calcium formate had a deleterious influence on the yield of methyl alcohol. With an addition of aluminium oxide to the calcium formate, the formation of oil was diminished. Barium formate[176] gave even better oil yields than calcium formate, about 70 per cent. of the theoretical amount of methyl alcohol being obtained. Lithium formate proved decidedly less suitable than the calcium or barium salts.

A review of these experiments with respect to the conversion of carbon monoxide into methyl alcohol and oils, shows that this conversion can be effected via calcium or barium formate with a yield of from 60 to 70 per cent. of the theory, that of carbon monoxide into formate being quantitative. If it should really prove necessary first to prepare, and then to decompose formate, the use of the calcium salt would be preferable to that of the barium salt, although the latter gives better results, because the recovery of the oxide from the calcium carbonate is easier than from barium carbonate.

If it is intended to combine the formation and decomposition of the formate in one process, say, by the reaction of carbon monoxide and steam under pressure with calcium carbonate as contact material, the temperature would have to be raised to at least 400°, at which calcium formate is decomposed. The question then arises whether a production of formate is still possible at that temperature. From previous experiments[177] it is known that a little formic acid is actually formed at this temperature by the combination of carbon monoxide and water vapour under pressure, the yield being limited by the stability of the acid; in the presence of calcium carbonate some formate may therefore be produced.

(*f*) SYNTHOL FROM CARBON MONOXIDE AND WATER VAPOUR UNDER PRESSURE *

The following experiments were made in the apparatus illustrated in Fig. 69. The apparatus, which is mounted on a tripod, consists essentially of three parts. The upper part, A, is a high-pressure cylinder made of Mannesmann steel tubing; it is filled with water and externally heated by a ring gas-burner, and supplies the steam to be added to the compressed carbon monoxide. The latter enters through a tube fixed in the cylinder cover, bubbles through the water and leaves the cylinder diluted with water vapour, through another tube which passes through the bottom of the vessel and terminates just below the cover, above the water level. The mixture of carbon monoxide and steam then enters into the contact vessel B, likewise a Mannesmann tube, 90 cm. long, 22 mm. internal diameter and 11 mm. wall thickness. An aluminium tube, 4 mm. wall thickness, fitted tightly over tube B serves to maintain an even temperature.

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* Unpublished experiments by Fischer and Tropsch.

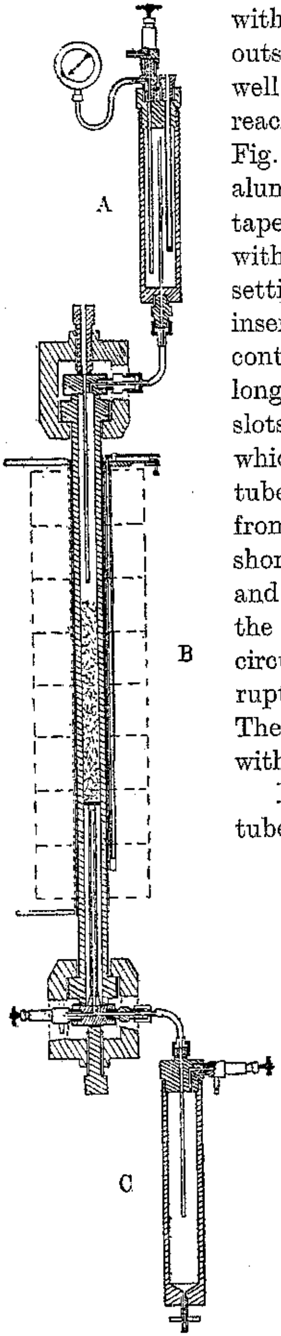

Fig. 69.

