

THE GAS FROM INDIAN OIL WELLS.

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Since the discovery of helium in the natural gas of the Kansas oil-fields by Cady and McFarland in 1907 (*J. Amer. Chem. Soc.*, 1907, **29**, 1524) the presence of this element has been reported in many natural gases (*cf.* Paneth, Gehlen and Pieters, *Z. Anorg. Chem.*, 1928, **175**, 383) but of these, comparatively few have their origin in oil-fields and those that have been examined in Germany and Japan contain only very small quantities of rare gas (Stockfish, *Z. angew. Chem.*, 1928, **41**, 472).

It was suggested by the Director of the Geological Survey of India that an investigation of the oil-gas obtained in large quantities in Assam and Burma might yield results of interest and consequently the following analyses have been undertaken.

As in many cases the gas is not allowed to escape from the wells but retained under high pressure, the securing of samples is a matter of considerable difficulty since special connections have to be made. The samples from Burma were drawn by the Geological Survey of India with the co-operation of the engineers of the Oil Companies and the samples from Assam were sent by the Burma Oil Company directly. We are greatly indebted to those concerned for the trouble they have taken. Most of the samples were in steel cylinders at pressures up to 300 lbs./sq. in., but three were collected over water in Winchester quart bottles and stored in an inverted position.

The origin of each sample is shown in Table I and also the pressure at which it was collected, this figure corresponding with the pressure of gas at the top of the well.

Samples 1-5 were from Burma and the remainder, with the exception of No. 15, from Assam. They were collected at well-distributed points so as to be as far as possible representative for the whole of each field. The last sample was not an oil-gas but natural gas from a spring in the Bombay presidency which was examined for the sake of comparison.

In addition to the determination of helium it was considered of interest to make a complete analysis of these gases and consequently the quantities of carbon dioxide, carbon monoxide, oxygen, nitrogen, hydrogen, methane, ethane and propane were estimated. As methane was the chief constituent, difficulty was experienced in obtaining

TABLE I.

Sources of Gas Samples.

No.	Pressure lbs./sq. in.	Origin.
1	300	Singu B.B.P.C. No. 70.
2	112	Yenangyaung B.O.C. No. 105.
3	34	Yenangyaung B.O.C. Gathering System F. Station.
4	200	Indaw.
5	3	B.P.C. Well at Payaye.
6	19	Main Line Gas Office.
7	24	Well No. 236.
10	24	No. 4 Collecting Line.
11	29	Well No. 215.
12	..	Well No. 35.
13	..	Well No. 22.
14	..	Masimpur No. 2.
15	..	Gogha, Bombay.

accurate results by absorption methods since it was found that this gas is appreciably absorbed by alkaline pyrogallol, by bromine and by ammoniacal cuprous chloride, while with the higher hydrocarbons the effect is still more marked. Ott (*Montash. Bull. Schweiz. Ver. Gas Wasserfach*, 1925, 6, 18) had already drawn attention to the absorption of methane by the latter reagent and while the experiments were in progress Pieters (*Z. anal. Chem.*, 1932, 89, 24) pointed out that pyrogallol absorbs methane and similar gases if it is allowed to remain in contact with the gas when the colour of its solution has changed from brown to violet. As an example, 0.5 c.c. of gases other than oxygen was absorbed from 100 c.c. by 10 c.c. of pyrogallol solution in 1 minute. In the case of ammoniacal cuprous chloride, 15 c.c. of reagent were found to absorb on the average 0.43 c.c. of hydrogen and 1.33 c.c. of methane at each shaking with about 90 c.c. of gas. Special precautions were therefore necessary in making the following experiments.

EXPERIMENTAL.

In the early experiments irregular and low values were obtained for the quantity of higher hydrocarbons present owing to their absorption by the reagents just mentioned, and it was consequently found essential to submit the gas to a preliminary fractionation, a method employed by Burrell and Siebert (*J. Amer. Chem. Soc.*, 1914, 36, 1537). At the temperature of liquid air, methane is the only hydrocarbon which is evolved from the mixture on pumping and the estimation of oxygen and carbon monoxide can be made with greater accuracy in this fraction than in the original gas.

