that very small proportions of a sufficiently strong base promoted oil formation. With very small quantities of a base and a fixed velocity of gas, the maximum oil yield cannot be expected in view of the insufficiency of time-contact between gas and catalyst. The following experiment, and the results in the next section, give a practical illustration of the efficiency of minute quantities of a strong base.

Experiment 265

In this experiment the usual 300 grams of iron filings were impregnated with 1/20 of the quantity of Rb_2CO_3 previously applied, *i.e.*, with 15 c.c. of N-Rb_2CO_3 solution; the conditions were as in Expt. 263. In 14 hours, 155 c.c. of water containing 10 per cent. of alcohol and 7 c.c. of oil were obtained, or an alcohol-to-oil ratio of 2 : 1. The experiments with ample impregnation had always yielded more oil than alcohol. It must therefore be concluded that the quantity of alkali is of importance in the formation of oil at the expense of alcohol.

4. *Experiments with Hydrogen Carriers other than Iron*

The need of the presence of a metallic hydrogen carrier, such as iron, has been pointed out and will further be discussed in the sections on the mechanism of the reaction. It was of interest to ascertain whether iron, which necessitates a careful purification of the gas from sulphur compounds, might be replaced by other hydrogen carriers less sensitive to hydrogen sulphide, whereby sulphur compounds formed in the contact tube might be continuously reduced by the reacting gases.

Antimony.—After having worked the apparatus for several weeks with an iron-rubidium catalyst for the purpose of obtaining large quantities of oil for chemical examination, the contact tube was emptied, rinsed with water, and charged with a catalyst consisting of pumice impregnated with potassium pyro-antimoniate. This compound was reduced to antimony in the course of the experiment. Antimony was chosen on the supposition that under pressure it would react with hydrogen in the water gas to form some stibine,* which on decomposition and re-formation would act as hydrogen carrier. Expt. 247, performed under the usual conditions, seemed to confirm this supposition. Oil and alcoholic water were produced, though the oil amounted only to 1 c.c. per hour. To make sure that the appearance of the oil was due to the antimony, the contact tube was emptied and rinsed with water, and an experiment was conducted with the uncharged tube. The surprising observation was made that the iron tube, though quite empty, now gave oil and alcohol, approximately in the same quantities as before. The explanation appears to be simple. The tube had been internally tinned, in order to exclude the catalytic influence of

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* The possibility of a synthesis of stibine from hydrogen and antimony is shown by its electrolytic formation on antimony cathodes (Sand, Weeks and Worrell, *Chem. Soc. Trans.*, 1923, **103**, 456).

the iron wall. In the course of the many and prolonged runs, the homogeneity of the tin-coating had suffered, iron became exposed and some rubidium salt was probably too firmly embedded in the rough surface to be washed out completely. The iron wall, impregnated in this way, was deceptive in showing activity of antimony.

The contact tube was therefore submitted to a thorough mechanical cleaning; it was then re-bored and re-tinned. In the freshly-tinned tube antimony catalysts proved quite ineffective for oil and alcohol formation. Iron with antimony (Expt. 259) gave some water and methane, which must be ascribed to the iron. Pumice stone and antimony (Expt. 257) merely yielded traces of water, and were otherwise ineffective.

Iodine.—A catalyst of copper turnings, superficially converted to cuprous iodide, had proved equally ineffective in a previous experiment made, when the tinning of the tube was still in good condition. The idea then was that hydrogen might momentarily form hydriodic acid, which could serve as hydrogen carrier.

In order to avoid an erroneous interpretation of further experiments owing to a damaged tin coating, a copper tube was closely fitted into the iron contact tube. It was specially tested to show that copper is completely inactive as to oil and alcohol formation, even in the presence of an alkali, in agreement with Expt. 107.

Nickel.—In conjunction with alkali, nickel behaved like iron and alkali, but it took longer to become active and required a higher temperature for the best yield, which even then was not so good as that with iron.

The copper sheath of the contact tube was charged with 135 grams of nickel turnings which had been evaporated to dryness with 135 c.c. of *N*-KOH. At 410°, a mean pressure of 100 atm. and a gas velocity of 40 litres per hour, practically no liquid reaction products were obtained in 50 hours. The gas remained almost unchanged, only 1·1 per cent. of methane being formed. The temperature was then raised to 450°, under otherwise unchanged conditions. After 80 hours' working, with a total consumption of 177 atm. of water gas taken from a 40-litre cylinder, which was recharged three times, 48 c.c. of aqueous and 67 c.c. of oily products were obtained. Table LXXIV gives the composition of the initial and final gases.