Temperature measurements were first attempted with the aid of a thermo-couple applied to the outside of the tube; later, a copper thermometer well was provided, fixed in the cover of B and reaching into the contact material, as indicated in Fig. 69. A mica insulation was wrapped round the aluminium sheath on which nichrome resistance tape was wound for the electric heating, itself lagged with asbestos. The whole tube was fixed in a setting of diatomite bricks. A thermostat was inserted in a recess in the brickwork, facing the contact tube, B. It consisted of a steel tube, 55 cm. long and 1 cm. diameter, provided with long internal slots and containing a close-fitting aluminium rod which was screwed into the lower end of the steel tube. The upper end of the steel tube, projecting from the brickwork, acted on a lever system. The short arm of the lever rested on the aluminium rod, and the lever moving with the thermal changes in the length of the rod opened or closed a battery circuit which actuated a Heraeus mercury interruptor connected with the heating current circuit. The arrangement secured temperature constancy within 5°.

Before giving further details of the contact tube, the third part of the apparatus should be

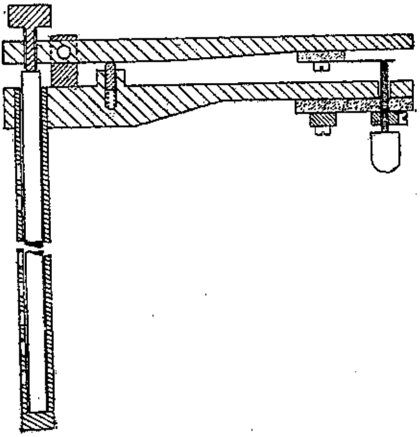

Fig. 70.

mentioned. It consisted of a Mannesmann steel tube acting as receiver for the liquid condensate from the gases which were cooled in the lower portion of B while still under pressure. The gas as freed from constituents condensable at ordinary temperature under pressure left the receiver through a reducing valve at the side and passed into a gas meter, in which the volume was determined at atmospheric pressure. The liquid condensate was withdrawn through a valve at the bottom of the receiver.

The contact tube B was tinned inside, and closed at either end by an annular copper washer held between strong steel flanges and the thick steel cover held by a clamp. The carbon monoxide entered the tube from the side through a right-angle bore so as not to be in the way of the clamp. The arrangement offered the advantage that the contact tube could easily be opened, examined and refilled without moving it. The tube was mounted vertically so as to avoid channelling in the contact material. The latter rested on a perforated plate fixed by means of clips at the lower end of the heating zone of the tube. The lower end of the tube projecting from the furnace setting was provided with a water cooler.

The carbon monoxide was stored in a steel cylinder of 40 litres capacity, from which it flowed through a copper capillary into a steel vessel charged with caustic potash to remove carbon dioxide, and then into the water vessel A.

The tubes connecting the water vessel with the contact tube B, and the latter with the receiver, were also copper capillaries. Another copper capillary penetrated through the steel cover from below into B nearly up to the perforated plate. This capillary was connected to a reducing valve in the cover. This arrangement made it possible to withdraw samples of gas at the point where it had left the catalyst; otherwise it would have been necessary when making changes in the working conditions (temperature, pressure, velocity, etc.) to wait until the whole receiver had been emptied and scavenged. The following experiments were made with this apparatus.

Experiment 99

The first contact material tried for the preparation of methyl alcohol and oil by way of calcium formate was potash lime. It was made by calcining a mixture of calcium hydroxide and potassium hydroxide in a silver dish. This mixture was used instead of calcium hydroxide, as the researches of Merz and Tibiriça [178] had shown that potash in the form of potash lime produces formate with special ease. It was also conceivable that potassium hydroxide acted as a carrier, transferring carbon monoxide to the calcium hydroxide. Potassium hydrate alone did not appear suitable, since on thermal decomposition potassium formate does not yield methyl alcohol as the calcium salt is known to do. 154·5 grams of potash lime of small grain size were charged into the contact tube to form a layer 45 cm. high in the uniformly-heated middle portion of the tube. The cylinder, A, was charged with 250 c.c. of water, and the whole apparatus was put under a carbon monoxide pressure of 80 atm. The contact material was heated to 420°, the water vessel to 250°. The rate of gas discharged was kept, on an average, at 150 litres per hour; later it was reduced to 30 litres. Commercial carbon monoxide was used of the composition :—

CO_2 . . .	5·1 per cent.	H_2 . . .	8·5 per cent.
C_nH_m . .	0·3 ,,	CH_4 . . .	0·3 ,,
O_2 . . .	0·2 ,,	N_2 . . .	3·4 ,,
CO . . .	82·2 ,,		