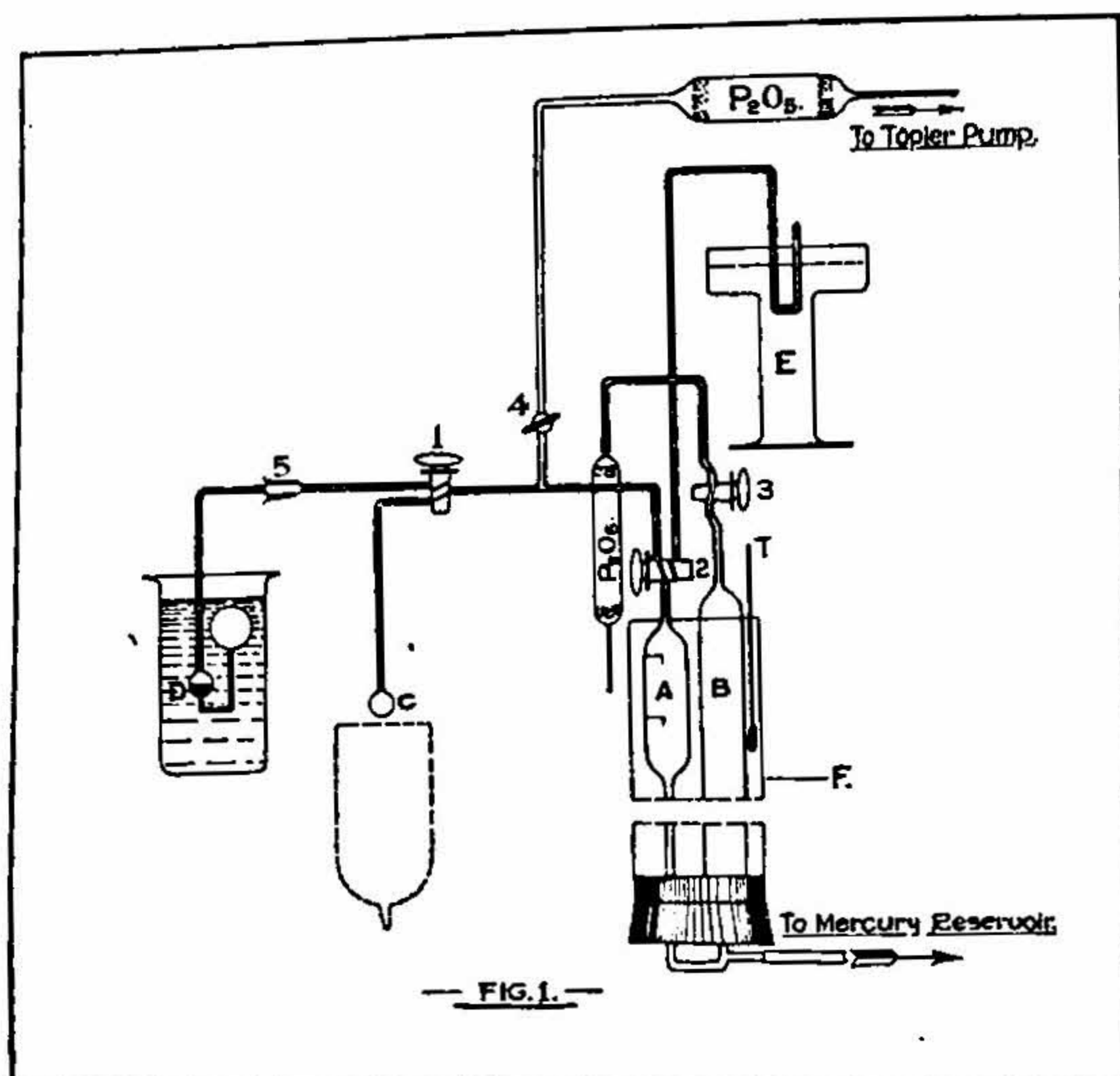
The absorption of methane was confirmed by shaking 8 c.c. of the pure gas with successive quantities of 5 c.c. of alkaline pyrogallol solution for 3 minutes and measuring the reduction in volume in a Bone and Wheeler apparatus. The quantities absorbed were 0.14, 0.15 and 0.18 c.c. which showed that the absorption was of the same order on each occasion. When absorbing oxygen from the fractionated gas, the process was conducted three times and the mean quantity absorbed in the two last operations deducted from the first figure. Thus, in the case of sample No. 3, four pressure readings were 898.6, 882.6, 874.0 and 864.8 mm. the differences 16.0, 8.6 and 9.2 mm. corresponding with the amounts absorbed and thus the partial pressure of oxygen was 16.0–8.9 or 7.1 mm.

