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CXXX.—The Equilibrium between Carbon, Hydrogen, and Methane.

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EQUILIBRIUM in the system $C+2H_2=CH_4$ is more suited to experimental study, in one respect, than the more commonly investigated high-temperature dissociations, such as those of water, carbon dioxide, and hydrogen chloride. The proportion of methane in equilibrium with carbon and hydrogen diminishes with increasing temperature, and hence when equilibrium is once established in the zone of reaction, the cooling of the gaseous mixture on its removal from the carbon is not accompanied by an alteration in composition. It is a simple matter to ensure the absence of elementary carbon from any but the zone of measured temperature in which the equilibrium is attained.

The synthesis of methane from its elements was achieved by Bone and Jerdan (T., 1897, **71**, 41; 1901, **79**, 1042), who found that when a stream of hydrogen was passed over carbon at about 1200° , the resulting gaseous mixture was hydrogen containing, roughly, 1 per cent. of methane and no other hydrocarbon. This synthesis was confirmed by Bone and Coward (T., 1910, **97**, 1219), who obtained an almost theoretical yield of methane from 0.0824 gram of carbon.

The decomposition of methane into carbon and hydrogen, without the permanent formation of any detectable amount of any other hydrocarbon, was demonstrated by Bone and Coward (T., 1908, **93**, 1197).

The above-mentioned experiments, the forerunners of those now to be described, indicated that the equilibrium mixture at 1000-1200° contained, roughly, 1 per cent. of methane.

The determination of equilibrium values in the system has been

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attacked in two other quarters. Mayer and Altmayer (*Ber.*, 1907, **40**, 2134) carried out experiments with the aid of a catalyst at temperatures ranging from 475° to 625° , and declared that Bone and Jerdan's methane formed at 1200° could not have arisen by the direct union of carbon and hydrogen. Pring (T., 1910, **97**, 498) found that a carbon rod lightly coated with platinum gave the value 0.55 per cent. of methane in equilibrium at 1200° and 0.30 per cent. at 1500° . Finally, Pring and Fairlie (T., 1912, **101**, 91) conducted experiments under high pressures, and, assuming the law of mass action to hold down to atmospheric pressure, calculated the following equilibrium values:

Amorphous carbon.			Graphite.			
1200°	0·36 p	er cent.	of methane	0.24	per cent.	of methane
1500°	0.21	,,	,,	0.07	,,	,,

The series of experiments, the results of which are recorded below, were conducted in essentially the same way as those described in detail by Bone and Coward (*loc. cit.*), except that the gaseous products of reaction were passed backwards and forwards over the carbon used until analysis showed the attainment of constancy of composition. The porcelain tube used to contain the reacting substances was, as before, set up coaxially with a wider one, through which dry hydrogen was passed. The wider tube was heated electrically by means of a platinum wire resistance. The temperature of the inner tube was, at 1100°, constant, within $\pm 6^\circ$, for a length of 10 to 15 cm. (in different furnaces), which was ample to contain the carbon used. The latter was held in a quartz boat or in an open quartz tube just narrow enough to pass freely into the porcelain tube.

The temperature of the reaction zone was measured by means of a platinum and platinum-rhodium thermo-junction lying in the inner porcelain tube, but encased in a thin quartz tube; one wire was insulated from the other by running it through a fine quartz tube. The thermo-couple was standardised by means of lithium chloride (m. p. 605°), antimony (m. p. 628°), an alloy of 80 per cent. of copper and 20 per cent. of tin (m. p. 738°), potassium carbonate (m. p. 835°), and electrolytic copper (m. p. 1084°).

The gaseous products were collected direct from the furnace over a mixture of glycerol and water, and before being re-passed into the furnace were dried by passage through a U-tube containing fragments of dry stick potassium hydroxide.

The electrolytic hydrogen and the carbon were prepared as described by Bone and Coward. The methane was obtained by interaction between aluminium carbide and water, washed with

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ammoniacal cuprous chloride and sulphuric acid, and collected after air had been displaced from the apparatus used for the preparation. Hydrogen was then removed by liquefaction of the gas by means of liquid air, and subsequent distillation. This procedure was proved to afford a satisfactory means for removing hydrogen from large volumes of methane. It cannot, however, be recommended for removing air from methane; methane must be prepared free from air in the first place unless large quantities of the gas are sacrificed during the fractional distillation after liquefaction.

Experiments at 1100°.