A trace of oil was produced in the experiment of 6 hours' duration, but nearly 19 c.c. of an aqueous fluid were withdrawn from the receiver. The liquid had a faintly acid reaction and contained possibly traces of alcohol. It required 9·1 c.c. of $N/10$-NaOH for neutralisation. Traces of esters seemed to be present, for after standing for some time the colour was discharged, and a further 0·6 c.c. of $N/10$-NaOH was required. On opening the contact tube a few drops of a liquid were found condensed on the lower part; they smelled distinctly of methyl alcohol and could be lighted with a match. The contact mass had caked to a cement in which some carbon was deposited. A sample of gas taken towards the end of the experiment showed a distinct change in composition :—

CO_2 . . .	15·8 per cent.	H_2 . . .	18·5 per cent.
C_nH_m . .	0·1 ,,	CH_4 . . .	0·0 ,,
O_2 . . .	0·2 ,,	N_2 . . .	3·1 ,,
CO . . .	62·3 ,,		

At least part of the carbon monoxide had therefore reacted with steam according to the equation: $CO + H_2O = CO_2 + H_2$. At the end of the experiment the water vessel contained only 12 c.c. of water; the rest had been evaporated and had combined with carbon monoxide. On the whole, the result was decidedly negative *; the occurrence of traces of alcohol was explained by subsequent experiments.

Experiment 103

On the supposition that the temperature of decomposition of calcium formate might be considerably above 420°, another catalyst was chosen with which the intermediate formation of a more easily decomposable formate

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* Two earlier experiments, in which pumice stone saturated with lithium carbonate, or lumps of quicklime, had served as catalyst, had likewise been failures; no alcohol was found in the water formed.

seemed likely. Temperatures above 500° could not be risked in view of the weakening of the steel tube and the accelerated deposition of carbon. The experiments of Hofmann and Shibsted[173] had shown that zinc formate decomposes about 100° below calcium formate. In this experiment, 73 grams of zinc oxide and 128 grams of potassium hydroxide were fused together and mixed with 68·5 grams of pumice stone crushed to pass through a sieve of 4 mm. mesh; 142·5 grams of this mixture were used as catalyst. The water vessel contained again 250 c.c. of water; the pressure of the carbon monoxide was 80 atm. as before, but the water was heated to 200° only. The contact tube was maintained at 400°, and the rate of gas at 90 litres per hour. In the earlier stages of the experiment, the escaping gases burned with a bright luminous flame. The luminosity was due to the presence of iron carbonyl, which is only formed at the commencement of an experiment; this observation was made in nearly all the experiments and will, therefore, not be mentioned again.

During a 5-hour experiment no trace of oil and only a little water was formed. The escaping gas had again undergone a change in that carbon monoxide and water reacted giving carbon dioxide and hydrogen. With respect to the desired products, the result was negative.

At the end of the experiment the water vessel still contained 180 c.c. of water; the catalyst had turned a little darker, but there was no appreciable deposition of carbon.

Experiment 107

The contact substance was copper and potassium hydroxide prepared by moistening copper turnings with 5*N*-KOH, drying and calcining on a copper sheet; 147 grams of the mass were used. The other conditions were those of Expt. 103. The result was negative.

Experiment 93

In this instance iron filings were used as a support for the catalyst, 215 grams of filings being wetted with 5*N*-KOH, dried on the water-bath and calcined in an iron crucible. The surface after cooling was grey-green and partly brown in colour. The experimental conditions differed very little from those before. There were 250 c.c. of water in the top vessel, heated to 250°; 178·7 grams of the catalyst mass were used, heated to 410° or 420°; the rate of gas discharge was 50 litres per hour. The escaping gas contained 30 to 40 per cent. of carbon dioxide. After 2 hours treatment 5 c.c. of a feebly acid liquid were withdrawn from the receiver, but no oil. After a further 3 hours 9 c.c. of liquid were obtained, this time including 1 c.c. of oil; the next hour yielded 5 c.c. of water and 3 c.c. of oil; the next, 5 c.c. of water and 1 c.c. of oil; and the next, 6·5 c.c. of water and 5 c.c. of oil. During this period of water and oil production the escaping gas had the following composition :—

