.c. of liquid) was attached to the bottom of the column. The liquefied sample was fractionated in the column at constant pressure, and distilled over into a glass bulb kept at constant temperature in a thermostat, the pressure on the receiver as indicated by M_2 (Fig. 3) being a measure of the volume distilled over. The sample was distilled with constant reflux, controlled as in the previous case by the pressure of hydrogen in the buffer and the level of liquid air in the cup. Frequent simultaneous readings of the pressure on the receiver and the b. p. of the gas were taken and plotted against each other to give a distillation curve, from which the composition of the sample could be deduced. A typical curve is shown in Fig. 4. If the rate of reflux is kept constant and a slow rate of distillation maintained,

FIG. 4.

Analysis of a hydrocarbon mixture in fractionation column.



very sharp cuts can be obtained, and an accuracy of 2% is given by the apparatus.

Preparation of Pure Hydrogen.—The hydrogen used in these experiments was prepared from the commercial gas by passing it at a pressure of 10 atm. over heated copper turnings and then over silica gel cooled in liquid air. The gas so prepared was found to be pure when analysed in the Bone and Wheeler apparatus. It was, however, found that any attempt to raise the pressure at which the preparation was carried out above 10 atm. resulted in an impure product. This may be due to the forcing out of the impurities absorbed by the gel at the lower pressures when the higher pressures are reached. As a result, pure hydrogen could not be stored at a pressure above 10 atm.

Summary.

1. The explosion method is found to be satisfactory for the analysis of a mixture containing two pure hydrocarbons, provided that certain precautions be taken.
2. For mixtures containing hydrogen in addition, the oxidation of this gas with palladium-black, followed by the explosion of the remaining hydrocarbons, affords a rapid and accurate method of analysis.
3. Two methods are given for the purification of ethane and methane, one involving fractional distillation of the liquefied gas. The fractionation column used is described, and its adaptation for the analysis of large samples of complex hydrocarbon gas mixtures is explained.
4. The use of activated silica gel for the purification of hydrogen is described.

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