TABLE LXXIV

	CO_2.	C_nH_m.	O_2.	CO.	H_2.	CH_4.	N_2.
Initial gas . . .	1·2	0·0	1·7	43·0	43·7	0·0	10·4
Final gas . . .	13·0	0·0	0·0	33·5	36·9	4·2	12·4

At the end of the experiment the catalyst was found strongly attacked and disintegrated, but there was no deposition of carbon.

Table LXXV shows the results of the examination of the products of this experiment compared with an experiment made with iron under the same conditions, but at a lower temperature (410°).

TABLE LXXV

Expt. No.	Catalyst.	Alcohol per hour.	Oil per hour	Boiling range of oil.					Ultimate composition of oil fraction 80–200°.		
				Drop. °C.	80°.	100°	150°.	200°.	% C.	% H.	% O.
402	Ni	0·1	0·8	74	2	40·5	80·5	90·5	61·10	12·08	26·82
386	Fe	0·1	1·24	72	12·5	34·5	62·5	80·5	67·02	11·25	21·73

The oils obtained with nickel as catalyst contained more low-boiling constituents, particularly near 140°, than those obtained with iron, and there were considerable differences in the ultimate composition.

Influence of the Composition of Water Gas *

At this point it seems useful to discuss the influence of the composition of water gas. Nearly all experiments were conducted with a water gas in which the proportion of hydrogen was considerably higher than, and sometimes twice as high as that of carbon monoxide. This was the case whenever the water gas had been produced at a comparatively low temperature and therefore contained 10 per cent. of carbon dioxide or more. A relative diminution of the oily reaction product was never observed. After the catalyst had developed its full activity, one part of oil was produced for one or two parts of alcoholic liquor; in the previous stages the oil-water ratio was smaller. Whilst carbon dioxide had been removed in the early experiments with water gas, it was later left in the gas, without detrimental results. On the contrary, the presence of carbon dioxide as well as an excess of hydrogen over carbon monoxide seemed to exert a favourable influence in keeping down the decomposition of carbon monoxide.

In order to test the influence of gas composition upon the nature of the reaction products, three experiments were made with gases in which the carbon monoxide–hydrogen ratio varied as 1 : 2, 1 : 1, 2 : 1. Considerable differences in yield and in the nature of the product were observed, both as regards the quantities of aqueous and oily products and their proportions. The oils showed particularly striking differences in their ultimate analyses and boiling ranges.

The catalyst used consisted of 135 grams of coarse iron turnings, impregnated with 135 c.c. of *N*-KOH. The temperature was 410° in all cases. The 40-litre cylinder containing the gas mixture was connected with the contact tube at

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* Unpublished research by Fischer, Tropsch and Zerbe.

full pressure, and the pressure was allowed to drop gradually. The rate of gas discharge from the apparatus was 40 litres per hour. In Expt. 383, made with gas rich in carbon monoxide ($2CO : 1H_2$), a considerable quantity of carbon was found deposited on the catalyst after 27 hours' working; the catalyst was renewed, and the experiment continued for another 30 hours with the same gas. After that time carbon deposition was considerable, and the catalyst was found disintegrated. A fresh catalyst was taken for Expt. 386 made with ordinary water gas. In this gas the turnings were little attacked and no carbon was deposited. The same catalyst was therefore used for Expt. 391, which likewise did not produce carbon deposition.

Table LXXVI

Expt. No.	Gas.	Gas composition.							Duration of Expt.	Gas used.	Products formed.	
		CO_2. %.	C_nH_m. %.	O_2. %.	CO. %.	H_2. %.	CH_4. %.	N_2. %.		Atm.	aqueous c.c.	oily c.c.
391	Initial	1·8	0·0	0·6	30·7	62·0	0·3	4·6	74	112	63·8	66·4
	Final	10·7	0·0	0·0	22·1	58·9	3·1	5·2				
386	Initial	1·7	0·0	0·8	44·3	47·0	0·4	5·8	55	72	40·8	68·8
	Final	7·4	0·0	0·0	38·7	43·4	2·9	7·6				
383	Initial	7·4	0·0	0·6	55·7	29·9	0·0	6·4	69	95	15·8	122·1
	Final	28·6	1·3	0·0	41·9	16·8	2·5	8·9				

Table LXXVI summarises the composition of initial and final gases, duration of experiment, gas used in atmospheres and quantities of reaction products. The analyses indicate that the conversion was not considerable, owing to the comparatively small active surface of the catalyst, which consisted of coarse iron turnings. The reaction tended decidedly to the formation of alcohol and oil, and only small quantities of methane were formed.