CO_2	42·5 per cent.	H_2	26·6 per cent.
C_nH_m	0·9 ,,	CH_4	1·0 ,,
O_2	0·4 ,,	N_2	4·5 ,,
CO	24·1 ,,		

The gross calorific value of the oil was 8750 cals. The 27 grams of aqueous liquid gave on fractionation 0·5 c.c. boiling between 50° and 70° in which acetone was found; 1·5 c.c. between 70° and 100°, of an ester smell; the rest of the liquid was acid, and required 83·6 c.c. of $N/10$-NaOH for its neutralisation. The experiment was stopped over-night and resumed on the following day for 3½ hours; the temperature of the water vessel was somewhat lower, 215°; that of the contact tube higher, 440° on average. In 3½ hours 3 c.c. of water and 6 c.c. of oil were collected; towards the end of the experiment oil only was formed.

After completion of the experiment the water cylinder was empty, an observation reflected in the composition of the last gas sample :—

CO_2	56·9 per cent.	H_2	9·0 per cent.
C_nH_m	2·0 ,,	CH_4	5·9 ,,
O_2	0·2 ,,	N_2	4·6 ,,
CO	21·4 ,,		

The small proportion of hydrogen along with the large proportion of carbon dioxide indicates that little steam entered the contact tube together with the carbon monoxide. The copious formation of CO_2 indicated decomposition of carbon monoxide according to the equation $2CO = CO_2 + C$; this was confirmed by an examination of the contact material when as much as 37·3 grams of carbon were found deposited in it.

The diminution of the steam–carbon monoxide ratio causes a decrease of the aqueous products instead of oil. With deficiency of water vapour at high temperatures, the side reaction: $CO + H_2O = CO_2 + H_2$ is substituted by the much less desirable reaction: $2CO = C + CO_2$, which leads to the clogging of the contact tube. The latter reaction is exothermic and is spontaneously accelerated, as becomes noticeable by the decreasing current required for maintaining the temperature.

Experiment 111

For this experiment commercial manganese dioxide was crushed and passed through a sieve of 4 mm. mesh. The screenings were mixed with 5N-KOH, evaporated to dryness in a porcelain dish, and reduced by a current of hydrogen in a glass tube at 400°; 200 grams of this contact substance of manganous oxide impregnated with KOH were used. Manganous oxide was selected in order to ascertain whether elements closely related to iron would favour the formation of oil although the presence of metallic manganese was not to be expected. The experiment was conducted much like the others and interrupted after 6 hours with the following result. The liquids which were not clear were extracted with ether giving 0·5 c.c. of oil; otherwise no oil was observed. As subsequent analysis revealed the presence of iron, the experiment does not prove the capacity of manganous oxide to induce even a small formation of oil in the presence of KOH. The water had been completely evaporated in this experiment. The temperature of the contact tube was varied occasionally between 340° and 430°, without any appreciable difference in the products. The liquid was slightly acid and it did not appear to contain methyl alcohol.

A review of these various experiments with carbon monoxide and water vapour shows that, contrary to all theoretical anticipation, considerable amounts of alcohol or oil were not formed, except when an iron support was used for the alkali. That contact with iron alone, in the absence of alkali, would not produce alcohol or oil had already been established by other experimenters.[179] According to the results so far obtained, the simultaneous presence of iron and alkali is required for the formation of alcohol and oil from carbon monoxide and steam. In a few further experiments nitrogen was added to the carbon monoxide in order to ascertain whether it had a disturbing influence. Large volumes of carbon monoxide are a waste product of the manufacture of calcium carbide, and still larger quantities of carbon monoxide–nitrogen mixtures are available in industry. Almost all the carbon in the coke consumed in blast furnaces reappears in the gas as carbon monoxide or dioxide. The following experiments were made, having regard to the nitrogen content of blast furnace gas, with gas containing more nitrogen than carbon monoxide.