A similar procedure was followed with carbon monoxide and in both cases the constant quantity of gas absorbed at each stage was taken to be methane. This method was not one of very high precision, but it was sufficiently accurate for these analyses. A check on the quantity of carbon monoxide was made in the case of sample No. 2 by passing a known volume of the gas through a U-tube at -120° followed by bulbs containing bromine, potassium hydroxide, sulphuric acid and finally iodine pentoxide, and the liberated iodine was collected in 10 per cent. potassium iodide solution and titrated with N/200 thio-sulphate. The amount of carbon monoxide found was 0.36 per cent. whereas the absorption method gave 0.40, a sufficiently good agreement.

The analysis of mixtures of hydrogen and methane with higher hydrocarbons has been discussed by several authors, references to their work being given in a recent paper by MacGillivray (*J. Chem. Soc.*, 1932, 941) which appeared while the present experiments were in progress. Most of these methods require large quantities of gas. Burrell (*Recovery of Gasoline from Natural Gas*, 1925, 80) who has published a large number of analyses of natural gas, in no case records the presence of hydrogen and this is in accordance with our results, only one abnormal sample appearing to contain a trace of this gas. Since the quantity of higher hydrocarbons is also small, solution of methane does not introduce a significant error and in practice it was found that if the gas was cooled to liquid air temperature and the non-condensable portion pumped off, a very sharp separation was obtained. If at the end of the operation the temperature was allowed to rise and the gas was then cooled, condensation was almost instantaneous and no more gas could be removed by pumping.

On replacing the liquid air by a mixture of solid ether and toluene, ethane and propane could be pumped off leaving a residue which was not analysed but designated as 'higher paraffins'. The separation in this case was not quite as sharp as previously but was fairly definite and gave concordant results.

The apparatus used is shown in Fig. 1. It consisted of a constant volume water-jacketted gas burette *A* with two fixed points and a manometer tube *B*. By opening or closing the tap 3 the mercury in this tube could be either exposed to the atmosphere or kept in a vacuum, the latter procedure being adopted when very small volumes of gas had



to be measured. *A* was connected through capillary tubing and suitable taps to a syphon *E* for admitting the gas, a bulb *C* for condensation and a small bulb *D* containing oxidised palladium sponge for absorbing hydrogen.

To make an analysis the whole apparatus was evacuated by means of a Töpler pump and the gas was introduced into *A* at slightly more than atmospheric pressure. The pressure was measured and the gas compressed into the bulb *C* which was cooled in liquid air. The gas was allowed to expand into *A* and again compressed, the operation being repeated two or three times to ensure thorough mixing, after which the non-condensable portion was pumped off, reintroduced into *A* and measured. The liquid air was then replaced by a toluene-ether bath at -130° and the second fraction removed and measured. Finally *C* was allowed to warm to room temperature and the residual gas pumped off, water being removed by a phosphorus pentoxide tube. As the volume of the burette was rather small (9.4 c.c.) two samples of gas were usually taken for each experiment and the fractions mixed.

The first fractions were tested for hydrogen by passing the gas over the oxidised palladium sponge in *D* which was heated to 100°. The reagent was prepared by heating ammonium palladium chloride to 180° in a current of dry hydrogen until no more hydrochloric acid was evolved, cooling and exposing to air. It was found very reactive when treated with pure hydrogen at low pressure, but in only one case was any diminution in pressure observed when the gases under examination were left in contact with it.