Table LXXVII

Expt. No.	Pressure drop of gas cylinders atmos./hr.	Aqueous products c.c./atmos. total gas.	Oily products c.c./atmos. total gas.	Oily products c.c./atmos. CO.	Oily products c.c./hour.	Mean ratio aqueous : oily products.
391	1·5	0·57	0·57	1·92	1·29	1 : 1·0
386	1·3	0·57	0·96	2·16	1·24	1 : 1·7
383	1·4	0·17	1·28	2·30	2·47	1 : 7·7

As shown in Table LXXVII, the pressure drop in the steel cylinder was in all experiments approximately equal. The yield of reaction products per atmosphere of total gas varied very considerably. The oil yield was greatest with gas rich in carbon monoxide. The yield per hour was also correspondingly greater with gas richer in carbon monoxide than with gas poorer in CO. These differences become less marked when the yield is calculated per atmosphere of carbon monoxide. The water–oil ratio was 1 : 7·7 with gas rich in CO, rising to 1 : 1 with gas rich in hydrogen. The formation of small quantities of water, when using gas rich in CO, is easily explained. The water formed in the reaction is, in the presence of a large excess of CO, converted into the water gas equilibrium, as shown by the high percentage of carbon dioxide in the spent gas. With water gas rich in hydrogen, this conversion takes place to a much smaller extent and larger amounts of water are formed. In carrying out the process it will be simpler to remove the oxygen of the carbon monoxide in the form of water, which can be easily condensed, than to scrub out carbon dioxide.

TABLE LXXVIII

Expt. No.	Boiling range.						Spec. grav. of fractions.			Ultimate composition of fraction 80–200°.		
	Drop ° C.	80°.	100°.	150°.	200°.	250°.	below 80°.	80–200°.	>200°.	% C.	% H.	% O.
391	73	9	38	70	86·5	93·5	0·8093	0·8546	0·9647	64·78	11·05	24·17
386	72	12·5	34·5	62·5	80·5	92·5	0·7895	0·8440	0·9636	67·02	11·25	21·73
383	65	8	27	53	70	87	0·7887	0·8419	0·9588	71·10	10·73	18·17

For the examination of the products, the oil was separated from the aqueous layer, and after passing through a dry filter was submitted to fractionation in an ordinary distilling flask. The figures of Table LXXVIII were obtained with 50 c.c of oil in each case. The oil from water gas rich in CO had the highest boiling range. The oil from gas rich in hydrogen boiled much lower, whilst that from ordinary water gas was midway between the two. The differences in boiling range are considerable. In the first case, 70 per cent. distil below 200°; in the second case, of gas rich in hydrogen, 86·5 per cent. The ultimate analyses of the fractions 80° to 200° reveal an appreciable rise in the carbon percentage with increasing percentage of the initial gas.

The specific gravity of the oil fractions was highest with the products resulting from gas rich in hydrogen.

The comparative examination of oils from water gas of different carbon monoxide percentages indicates the decided advantage of starting with a gas rich in hydrogen, for carrying out the process without deposition of carbon and for obtaining low boiling products. Further, to secure a high rate of conversion, and when liquid products are desired, an excess of hydrogen over carbon monoxide is indispensable, and oxygen is to be removed in the form of water and not of carbon dioxide.

6. *Influence of Impurities in Water Gas*

The sulphur compounds in water gas consist of hydrogen sulphide, carbon oxysulphide and carbon disulphide. The elimination of the hydrogen sulphide can be effected without difficulty by means of the ordinary gas purifying material. A preliminary treatment with slaked lime is not advisable, as the lime would also absorb carbon dioxide, which should be avoided. It is claimed to be possible to remove all sulphur compounds from the gas by passing it mixed with oxygen through activated carbon, which oxidises hydrogen sulphide to sulphur and retains the latter. The removal of carbon oxysulphide and carbon disulphide is more difficult. Whether thiophene is present in water gas is uncertain. Water gas purified with iron oxide does not blacken lead paper, but still contains other sulphur compounds easily recognised by passing the purified gas through a red-hot iron tube. Owing partly to the hydrolysing effect of water vapour in the gas, and partly to reduction by the hydrogen, hydrogen sulphide is again formed from these compounds and can, after cooling, be removed by means of iron oxide. After repeated heating and purifying, the bulk of the sulphur compounds can be transformed into hydrogen sulphide, and be removed as such.[180] That the removal of the sulphur from water gas cannot be carried out in a single operation is probably due to the existence, say, at 900°, of an equilibrium between carbon dioxide, hydrogen sulphide, carbon disulphide and water vapour, when most of the sulphur is present as hydrogen sulphide, but a certain amount of carbon disulphide persists. The removal of the hydrogen sulphide from the cooled gas leaves a little carbon disulphide in the gas. On reheating the gas, possibly after moistening it, the bulk of carbon disulphide is converted into hydrogen sulphide and so becomes removable. The last traces of sulphur and other impurities can be eliminated if needs be by preheating the gas with a contact material under pressure.