(*g*) CATALYTIC EXPERIMENTS IN THE PRESENCE OF NITROGEN

Experiment 139

Nitrogen was pressed into a steel cylinder containing carbon monoxide until the pressure rose to 113 atm. The cylinder was rolled about and turned upside down to ensure thorough mixing of the gases. The analysis of the mixed gas gave :—

CO_2 . . .	0·0 per cent.	H_2 . . .	1·6 per cent.
C_nH_m . . .	0·0 ,,	CH_4 . . .	0·0 ,,
O_2 . . .	0·0 ,,	N_2 . . .	56·9 ,,
CO . . .	41·5 ,,		

The water vessel contained 250 c.c. of water. The contact material consisted of 230 grams of iron filings impregnated with KOH. The temperature of the water vessel was kept at 170°; that of the catalyst was varied between 400° and 440°. The rate of gas flow averaged 150 litres per hour. The gas discharged from the apparatus contained 20 to 22 per cent. CO_2. Strangely enough, no aqueous liquor was produced; when the temperature rose to 240°, oil appeared, altogether 3 c.c. in 3 hours, but no water. At the end of the experiment only 15 c.c. of water were found to have evaporated, 235 c.c. remaining in the water vessel. As there was very little steam admixed to the carbon monoxide, the conditions recall those at the end of Expt. 93, when in the absence of water, oil and no aqueous liquor was formed. On opening, the contact tube was found clogged with carbon, as in Expt. 93, the weight having increased by 24·4 grams. The experiment showed that the presence of nitrogen does not exert a disturbing influence; an appreciable formation of ammonia was not observed, and the oil yield was small. This may be partly attributed to an inadequate partial pressure of carbon monoxide. This was about 50 atm., as against the usual 80 atm. If blast furnace gas were used, it would have to be compressed to upwards of 300 atm., to ensure a carbon monoxide pressure of 80 atm., since this gas frequently does not contain more than 28 per cent. CO, as the following analysis of an average sample shows: CO_2 10 per cent., CO 28 per cent., H_2 3 per cent., N_2 59 per cent. The composition of blast furnace gas may vary between these limits:—

	I	*II*
Carbon dioxide . .	15 per cent.	6 per cent.
Carbon monoxide . .	20 ,,	34 ,,
Hydrogen . . .	1 ,,	4 ,,
Nitrogen . . .	64 ,,	56 ,,

The saturation of the compressed gas with water vapour may offer difficulties. These might be obviated by mixing blast furnace gas with steam at ordinary pressure, and then passing the mixture at ordinary pressure over a contact material which will convert it into carbon dioxide and hydrogen, which can be compressed and will not require any further addition of steam. That carbon monoxide will again be formed in the apparatus was shown by the results of Expt. 144. The gas applied contained:—

CO_2 . . .	32·8 per cent.	H_2 . . .	60·5 per cent.
C_nH_m . . .	0·0 ,,	CH_4 . . .	0·0 ,,
O_2 . . .	0·4 ,,	N_2 . . .	5·4 ,,
CO . . .	0·9 ,,		

Under the usual conditions the resulting gas had the composition:—

CO_2 . . .	33·2 per cent.	H_2 . . .	49·8 per cent.
C_nH_m . . .	0·1 ,,	CH_4 . . .	2·4 ,,
O_2 . . .	0·2 ,,	N_2 . . .	6·2 ,,
CO . . .	8·1 ,,		

(*h*) CATALYTIC EXPERIMENTS WITH CARBON DIOXIDE AND HYDROGEN UNDER PRESSURE

Experiment 144

The composition of the gas used was as stated above. The pressure was 82 atm., temperature 420°, rate of gas flow 55 litres per hour, contact material as in Expt. 139, water vessel empty. Five to 10 c.c. of an aqueous liquid of acid reaction were made per hour; a sample on boiling yielded inflammable vapours; oil was not found. Fractionation of 37 c.c. of the alcoholic solution yielded 0·8 c.c. between 50° and 70°, in which acetone was present, and 1·7 c.c. between 70° and 100°. Later experiments indicate that the escaping gas which (as stated) contains carbon monoxide, yields oil but less water when passed a second time over the catalyst.

