

X.—*The Methane Equilibrium.*

By JOHN NORMAN PRING and DORIAN MACEFIELD FAIRLIE.

It has been found that hydrogen and carbon when in the purest condition combine directly to form methane at temperatures between 1200° and 1500°; ethylene at all temperatures above 1200° (although not in any considerable quantity below about 1500°); and acetylene at all temperatures above 1700° (Pring, *Trans.*, 1910, **97**, 498; Pring and Fairlie, *ibid.*, 1911, **99**, 1796).

Ethylene and acetylene were found to unite readily with hydrogen to give methane at all temperatures above about 700°.

A careful investigation of the equilibrium between carbon, hydrogen, and methane at different temperatures will be of particular value with regard to its application to the calculation of specific heats at temperatures where direct measurements cannot be made with any accuracy.

This application of thermodynamics to the calculation of chemical equilibria from heat data has been developed and verified by van't Hoff, Nernst, Haber, and others, but there are very few cases where accurate data are available to enable the extension of these formulæ to high temperatures.

In the work hitherto carried out on the synthesis of methane under atmospheric pressure, it was not possible to measure the precise equilibrium values, as the whole apparatus was not at a uniform temperature, and traces of ethylene formed at the higher temperature of the carbon would combine with hydrogen in zones of lower temperatures and give methane, thus raising the quantity of this latter to an amount greater than the equilibrium value at the higher temperature.

It is not practicable to use a reaction vessel, the walls of which can be heated to temperatures above 1200° and remain gas-tight.

A calculation of the methane equilibrium at high temperatures has been made by Mayer and Altmayer (*Ber.*, 1907, **40**, 2134) on the basis of experimental measurements made between 250° and 850°, and by making use of thermodynamical deductions. The formula as applied in this particular case is expressed by Haber \* as follows:

$$\log_e K = \frac{Q_0}{RT} - \frac{\sigma \log_e T}{R} - \frac{\sigma_1 T}{R} + \frac{k}{R}, \dagger$$

$K$  is here the reaction constant, or  $\frac{p\text{-CH}_4}{p\text{-(H}_2\text{)}^2}$ ,  $Q_0$  the heat of

\* "Thermodynamics of Technical Gas Reactions." 1908. p. 345.

† The term  $\frac{1}{2}\sigma_1 T^2$  is omitted from this equation.

reaction at absolute zero,  $\sigma + \sigma_1 T + \sigma'' T^2$  the sum of the specific heats, at constant pressure, of the substances disappearing ( $C + 2H_2$ ) and that appearing ( $CH_4$ ) in the reaction, the value for methane being taken as negative.  $T$  is the absolute temperature, and  $k$  an indeterminate constant. On examining experimentally the equilibrium at temperatures between  $250^\circ$  and  $850^\circ$ , the value of  $k$  was found to be 21.1. Taking 18,500 as the heat of formation of methane at absolute zero, the above equation took the form:

$$\log K = \frac{4050}{T} - 3.027 \log T - 0.0006424T + 4.617.$$

At  $1200^\circ$  this gives as the equilibrium ratio of methane to hydrogen the value 0.07 per cent.

It is obvious, however, that the variables in this equation are not known with sufficient precision to enable its application at high temperatures; for instance, in the above calculation, the term  $\sigma_1$  in the specific heat of methane was omitted as the value is unknown, and for  $\sigma$ , the value 9.106 found by Wüllner between  $0^\circ$  and  $200^\circ$  was used. A large departure will thus be produced at the higher temperatures. A still greater discrepancy than the above arises from taking for the heat of formation of methane a value which is based on data relating to amorphous carbon. Diamond is known to be the stable form of carbon at the ordinary temperature, and graphite at higher temperatures. In consequence of this, graphite has at the ordinary temperature a heat of combustion 2840 calories (per gram-atom) less than the value for amorphous carbon (Berthelot, *Compt. rend.*, 1889, **108**, 1144).

The difference at absolute zero can be calculated from Kirchhoff's law, according to which:

$$Q_0 = Q_T - T(C_{(r)} - C_{(p)}),$$

where  $Q_0$  and  $Q_T$  denote the heat of transformation of amorphous carbon into graphite at the temperatures  $0^\circ$  and  $T^\circ$  (absolute).  $C_{(r)}$  and  $C_{(p)}$  are the mean specific heats of carbon and graphite respectively.

The atomic heat of amorphous carbon is given by Kunz (*Ann. Physik*, 1904, [iv], **14**, 327) as  $2.0094 + 0.00173T$ , and the value for graphite as determined by Behn (*ibid.*, 1900, [iv], **1**, 264) is  $0.0 + 0.0075T$  (compare also Nernst, *ibid.*, 1911, [iv], **36**, 395).  $Q_0$  is therefore equal to 2506 cal., and the heat of formation of methane from graphite will consequently be 16,000 cal. at absolute zero. When the unstable substance, amorphous carbon, takes part in a gaseous equilibrium, a false value will be produced and maintained for some time.