7. *Influence of Temperature, Pressure and Gas Velocity*

By varying the temperature, leaving other conditions constant, it was ascertained that below 380° the reaction proceeds at a very slow rate. At temperatures above 450°, the tendency to deposit carbon grows. Between these limits the reaction velocity increases with rising temperature until that maximum of oil is obtained which is conditioned by its equilibrium with the other constituents in the gas. If the temperature is lower, more alcohol and less oil is produced; if higher, more oil will be found, whilst the alcohol in the aqueous liquid is diminished. Under our conditions of working, the best results were realised at 410°. This only holds good in cases where the gas velocity is adjusted so as to leave sufficient time for the establishment of equilibrium conditions even at the lowest temperature.

As regards pressure, the ratio of oil produced to the gas discharged is proportional to it. A higher pressure accelerates by mass action the establishment of equilibrium conditions in the contact tube, and shifts the equilibrium towards the formation of the larger oil molecules. It makes their production at 410° possible to a greater extent than would a lower pressure, which would favour a tendency to decomposition of these molecules. At the maximum pressure of 150 atm. and a temperature of 410°, the formation of large molecules seems to reach a limit, for the oils obtained were almost completely volatile below 200°. It is not unlikely that at pressures of 1000 atm. and higher, the building up of large molecules might be pushed so far that solid waxes would be obtained instead of oils. It is well known that the larger the molecules of aliphatic compounds, the lower is the temperature of their thermal decomposition; the pressure must therefore be so much higher to render their formation possible. Indications of the formation of small quantities of wax-like compounds were observed (Expt. 120) when the high-boiling portions were diluted with acetone and strongly cooled, a white substance of paraffin character separating.

Thus, improved results are secured by increasing the pressure; the oil yield decreases with lower pressure, but no sharp boundary line can be drawn. Below 50 atm. the oil formation vanishes, though alcoholic liquor is still formed. Near atmospheric pressure alcohol also disappears and only methane appears as some experiments with water gas and an alkaline iron catalyst have shown.

The influence of the gas velocity is such that the maximum of oil formation is obtained at a low rate. As the velocity is raised, the oil formation decreases and more alcohol appears by comparison with the oil, as proved by the tests made with short catalyst columns (p. 223).

To sum up the influence of the three factors, pressure, temperature and velocity of gas, the most favourable temperature is about 410°, at a pressure of 150 atm.; the pressure should be as high as possible; the gas velocity should, when oil production is aimed at, be lowered until the best oil yield is reached. It is obvious that the treated gas after being freed of the liquid products may be pumped back into the cycle, over and over again,* until it is practically spent, when its composition can be corrected by adding either hydrogen or carbon monoxide. Alternatively, it may, without the aid of a pump, be passed under its own pressure over a fresh catalyst until it is spent. Experiments with a continuous circulation apparatus are described in the next section.

To discuss all factors which were found to affect the yields and the safety

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* Carbon dioxide might be continually removed and olefines extracted with concentrated H_2SO_4. The oil formed has the general formula C_nH_{2n}.

of working, in the course of several years of investigations, is beyond the scope of this book, which is intended merely to outline the essential conditions for the production of oil from water gas.

8. *Determination of Yields in the Circulation Apparatus*

In the preceding experiments water gas was only once passed through the contact tube and thus badly utilised, since only a certain quantity of oil and alcohol could be formed in equilibrium with unchanged water gas, carbon dioxide, steam, and methane. It was to be expected that the gas might be re-used after the removal of the liquid reaction products, oil, alcohol and water. For this purpose, 6 cb.m. of the discharged gas were collected and compressed again to 150 atm. in a cylinder of 40-litre capacity. This gas was then fed into the contact tube under the usual conditions and yielded some oil, alcohol and water, but, in keeping with the changed composition, less than the original water gas.

Description of the Apparatus for Continuous Circulation.—In order to arrive at some estimate of possible yields, the apparatus illustrated in Fig. 71 was constructed.

The contact tube of the apparatus consists of a Mannesmann tube, 110 mm. external diameter and 10 mm. wall thickness, closed by a cap at the lower end. The compressed gas enters through the cap and rises through an annular space, of 17 mm. clearance, between the outer steel tube and a copper tube reaching nearly to the top. The upper portion of the copper tube is charged with the catalyst, resting on a perforated disc. The upper end of the steel tube is closed and drilled to admit a pocket for the thermo-couple with its junction close to the catalyst.