Having thus demonstrated that it made little difference whether carbon monoxide and steam, or carbon dioxide and hydrogen, were used, it seemed likely that commercial water gas should give similar results. Water gas is easily produced commercially and need only be freed from sulphur compounds. The following experiments were made with water gas. Carbon dioxide was at a later stage left in the gas when it was found to have actually a favourable effect in preventing deposition of carbon which the excess of hydrogen over carbon monoxide tends to cause.

(*i*) SYNTHOL FROM WATER GAS UNDER PRESSURE *

In discussing these experiments with water gas, mention should first be made of Expt. 125, which was undertaken to test the statements contained in the British Patent No. 20,488/1913 (German Patent No. 293,787), of the Badische Anilin- und Soda-Fabrik (p. 206).

1. *On the need of a Metallic Hydrogen Carrier in the Contact Material.*

Experiment 125.

Commercial water gas was, before the compression, carefully freed of sulphur compounds, particularly H_2S, in the usual way. The contact substance was prepared by impregnating pumice stone with a concentrated solution of potassium carbonate and drying it. It was then put into a concentrated zinc nitrate solution and heated gently; the solution was poured off from the pumice, and the latter, now impregnated with alkali and zinc carbonate, was dried and heated. The catalyst was, therefore, made exactly as directed in

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* Unpublished experiments by Fischer and Tropsch.

example 2 of the specification quoted. The water gas used had the following composition :—

CO_2	4·1 per cent.	H_2	51·0 per cent.
C_nH_m	0·2 ,,	CH_4	0·0 ,,
O_2	0·2 ,,	N_2	6·3 ,,
CO	38·2 ,,		

The contact tube was charged with 84·4 grams of the catalyst; the water gas pressure was adjusted to 90 atm.; the temperature was maintained between 400° and 420°, and the rate of gas flow at 110 litres per hour.

In this experiment not a trace of oil was obtained, and water only in minimal quantities. The water gas leaving the apparatus proved little changed by its passage over the catalyst :—

CO_2	5·9 per cent.	H_2	49·5 per cent.
C_nH_m	0·2 ,,	CH_4	0·6 ,,
O_2	0·2 ,,	N_2	6·2 ,,
CO	37·4 ,,		

Experiment 127

The following experiment, which was made immediately after the failure of Expt. 125, demonstrates that example 2 of the specification had omitted to state some indispensable factor. The catalyst used this time consisted of 63 grams of pumice stone, which was impregnated with 30 grams of calcium acetate and 30 grams of concentrated ferric acetate solution, dried and calcined in an iron dish. Of this material, 71·5 grams were used; the pressure of the water gas, which came from the same cylinder as in Expt. 127, was slightly lower than before, viz. 85 instead of 90 atm.; temperature and rate of gas flow remained unchanged. By contrast with the last experiment, 10 c.c. of a feebly acid alcoholic liquid were obtained per hour.

The composition of the escaping gas differed considerably from that of the original water gas. It was :—

CO_2	19·7 per cent.	H_2	29·4 per cent.
C_nH_m	0·7 ,,	CH_4	16·2 ,,
O_2	0·8 ,,	N_2	6·8 ,,
CO	26·4 ,,		

Why no oil was formed in Expt. 125 with potassium carbonate and reduced iron will be explained by later experiments on the influence of the bases. This experiment proves the production of an alcoholic liquor, and the changed composition of the gas further proves that the substitution of iron for zinc is essential.

2. *Influence of the Form and Length of the Contact Material*

Although in the examples set out in the patent specification iron is not mentioned, this metal has in our method of working proved to be an essential constituent of the catalyst and is, according to our observations, far superior to cobalt and nickel.

As regards the physical condition of the metal, we found turnings preferable to fine powders; the activity of turnings sets in more slowly, but it lasts for weeks. Finely-divided iron becomes immediately active but loses its activity quickly; moreover, it always causes deposition of much carbon. The difference in behaviour of the iron turnings and powder in exothermal reactions is probably to be accounted for in the following way. The heat of reaction liberated per unit of time in 1 c.c. of contact material is proportional to the surface of the catalyst exposed within this cubic centimetre. The rise of temperature in the contact material will be inversely proportional to its heat capacity and the loss by conduction. In the finely-divided iron the heat capacity is small in comparison with the surface, and the smallness of the particles does not favour transference of heat by conduction. Conduction is further impeded by the impregnation of the iron with alkalis or alkaline earths, which are poorer conductors of heat than metallic iron. It is conceivable that finely-divided iron, properly impregnated, will immediately be fully active; but the catalyst quickly heats-up in uncontrollable fashion and accelerates the undesirable reaction: $2CO = CO_2 + C$, thereby clogging itself with carbon and choking the contact tube.