The first fractions were treated in succession with alkaline pyrogallol and ammoniacal cuprous chloride in a Bone and Wheeler apparatus, absorption being repeated three times as already explained. This gave the quantity of oxygen and carbon monoxide. The residual gas consisting of methane with about 10 per cent. of nitrogen required careful treatment to ensure complete combustion. About 2.5 times its volume of oxygen was introduced into the eudiometer and the methane admitted while sparks were passing. Carbon monoxide was always present after this operation and consequently the carbon dioxide was removed with potassium hydroxide and the residue again sparked. This resulted in a mixture of carbon dioxide and nitrogen only. The quantity of methane calculated from the carbon dioxide formed was usually lower than that calculated from the contraction, typical results being :—

	CH ₄ from CO ₂	CH ₄ from contraction
No. 5	85.5	86.5
No. 12	81.5	82.7

This discrepancy arises from the solubility of the carbon dioxide in the sulphuric acid solution used for washing (*cf.* MacGillivray, *loc. cit.*) so that the contraction is too large and the CO₂ measured by absorption is too small. In calculating the results the mean value has been adopted.

The second fraction was treated with potassium hydroxide solution to absorb carbon dioxide and then exploded with excess of oxygen. From the amount of carbon dioxide formed and the contraction, the quantities of ethane and propane could be calculated assuming that only these two gases were present.

It is well known that air is very soluble in liquid methane and is difficult to separate by fractionation. Nitrogen also appears to dissolve readily in solid ethane, since, after applying a correction for traces of nitrogen in the oxygen used for exploding, the second fraction always left a residue of about 5 per cent. of its volume. In most cases this amount was negligible when calculated on the total quantity of gas but in one or two samples in which the amount of ethane and propane was large it was appreciable. If these gases retain nitrogen so tenaciously it seems highly probable that methane is also present in the second

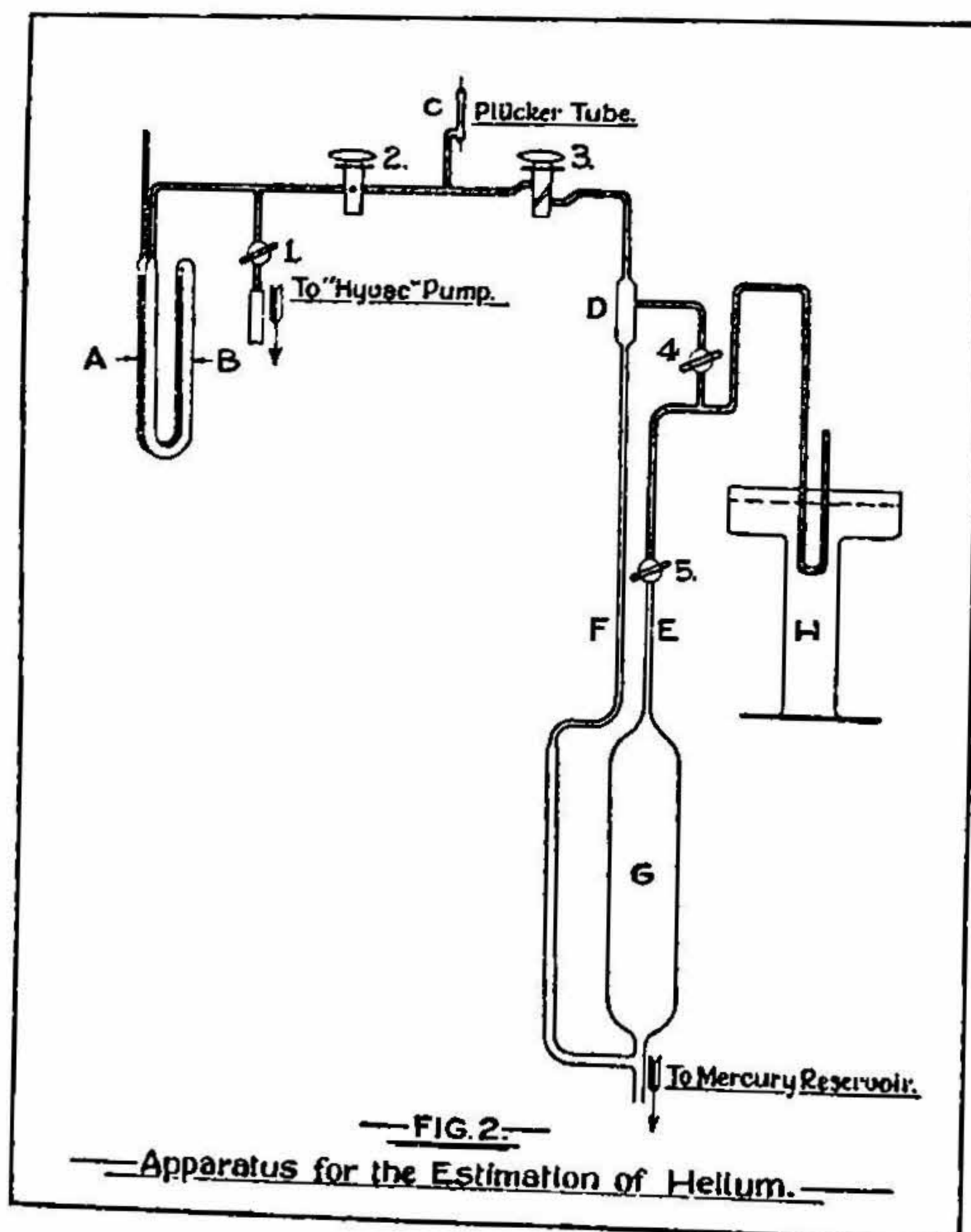
fraction and this would result in high values for ethane and low for propane.