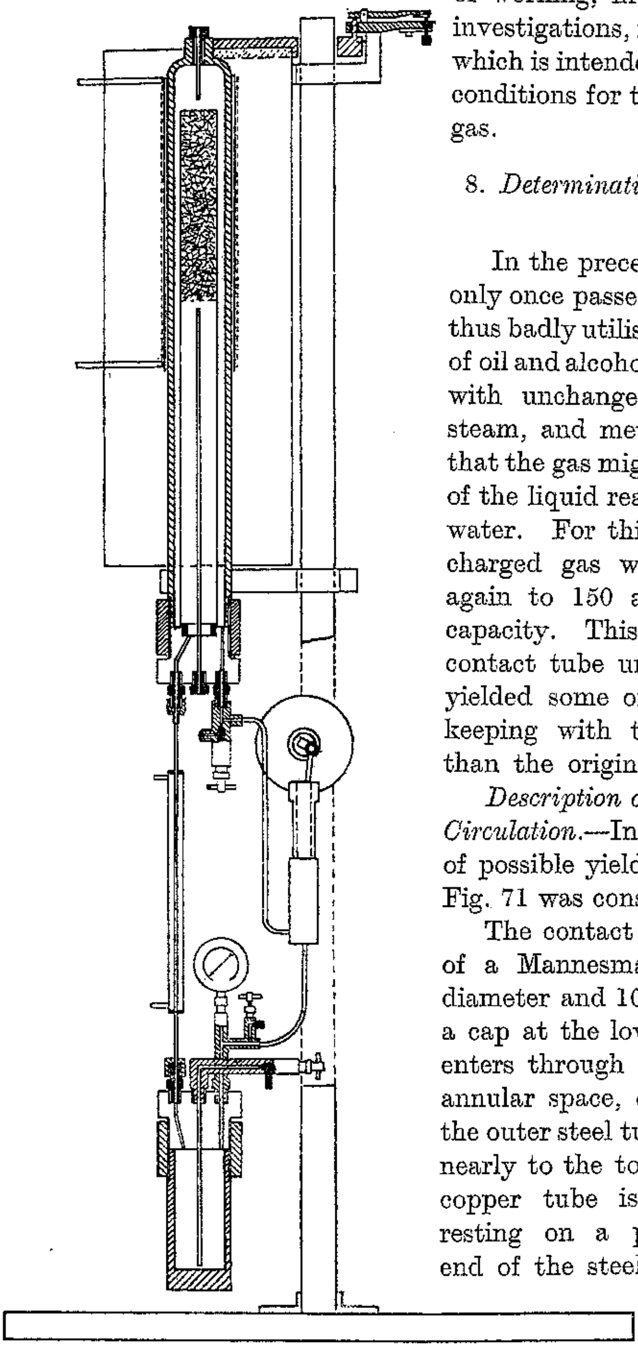

FIG. 71.

After rising, the gas flows down the copper tube, leaves through a bore in the cap and flows through a high-pressure condenser into the receiver, where the liquid products are deposited. From the receiver the gas is withdrawn by the circulation pump and returned to the contact tube.

Only the upper portion of the steel tube is electrically heated; the lower half together with the copper tube serves as heat exchanger. The rising gas is preheated to the reaction temperature in the annular space before it reaches the catalyst on its downward path. After leaving the catalyst, it heats the lower part of the tube and the ascending gas outside it. An efficient temperature equalisation and control was thereby secured. The catalyst consisted of fairly coarse iron turnings, about 1 sq. mm. cross-section, impregnated with potassium carbonate and loosely packed in the copper tube to admit of a rapid passage of gas. The circulation pump was mostly set for moving 150 c.c. of compressed gas per minute. Without circulation the gas was clear of the catalyst after 20 minutes; with the aid of the pump it could be returned five times per hour. In addition, it was possible to keep one charge of the contact tube in circulation by itself. The steel vessel had 3 litres free space; the receiver could accommodate 1 litre of liquid. The pressure fluctuations of the alternating currents used for heating made an automatic temperature control necessary. This was simply effected by allowing the expansion of the steel tube to open or close, through lever mechanism, a low-tension circuit, which actuated a Heraeus mercury interruptor, which in its turn controlled the heating current. For this purpose the lower end of the steel tube was firmly clamped in a standard; a clip round the upper end of the tube was free to move up and down on the standard. By this very crude method, the temperature was easily kept constant within 5°, though fluctuations in the current supply were considerable. The steel tube was wound with nichrome wire, which could easily be detached, and required 14 amperes for heating. It was lagged with diatomite bricks 5 cm. thick.