If the finely-divided iron particles are replaced by filings or turnings likewise impregnated, the position is at first less favourable. The active surface is small, and heat capacity and thermal conductivity are relatively very large. After starting an experiment with turnings, the catalyst gradually acquires activity. The maximum activity may only be attained after several days of continuous operation. During that period the surface of the turnings is loosened, possibly owing to an intermediate formation and decomposition of iron carbonyl. Other factors may participate in the gradual shaping of the surface of the iron turnings. It is a fact that turnings do not promote the deposition of carbon as much as finely-divided metal. In this respect, our observations are in accord with the directions given in the patent specification, that contact masses of high thermal conductivity should be applied. Expt. 263 shows the influence of the length of the contact column upon the products. In this experiment only 20 grams (instead of the usual 300 grams) of iron turnings were used; they were impregnated with 20 c.c. of $N{\cdot}Rb_2CO_3$ solution, dried and heated. This small quantity of catalyst was held by a special contrivance in the middle of the contact tube; the length of the column was only 1/15 of that in the other experiments. The gas pressure, initially 132 atm., fell to 109 atm.; the temperature of the catalyst was 460°, and the rate of gas flow 40 litres per hour. The experiment yielded 5 c.c. of an aqueous liquid per hour, containing 12 per cent. of alcohols, but only traces of oil. In 20 hours about 100 c.c. of liquor were obtained, but less than 1 c.c. of oil. The results suggest that the primary process is alcohol formation, and that the oil formation sets in at a later stage. Once the gas has left the short catalyst column, oil formation comes to an end. Oil formation thus requires for every gas velocity a minimum length of catalyst column.

3. *Influence of Bases and their Quantity upon the Oil Yield*

Iron without Impregnation.—If iron turnings are used alone as catalyst for water gas at 100 atm. and about 400°, methane and carbon dioxide are the chief products, whilst no oil is formed, and water only in minor quantity with no methyl alcohol.[179] Hence, iron without some impregnation is as ineffective, as regards alcohol and oil formation, as alkali is without iron.

Iron with Potassium Hydroxide.—The situation changes entirely as soon as the iron turnings are impregnated with caustic potash.* The combination may furnish the condition for formate production. Alternatively, the alkali may act by catalytically transforming the formaldehyde, appearing as an intermediate product of the union of hydrogen and carbon monoxide, before it is reduced to the methane stage. The mechanism of the reaction will be considered in a subsequent chapter. References in the Patents of the B.A.S.F. to the impregnation of the metal as merely suitable or advantageous, but not essential, may be misleading, as according to our experience it is absolutely indispensable; without impregnation, neither alcohol nor oil is obtained, as the following experiments will demonstrate.

Experiment 175

300 grams of iron filings were stirred into 60 c.c. of 5*N*.-KOH in an iron dish until the mass was dry; it was then calcined. The water gas used had the composition :—

CO_2	0·0 per cent.	H_2	60·3 per cent.
C_nH_m	0·0 ,,	CH_4	0·1 ,,
O_2	0·1 ,,	N_2	4·4 ,,
CO	35·1 ,,		

The absence of carbon dioxide in this and the further experiments in this section was secured by first passing the water gas through a steel vessel containing 2 litres of 32 per cent. caustic potash. The average temperature was 420°, the pressure 146 atm., the rate of gas flow 150 litres per hour. The average hourly yield was 9 c.c. of an aqueous liquor containing 17 per cent. of alcohols

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* Carbonate serves equally well, since the hydroxide is soon converted into carbonate.

and 3 c.c. of oil. During the 8 hours of the experiment spontaneous heating was occasionally noticed, but was quickly suppressed by cutting off the heating current; the reactions then proceeded again normally, but there was always considerable deposition of carbon in the upper portion of the catalyst. The composition of the gas leaving the contact tube was :—

CO_2	23·8 per cent.	H_2	41·7 per cent.
C_nH_m	3·6 ,,	CH_4	11·5 ,,
O_2	0·5 ,,	N_2	5·6 ,,
CO	13·3 ,,		

The difference in these results from those of the experiments without impregnation or without iron (Expt. 125) is manifest both as regards alcoholic liquor and oil, and the composition of the discharged gas.