Synthesis of Methane.—Pure dry hydrogen was passed over 1 gram of carbon (ash, 0.06 per cent.) at the rate of about 1 litre per hour until from 5 to 6 litres of gas had been collected. A litre of this was measured and treated with palladium foil; the resulting concentrate was measured and analysed. The residual 4 to 5 litres of the gas, once passed over carbon, were re-passed at the same rate as before, and a sample was taken for analysis after concentration. The residual gas was then passed twice again over the heated carbon, and again sampled for analysis. The results of the analysis, calculated back to the unconcentrated mixtures, are (in percentages):

	1st passage.	2nd passage.	3rd passage.
Carbon monoxide	0.07	0.16	0.51
Methane	0.46	0.70	0.62
Nitrogen	0.21	0.51	0.67

The experiment was repeated with the same sample of carbon:

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Each experiment shows an accumulation of methane during the first and second passage of the gas over the carbon, but thenceforth the methane content remained practically constant.

The nitrogen content is a measure of the leaking in of air during the experiment and analysis, and in itself is unimportant. The carbon monoxide, due in part to air and in part to a slight oxidising action by the glaze of the heated tube, raises the question as to whether carbon monoxide may play some important part in the synthesis. It is just conceivable, although contrary to the results of other investigations,* that carbon monoxide would be

^{*} Bone and Coward (T., 1908, 93, 1987) showed that when a mixture of 98 per cent. of hydrogen and 2 per cent. of carbon monoxide was passed through a porcelain tube at 1100° in the absence of carbon, no more than 0.03 per cent. of methane was present in the issuing gas.

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reduced by the large excess of hydrogen present to methane and water; the latter would regenerate carbon monoxide by reaction with carbon. If carbon monoxide acted as a catalyst in the synthesis, then the two reactions—whatever they might be precisely —indicated as A and B in the scheme

 $\begin{array}{ccc} C \longrightarrow CH_4 \\ \swarrow & \swarrow \\ & \swarrow & \swarrow \\ & & CO \end{array}$

would each be fast in comparison with the rate of the direct synthesis. Hence the accumulation of carbon monoxide exhibited in the experiments would only be possible provided that the reversion of methane to carbon and hydrogen were a very rapid reaction indeed when the methane was increased above about 0.7 per cent. That this is not the case is shown by experiments (below) on the decomposition of methane at 1100° . The carbon monoxide is therefore produced as a side reaction between carbon and water vapour, and plays no part in the formation of at least the great proportion of the methane found.

Decomposition of Methane.—A mixture containing 2.0 per cent. of methane and 98.0 per cent. of hydrogen was passed over the same sample of carbon, eight times in all. The gas was sampled from time to time for analysis as before. The results were (in percentage):

0 /	2nd passage.	5th passage.	8th passage.
Carbon monoxide	0.45	0.65	0.92
Methane	1.18	0.64	0.61
Nitrogen	0.49	0.52	1.04

Here, again, the steady formation of carbon monoxide is evident, whilst the methane-content becomes constant at or before the fifth passage, and shows the attainment of equilibrium, as in the synthetic experiments.

Synthesis and Decomposition of Methane in the Presence of Nickel.—One gram of the pure carbon was intimately mixed with 1 gram of nickel oxide, obtained by igniting the nitrate, and the mixture heated to 300° in hydrogen until no more water vapour was formed, and then raised gradually to 1100° in a current of hydrogen. The gas issuing from the tube was collected and repassed three times; analysis showed it to contain: carbon monoxide = 1.29, methane = 0.61, nitrogen = 0.49 per cent.

The decomposition of methane was conducted with a mixture containing 5.7 per cent. of methane and 94.3 per cent. of hydrogen. After five passages over the same mixture of carbon and nickel, the gas contained: carbon monoxide = 1.27, methane = 0.57, nitrogen =

1.33 per cent. The increase in carbon monoxide is ascribed to the well-known difficulty of reducing finely divided nickel oxide completely in hydrogen.

Collection of Results at 1100°.-The equilibrium values indicated above are:

		Carbon–Nickel
	Pure carbon.	mixture.
Synthesis	(i) 0.65; (ii) 0.67	0.61
Decomposition	0.61	0.57

The mean value for the equilibrium amount of methane at 1100° is therefore 0.62 per cent.

Experiments at 1000°.

Synthesis of Methane.-The synthesis of methane from the highly purified carbon used in the experiments at 1100° proved to be too slow for the attainment of equilibrium at 1000°. A less pure sample containing 0.5 per cent. of incombustible matter (silica) gave the following percentage results in an experiment conducted in a similar manner to the corresponding experiment at 1100°.

	lst passage.	2nd passage.	3rd passage.	4th passage.
Carbon monoxide	0.05	0.10	0.17	0.28
Methane	1.06	0.97	0.96	1.06
Nitrogen	0.12	0.44	0.32	0.31

Equilibrium is evidently established from the first. The carbon monoxide-content is much lower than in the experiments at 1100°, and although increasing throughout, has no appreciable influence on the methane-content of the gases. The high value for nitrogen in the second experiment is most probably due to a small in-leakage of air during the concentration of the sample of gas analysed.