Experiment 316

The catalyst for this apparatus was prepared by evaporating 740 grams of coarse iron turnings with 740 c.c. of *N*-KOH, and calcining in an iron crucible. The catalyst was charged into the upper half of the copper tube. The temperature was 410°; the pressure 102 atm. The gas leaving the apparatus * had the composition :—

CO_2	22·8 per cent.	H_2	55·0 per cent.
C_nH_m	1·0 ,,	CH_4	0·8 ,,
O_2	0·4 ,,	N_2	6·6 ,,
CO	19·3 ,,		

The apparatus having been heated to constant temperature, the connection with the steel cylinder and the outlet valve was closed. The pump was then

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* The composition of the gas from the cylinder is here immaterial.

started, and the gas circulated through the catalyst.[*] The pressure fell in 4 hours from 102 to 42 atm., at a rate shown in Table LXXIX.

TABLE LXXIX

Time minutes.	Temperature.	Pressure Atm.
start.	410°	102
70	410	75
100	410	68
160	410	56
180	410	52
240	410	42

As the pressure decreased, the formation of alcohol and oil diminished, but it continued right to the end. The final gas had the composition :—

CO_2 . . .	32·1 per cent.	H_2 . . .	10·3 per cent.
C_nH_m . .	1·1 ,,	CH_4 . .	19·8 ,,
O_2 . . .	0·5 ,,	N_2 . .	11·8 ,,
CO . . .	19·4 ,,		

Thermal Balance.—In order to ascertain the portion of heat units supplied with the gas, those present at the end of the experiment in the form of oil and alcohol, and those lost by exothermal reactions, the following calculation was made : Initial gas pressure 102 atm. Volume of apparatus [†] 2·8 litres = 286 litres at atmospheric pressure, or 268 litres at N.T.P. Heating value of the gas (calc.) 2480 cals. per cb.m. Heat used therefore = 665 cals.

Total calorific value of 20 c.c. of oil and 9·3 c.c. of alcohol = 192 cals. (Total yield : 20 c.c. of oil and 62 c.c. of liquor containing 15 per cent. of alcohol.)

Final pressure 42 atm. Volume of apparatus 2·8 litres = 118 litres at atmospheric pressure, or 111 litres at N.T.P. Calorific value (calc.) 3900 cals. per cb.m. Heat found therefore = 433 cals.

The output represents 192 + 433 = 625 cals., about 40 cals. less than the input, a loss of 6 per cent.[‡] The oil and alcohol contained $\frac{192 \times 100}{665} = 29$ per cent. Expt. 316 demonstrates that it is possible to obtain at least 29 per cent. of the calorific value of the water gas in the form of oil and alcohol. Considering that alcohol and oil production was still proceeding at the end

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[*] The condensible products, oil, alcohol and water, were collected in the receiver.

[†] The volume was determined with the contact tube hot, by letting off gas, until the pressure had been reduced by 10 atm., and measuring its volume.

[‡] A loss of this kind occurs, for instance, in the formation of methane according to : $CO + 3H_2 = CH_4 + H_2O + 49{,}000$ cals. The heat value of 4 cb.m. of $(CO + 3H_2)$ is about 12,000 cals.; that of the resulting CH_4, only 9500 cals.

of the experiment, though the pressure had dropped to 42 atm., it may be safely concluded that even higher calorific yields in the form of liquid fuels are possible. The results would certainly have been better by working at constant, instead of diminishing, pressure.

Experiments in this direction will be made with eight contact tubes connected in series; condensers for the reaction product will be inserted after every two tubes.

On calculating the results of Expt. 316 for the quantity of water gas, disregarding difference between calorific values of initial and final gas, it is found that 268 litres of water gas gave about 30 c.c. of liquid fuel; that would be approximately 112 c.c. = 100 grams per cb.m. From 10 cb.m., or 7 kg., of water gas about 1 kg. of liquid fuel is even now obtainable with a thermal efficiency of 29 per cent. On the basis of the latter, one may, under favourable conditions, reckon upon 3 kg. of liquid fuel from 10 cb.m. of water gas, provided no combustible gas is left. The spent gas from Expt. 316 had a calorific value of 3900 cals. in spite of the high carbon dioxide content of 32·1 per cent. If carbon dioxide were washed out, a gas of about 6000 cals. would remain, with a consequent rise in nitrogen from 12 per cent. to 18 per cent.

(*k*) CARBON DIOXIDE AND HYDROGEN IN THE CIRCULATION APPARATUS

Experiment 329

It has been shown (Expt. 144, p. 221) that from carbon dioxide and hydrogen in the ratio 1 : 2 no oil but much water and a little alcohol were obtained. It was also observed that the spent gas contained 8·1 per cent. carbon monoxide formed by a reduction of carbon dioxide, though steam was present. It was then suggested that the spent gas would yield oil on passing it, after cooling, a second time through the catalyst. This was tested in the circulation apparatus, but the excess of hydrogen was made larger than in Expt. 144, so as to reduce the carbon dioxide to the CH_2 stage.