Comparative Experiments with Different Bases.—In a similar way a number of experiments were made, summarised in Table LXXII, in which the catalyst always consisted of 300 grams of iron turnings of the same origin and properties, which were impregnated in each case with a different base, but in equivalent quantity.

TABLE LXXII

Expt. No.	Iron filings with	Oil/hour c.c.	Water/hour c.c.	Alcohol. %
173	LiOH	0	0·7	28
171	NaOH	0·7	4·0	24
175	KOH	3·0	8·5	17
167	RbOH	4·0	8	25
183	CsOH	3	7	19
179	$Ca(OH)_2$	0	9	7·5
185	$Sr(OH)_2$	0	0·9	22
181	$Ba(OH)_2$	1·2	8·7	19

The five alkalis and the three alkaline earths are arranged in ascending order of atomic weight and therefore of basicity. It at once becomes evident that the weaker bases do not yield any oil, and that the quantity of oil, produced under otherwise equal conditions, increases with the strength of the base used for impregnation. If the weaker bases will not cause oil production, it is only to be expected that iron not impregnated at all is unable to do so. As regards oil formation, cæsium hydroxide, the strongest base, seems to be an exception. This is only apparent, for on account of lack of material, impregnation was effected in this case with only 40 per cent. of the equivalent quantity. For industrial operation the provision of large amounts of cæsium would be a matter of some difficulty, but rubidium should be more easily procurable. With an output of 2,000,000 tons of carnallite per annum nearly 700 tons of rubidium chloride go into fertilisers and potassium compounds consumed by chemical industry.

Comparative Experiments with some other Compounds.—The experiments summarised in Table LXXII had shown that the weaker bases, though not yielding oil, would at any rate promote the formation of alcohol. Iron itself being unable to do this, it was of interest to investigate the effect of impregnating iron with basic salts and other compounds.

TABLE LXXIII

Expt. No.	Iron filings with	Oil/hour c.c.	Water/hour c.c.	Alcohol. %.
219	K_2HPO_4	3–0·3	11–1·6	20
221	H_3PO_4	0	2	8
223	K_2SiO_3	1·5	10	20
268	KCN	1	7	?
233	$Ba(OH)_2 + KOH$	2	5	?

The impregnation of the iron turnings was effected in the way described and all compounds were applied in equivalent proportions. The impregnation with K_2HPO_4 had at first a very good effect on the formation of both oil and alcoholic liquid, but its activity diminished very much in the course of a day. An examination of the catalyst furnished the explanation; the phosphate, which to begin with had reacted strongly alkaline, had been converted into pyrophosphate, which is evidently less active.

In Expt. 221 impregnation with phosphoric acid was found to have no effect on oil formation; the want of basic properties would account for that. A little water had been formed, but it contained alcohol. It may safely be assumed that phosphoric acid had reacted with iron forming iron phosphate; it is questionable whether the phosphate was again reduced to iron in the course of the experiment. The formation of alcohol may be due to iron phosphate, and not to phosphoric acid.

Potassium silicate and potassium cyanide, being basic salts, yielded both oil and alcoholic liquor.

In Expt. 233 a mixture of bases was used, but it was found that mixed bases offered no advantages over single bases.

Influence of the Quantity of Bases.—Oil formation having been found to be connected with the presence of strongly basic compounds, the relation of the quantity of these compounds to the exposed surface of iron turnings was investigated. It is evident that an increase in the quantity of a weak base cannot make up for its lack of basicity; with too weak a base, no oil will be obtained, irrespective of the quantity of base used. Conversely, it was observed