This has indeed been observed by Schenck and Heller (*Ber.*,

1905, **38**, 2139), who studied the equilibrium in some reactions in which carbon in different modifications takes part.

In the case of the equilibrium between carbon dioxide, carbon monoxide, and carbon in different modifications, the reduction of carbon dioxide was greatest when amorphous carbon was used. A similar result was obtained in the reaction between iron oxide, carbon, and carbon monoxide; thus, in this case, at 550° the pressure of carbon monoxide obtained when in "metastable equilibrium" was, with amorphous carbon, 59 mm., diamond, 22 mm., and graphite, 12 mm.

In the present work an investigation was made of the reaction between carbon and hydrogen at high gaseous pressures, with a view to find the equilibrium values at high temperatures, and incidentally to obtain some idea of the effect of pressure on the progress of the synthesis. Since the formation of methane proceeds according to the equation  $C + 2H_2 = CH_4$ , it follows, from the law of mass action, that  $\frac{p\text{-}CH_4}{p\text{-}(H_2)^2} = k$ , a constant at any given temperature. It

is seen from this that an increase of pressure of  $n$  times will increase the ratio of methane to hydrogen  $n$  times; further, if in a series of experiments a constant value is obtained for  $k$  at different pressures, we have an indication that this represents the true equilibrium constant.

The objections, enumerated above, to the determination of the methane equilibrium in the form of apparatus used in the earlier work (*loc. cit.*) at atmospheric pressure were largely overcome in these experiments at high pressures.

It was found in the preliminary experiments made at high pressures that in these cases the formation of methane attains the equilibrium value much more rapidly, even when the carbon is used in absence of any catalyst, and the disturbance of the equilibrium due to the formation of ethylene will be very much diminished on account of the rapid cooling of the gaseous product by the water-cooled steel walls of the reaction vessel.

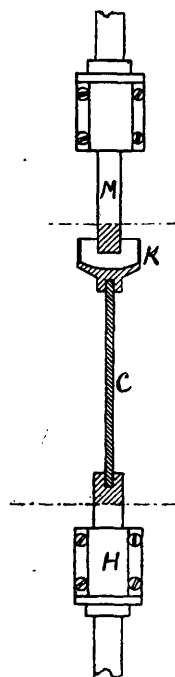
Methane is, of course, stable in larger amounts the lower the temperature, so that apart from the slight disturbance through the traces of ethylene formed, the quantity of methane finally obtained will correspond with the equilibrium at the temperature of the heated carbon.

#### *Part I.—Experiments with Pressures up to 100 Atmospheres.*

*Apparatus.*—This series of experiments were carried out with a pressure furnace designed by Hutton and Petavel (*Phil. Trans.*,

1908, *A*, 207, 428). This apparatus was constructed for investigating reactions produced by the electric arc at high pressures. For the present work it was adapted for heating carbon in the form of a rod, uniformly, and at definitely controlled and measured temperatures between  $1100^{\circ}$  and  $2100^{\circ}$ . The carbon (*C*, Fig. 1), which was 6 to 8 mm. diameter and 8 to 12 cm. long, was inserted in graphite end-pieces, the bottom one of which was clamped by one of the brass electrode holders (*H*). The top graphite piece

FIG. 1.



was turned in the form of a cup (*K*), which was filled with pure graphite powder. A graphite rod (*M*) was fastened in the top clamp, and after the furnace top had been fastened down and the pressure admitted, this electrode could be lowered by screwing down (compare Hutton and Petavel, *loc. cit.*), and a satisfactory electrical connexion established between the carbon rod and the top electrode by means of the graphite in the cup. The temperature was estimated by means of a Wanner optical pyrometer, by sighting through the glass window mounted in the furnace walls.

In a number of the earlier experiments, before admitting the hydrogen, the furnace was exhausted and filled with methane, so as to introduce a small percentage of this gas and accelerate the attainment of the equilibrium value.

#### *Preparation of Materials.*

*Hydrogen.*—This was prepared by acting on zinc (prepared electrolytically) with sulphuric acid (compare Hutton and Petavel, *J. Soc. Chem. Ind.*, 1904, 23, 88), and after washing, the gas was compressed in steel bottles. On analysis it was found to contain 98.0 per cent. of hydrogen and 2.0 per cent. of nitrogen.