The apparatus was charged from a gas cylinder at a pressure of 135 atm., and the connection with the cylinder was closed. The composition of the gas was :—

CO_2 . . .	24·0 per cent.	H_2 . . .	73·6 per cent.
C_nH_m . . .	0·0 ,,	CH_4 . . .	0·0 ,,
O_2 . . .	0·1 ,,	N_2 . . .	2·3 ,,
CO . . .	0·0 ,,		

The catalyst consisted of 470 grams of coarse iron turnings impregnated with *N*-KOH, as in Expt. 316. The pressure rose while the apparatus was heated to 410°; circulation was then started at a rate at which the gas charge passed 5 times per hour through the catalyst. The pressure and composition of the gas and the yield of oil and water at progressive stages are specified in Table LXXX; the water contained 5 per cent. of alcohol.

This table shows that the brisk water formation diminishes gradually; methane appeared almost suddenly after 5 hours, and heavy hydrocarbons 1 hour later. The first oil was observed simultaneously with methane. It is interesting to note that oil formation had not ceased when the pressure had gone down to 7 atm., at which the experiment was stopped. The expectation that oil would be obtained from carbon dioxide and water is confirmed by the experiment. Repeated passage * through the catalyst and condenser was required before the composition of the gas mixture had become amenable to oil formation, which seems to be conditioned by the presence of carbon monoxide. This appeared soon after starting, and temporarily rose to 19·3 per cent. Certain irregularities in the table disappear if the percentages are multiplied by the total pressures and divided by 100. The partial gas pressures of the graphs of Fig. 72 were obtained in this way. It is then seen that the pressures of hydrogen and carbon dioxide were continuously falling and do not show maxima and minima as in Table LXXX. The rise and fall of the carbon monoxide, methane and unsaturated hydrocarbons are well brought out. "Methane" probably includes some of its homologues; its decrease may be due to the formation of oil and alcohol, or to its conversion into homologues with loss of hydrogen.

TABLE LXXX

Time. minutes.	Temp.	Pressure Atm.	CO_2 %.	C_nH_m. %.	CO. %.	H_2. %.	CH_4. %.	N_2. %.	Water c.c.	Oil c.c.
start	410°	115	24·0	0·0	0·0	73·6	0·0	2·3		—
30	410	105	14·4	0·0	11·4	69·6	0·0	4·6	8·5	—
100	410	89	8·7	0·0	19·3	66·6	0·0	5·2	27	—
215	410	28	13·4	0·0	11·1	51·7	15·7	7·9	49	1
275	410	14	11·3	11·7	11·9	33·7	25·3	11·9	13·5	4
365	410	7	8·5	15·2	6·3	20·7	35·4	13·9	7·5	2·5

Somewhat surprising is the occurrence of carbon monoxide when carbon dioxide is on the decrease and much water is formed. One would expect that carbon monoxide at 410° would react with steam to give carbon dioxide and hydrogen. Oil formation at such low pressures as 14 and 7 atm. is another new fact not observed in the previous experiments, which indicates that certain gas mixtures yield synthol at very low pressures. Heavy hydrocarbons (absorbed by fuming H_2SO_4) appear together with "methane." They amount to not less than 15 per cent. of the final gas, a higher percentage than that of carbon monoxide and carbon dioxide in the same gas sample.

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* The gas was pumped 5 times per hour over the catalyst.