An experiment with 1 gram of carbon containing 4 per cent. of platinum, finely disseminated, gave similar values:

	lst passage.	2nd passage.
Carbon monoxide	0.07	0.16
Methane	1.09	1.08
Nitrogen	0.09	0.19

Decomposition of Methane.—A mixture containing 2.0 per cent. of methane and 98.0 per cent. of hydrogen gave in two separate experiments:

	First experiment.		Second
	3rd passage.	5th passage.	2nd passage.
Carbon monoxide	0.19	0.41	0.55
Methane	1.16	1.13	1.06
Nitrogen	0.83	0.84	0.69

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Synthesis and Decomposition of Methane in Presence of Nickel. —The same sample of a carbon-nickel mixture as was used for the experiments at 1100° gave the following results at 1000°. Starting with pure hydrogen, samples of the unconcentrated gases showed on analysis an approximately constant content of methane from the second to the sixth passages. The methane then present was determined accurately after concentration of the mixture: carbon monoxide = $2 \cdot 2$, methane = $1 \cdot 23$, mitrogen = $0 \cdot 7$ per cent. The decomposition of a $3 \cdot 7$ per cent. methane mixture gave, in similar circumstances, a constant content of methane from the third to the seventh passage. The final composition was: carbon monoxide = $1 \cdot 1$, methane = $1 \cdot 18$, mitrogen = $1 \cdot 2$ per cent.

Collection of Results at 1000°.—The equilibrium values indicated above are:

	Carbon (0.5 per cent. of ash).	Carbon-4 per cent. of platinum.	Carbon-Nickel.
Synthesis	1.01	1.09	1.23
Decomposition	1.13; 1.06		1.18

The mean value for the equilibrium amount of methane at 1000° is therefore 1.12 per cent.

Experiments at 850°.

The reaction between carbon and hydrogen proved to be too slow at 850° for equilibrium to be reached at that temperature within a reasonable period of time in the apparatus employed. Experiments with the nickel-carbon mixture were more successful. Synthetic experiments with a slow stream of gas showed that from the sixth to the eighteenth passage the methane content remained constant, according to the approximate results of analyses of unconcentrated samples of the mixture. The methane present at the end of the eighteenth passage was determined after concentration: carbon monoxide=0.5, methane=2.60, nitrogen=1.3 per cent. Corresponding experiments on the decomposition of methane, carried out with a very slow stream of gas, showed constant composition between the second and fifth passages of the gas: carbon monoxide=0.2, methane=2.4, nitrogen=0.6 per cent.

The equilibrium amount of methane at 850° is therefore 2.5 per cent.

Experiments at 650°.

Hydrogen and methane were separately heated for prolonged periods in contact with carbon at 650°. In no case did the analyses of the resulting mixtures indicate that equilibrium could be attained within any reasonable period of time, although attempts

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were made to activate the carbon by means of finely divided nickel, (a) by grinding together nickel oxide and pure carbon and reducing in hydrogen at 300° ; (b) by igniting a mixture obtained by evaporating nickel nitrate in the presence of excess of finely divided carbon, and heating finally in hydrogen at 300° ; (c) by absorbing nickel nitrate in small pieces of porous porcelain, igniting; and depositing carbon by the prolonged passage of methane over the heated solid.

It is not concluded that it is impossible to prepare carbon in a sufficiently active state to attain equilibrium at this temperature, but the claim of Mayer and Altmayer (*loc. cit.*) to have succeeded at still lower temperatures is much weakened by the fact that they record no attempt to discover whether their gaseous products contained carbon monoxide. If, as it seems fair to assume, therefore, they overlooked carbon monoxide, much of their so-called methane may have had no actual existence. That there must have been carbon monoxide present in their products can scarcely be doubted in view of, first, the presence of large amounts of nitrogen, and, secondly, their use of somewhat large amounts of nickel, which, as is known, is difficult to obtain free from nickel oxide by reduction of the latter at a low temperature.

Summary and Conclusions.

The percentage composition of the equilibrium mixtures of methane and hydrogen in contact with amorphous carbon at atmospheric pressure is

	1100°.	1000°.	8 50°.
Methane	0.6	1.1	2.5
Hydrogen	99·4	98.9	97.5

These values will doubtless be capable of correlation by means of a thermodynamical equation, when the specific heats of the three reacting substances are known, together with the heat of formation of methane. Information as to the specific heat of methane at high temperatures is, however, wanting at present, and the heat of combustion of methane has apparently not been determined with a gas of sufficient purity. Calculation of the mean value of the latter between 850° and 1100° from the experimental values for the equilibrium, by means of the integrated form of the equation

$$\frac{d \log K}{dT} = - \frac{Q}{RT^2},$$

gives the value 18,000 calories, with a possible error of perhaps a couple of thousand calories.

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