In one case (sample 11) in which nitrogen was present to the extent of 31 per cent. the residue was admitted into a tube containing magnesium heated to 550° and maintained in contact until no further contraction took place. The remaining gas, found by its spectrum to be argon, amounted to 0.6 per cent. of the original.

Tests were made for unsaturated hydrocarbons by taking the portion of the gas which could be pumped off at -130° and treating it with bromine in potassium bromide solution. Absorptions of the order of 1 per cent. were recorded but on adding a fresh quantity of bromine an equal amount was again absorbed showing that it was the saturated hydrocarbons which were dissolved or absorbed and that unsaturated hydrocarbons were absent.

Estimation of Helium.

In order to estimate helium, the gas was allowed to remain in contact with charcoal at liquid air temperature until no further absorption occurred and the helium was removed and measured. The apparatus used is shown in Fig. 2.



A is a U-tube containing 4 g. of coconut charcoal and *B* a plain U-tube for condensing higher hydrocarbons. Before starting an experiment these tubes were heated in a sulphur bath and the whole apparatus exhausted. After cooling *A* and *B* in liquid air, the gas was admitted through the tap 4, *G* being previously filled with mercury. To hasten absorption, the whole of the gas on the right-hand side of the apparatus was displaced by mercury as far as the tap 3, the bore of which was also filled with mercury. Since the remaining dead space was constructed of capillary tubing its volume was very small and absorption was complete in about 5 minutes. By closing the tap 5 and lowering the mercury in *G* below the level of the side tube any residual gas diffused into *G* and after compression into the narrow tube *E* which was calibrated, its pressure could be measured. The volume of *G* was known and hence the quantity of gas was determined. The effective volume of the rest of the apparatus taking into account the low temperature of the U-tubes was about 33 c.c. while that of *G* was 140 c.c. so that the total volume of gas was 1.24 times that measured in *E*. This correction was sufficiently accurate in ordinary cases when the volume of gas was very small, but if more precise values were required, the gas after measurement could be displaced through the tap 5 and the residue allowed to enter *G* and be measured as before. Alternatively *G* could be used as a pump and the gas collected in a tube over the syphon, returned to *E* and measured at one time. Since the capillaries used were fine and the tap 5 was very small, there was little risk of loss of gas by this method.