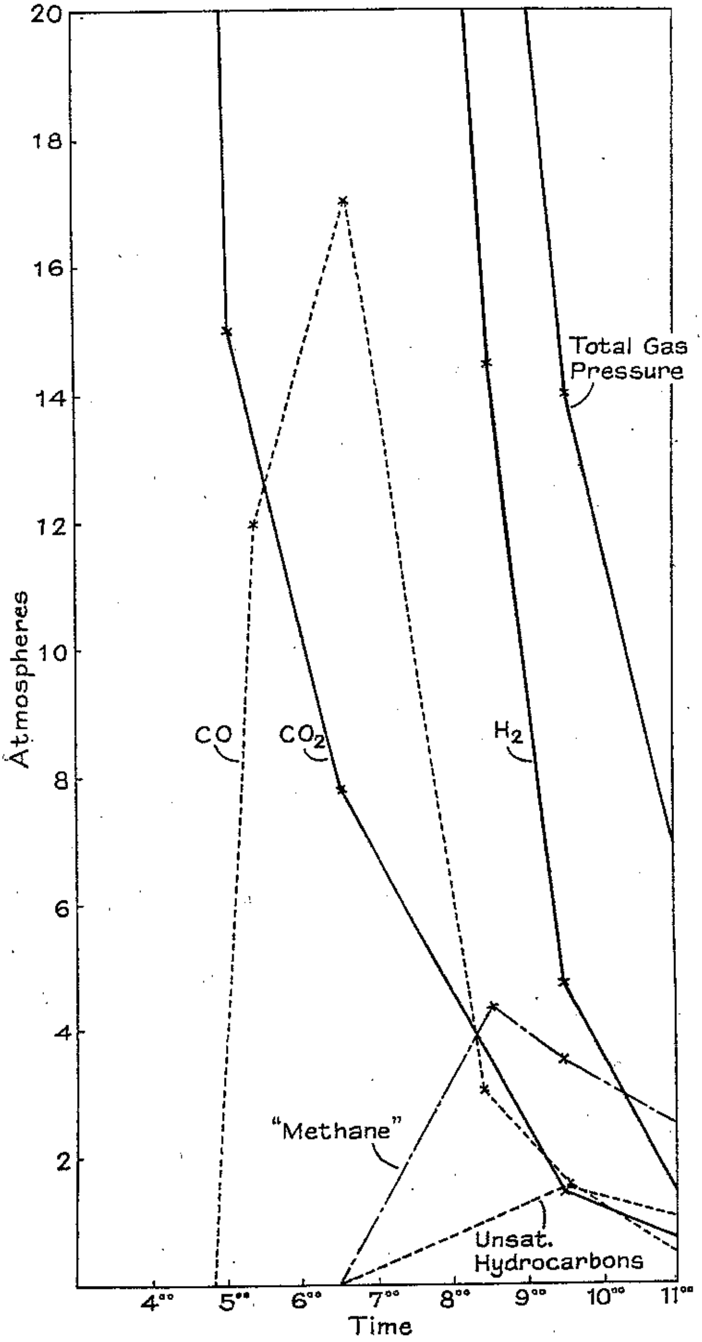
Atmospheres
20
18
16
14
12
10
8
6
4
2
Time
4⁰⁰
5⁰⁰
6⁰⁰
7⁰⁰
8⁰⁰
9⁰⁰
10⁰⁰
11⁰⁰
Total Gas Pressure
CO
CO_2
H_2
"Methane"
Unsat. Hydrocarbons

FIG. 72.

Probably the primarily-formed alcohols, found under other conditions in the water, were in this case converted with loss of water into olefines. If, for example, ethyl and propyl alcohol were converted into ethylene and propylene, the liquor would become poorer in alcohols and the gas richer in olefines. It was further observed that the high olefine content of the gas still in the apparatus decreased during cooling overnight. The olefines in the contact tube were probably converted into methane hydrocarbons by hydrogen, a reaction favoured by lower temperatures. It was indeed found that the decrease in olefines was accompanied by an increase in paraffin hydrocarbons.

The occurrence of gaseous olefines, due to the dehydration of water-soluble alcohols, has a parallel in the composition of the oil. Whilst in all previous experiments with a small excess of hydrogen the oil obtained was almost completely soluble in concentrated sulphuric acid, the oil from this experiment contained 40 per cent. of hydrocarbons of pronounced petroleum smell, insoluble in concentrated sulphuric acid. The formation of these hydrocarbons, analogous to the synthin experiments to be described later, indicates that alcohols are converted by longer treatment into hydrocarbons with the liberation of water. According to our more recent observations the formation of olefines is favoured by the presence of carbon monoxide, which reacts with liberated water yielding $CO_2 + H_2$, stimulating progressive dehydration.

(*l*) CARBON DIOXIDE AND METHANE IN THE CIRCULATION APPARATUS

Experiment 343

A mixture of 1 part of CO_2 and 3 parts of CH_4 was kept circulated over the catalyst of Expt. 229 and under otherwise equal conditions. Only traces of water, and neither alcohol nor oil, were produced. As the failure of any reaction between carbon dioxide and methane might have been due to the exhaustion of the catalyst, its activity was checked by withdrawing the gas mixture, and charging the apparatus with water gas at 120 atm. (Expt. 345). At once, ample quantities of water, alcohol and oil were obtained, proving the catalyst to be undoubtedly still in good condition.

Experiment 347

The water gas was blown off and the apparatus recharged with a 1 : 3 mixture of carbon dioxide and methane at a total gas pressure of 88 atm. After 2½ hours' working, the pressure was still exactly 88 atm.; neither water nor oil had been formed, proving definitely that under the experimental conditions employed carbon dioxide and methane do not react.