In order to identify and check the purity of the gas, the syphon was closed by the finger or a rubber cap and the gas passed through taps 5 and 4 into the small spectrum tube *C* made from capillary tubing, the tap 2 being closed. The yellow helium line could usually be seen, but small quantities of impurity from the walls of the apparatus were generally present. These could be removed by cooling the tube leading to the spectrum tube with liquid air when the complete helium spectrum made its appearance. The error in volume caused by this impurity was probably less than the experimental error.

This apparatus was convenient to use and three analyses could be made in one day. 25 c.c. of gas were sufficient for a determination, 0.44 c.mm. giving a pressure of 1 mm. so that 1 part of helium in 100,000 could be readily detected.

RESULTS.

The results found for the different samples are given in Table II which shows the quantities obtained by fractionation and the amounts of the different gases present expressed as percentage on the dry gas. The helium content is in parts per 100,000.

TABLE II.

Sample No.	1	2	3	4	5	6	7	10	11	12*	13	14	15
Volatile at -190°	91.0	89.6	87.7	97.1	96.9	80.2	82.9	73.0	83.4	90.0	84.8	97.8	99.4
Volatile -190° to -130°	7.3	8.1	6.1	2.8	3.1	12.3	10.8	18.0	10.0	9.8	15.2	2.2	0.6
Residue	1.7	2.3	6.2	0.1	0.0	7.5	6.3	9.0	6.6	0.2	0.0	0.0	0.0
Oxygen	0.5	0.8	0.7	0.5	0.4	0.8	1.3	0.5	0.6	0.6	1.3	0.9	1.2
Carbon dioxide	0.3	0.3	0.2	0.5	0.3	0.6	0.4	0.5	0.4	8.4	14.6	1.9	0.6
Carbon monoxide	0.4	0.4	0.4	0.3	0.6	0.4	0.9	0.2	0.6	0.5	0.6	0.4	
Methane	87.0	84.4	69.0	88.2	88.1	75.5	75.7	70.6	51.7	84.5	75.2	80.8	92.2
Ethane	3.8	4.4	2.8	1.7	2.4	7.6	3.0	7.3	3.5	0.6	0.5	0.4	0.0
Propane	3.2	2.9	2.3	0.3	0.1	3.0	6.1	9.5	5.3	0.3			
Higher hydrocarbons	1.7	2.3	6.2	0.1	0.0	7.5	6.3	9.0	6.6	0.2	0.0	0.0	0.0
Nitrogen	3.9	4.5	18.4	8.4	8.1	4.6	6.3	2.4	31.3†	4.8	7.8	15.6	6.0
Helium in 10 ⁵	4	7	0	3	3	1	0	0	3	6	4	7	12

* No. 12 contained 0.1 per cent. of hydrogen.

† Includes 0.6 argon.

The samples from Burma (1-5) with the exception of No. 3 are somewhat similar in composition and contain a high proportion of methane. In Nos. 1 and 2 the excess nitrogen (above the quantity required to form air with the oxygen present) is very small whereas in Nos. 4 and 5 it is 6.4 per cent. The high proportion of nitrogen in sample 3 is abnormal and the higher hydrocarbons are also present in much larger quantity than usual. Of the Assam samples, No. 12, except for its high content of carbon dioxide, resembles the Burmese gases, while No. 11 and in a less degree No. 14 are remarkable for their very high nitrogen content. In No. 13 the amount of carbon dioxide is very large. In Nos. 6, 7, 10 and 11 the ratio of methane to other hydrocarbons is much lower than in the remaining samples. The Bombay gas No. 15 consists of nearly pure methane mixed with air. The amounts of helium have little significance, the proportion of this gas being in most cases of the same order as in air. The results are not in accordance with the suggestion of Cady and McFarland (*loc. cit.*) that the amount of helium varies with the nitrogen-content, there being no correlation between the two quantities. None of the gases contains sufficient helium to render feasible its commercial extraction.

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