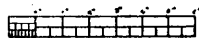
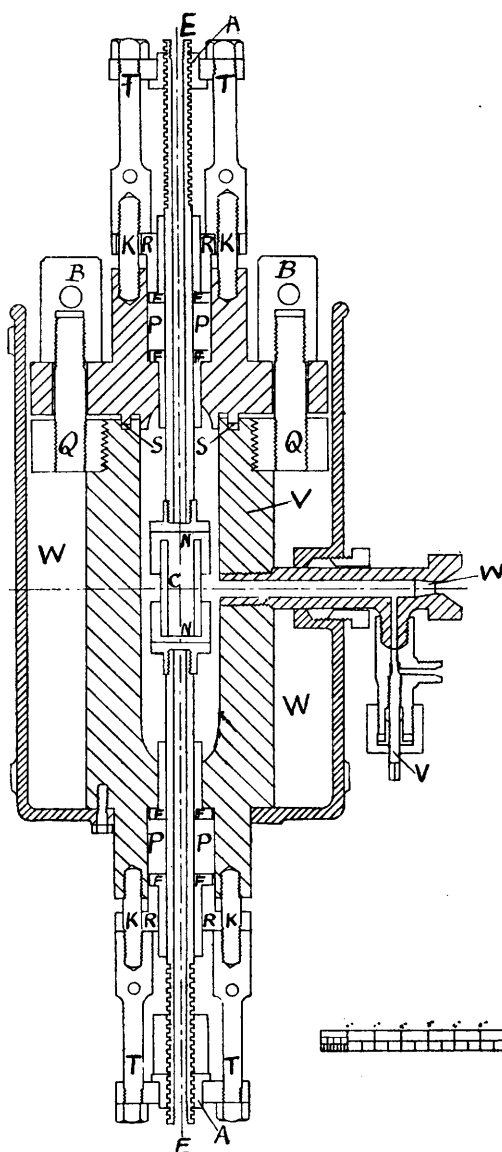
*Carbon.*—This was used in the form of rods of retort carbon, usually 8 mm. in diameter and about 10 cm. long. They contained originally about 2 per cent. of ash (oxides of iron, silicon, etc.) and about 0.2 per cent. of combined hydrogen. They were purified by supporting with water-cooled electrodes in a large glass tubular flask, heating electrically to  $1400$ – $1500^{\circ}$  in a stream of chlorine, and then in hydrogen in the same manner.

When the carbon was used in presence of a catalyst (platinum or

palladium), a layer of either of these metals was coated on the carbon by electro-deposition from a chloride solution before heating in hydrogen.

*Methane.*—This was prepared by decomposing commercial aluminium carbide with water, passing the gas through ammoniacal cuprous chloride to remove acetylene and hydrogen sulphide, and then liquefying with liquid air. After evaporation, the gas was collected over water in a large holder of 20 litres capacity. In some experiments carbon was used which had received no purification treatment beyond heating a short time in the furnace in hydrogen at a high pressure. In all these cases, however, it was estimated that the amount of combined hydrogen present as impurity always corresponded with a quantity of methane well below that subsequently produced in the synthesis.

FIG. 2.



*Part II.—Experiments at Pressures from 100 to 200 Atmospheres.*

In these experiments a new form of pressure furnace of smaller capacity was constructed, and is shown in diagram in Fig. 2. The inner cylinder (*V*) was forged from a piece of nickel steel of high tensile strength. The electrodes consisted of steel tubes (*EE*), which were cooled by water circulation, and contact with the carbon was made by means of nickel clamps (*NN*), which were brazed to the ends of these electrodes. The carbon rods or tubes (*C*) were always fitted into graphite end-pieces (not shown in the diagram), which were held in the nickel clamps. [The tube or rod (*C*) was always longer and narrower than the one shown in the figure.]

The electrodes emerged from the furnace at the stuffing boxes (*PP*). Small tubes of ebonite or fibre (*FF*) insulated the electrodes from the walls of the latter. Asbestos cord mixed with a little tallow or wax was used as the packing material for the boxes (*PP*), and was compressed by the brass rings *RR*, which were forced down on to the ebonite rings by six bolts, as at *KK*. The outward thrust of the electrodes was secured by the bolts (*TT*), of which there were two at each end of the furnace. The top part of the furnace was fastened down by six bolts as at *BB*, and a gas-tight joint was made by means of the lead spigot *SS*. By opening the bottom stuffing-box and removing the packing, the bottom electrode could be lifted while clamped to the carbon rod and top electrode, and removed with the furnace top. Water circulation was provided in the annular jacket *W*. The glass window, *X*, was placed at a sufficient distance to be protected from the heat of the carbon.

Temperature readings were made by means of the light radiated from the carbon, after passing through the window and being reflected from a mirror placed in front of the window at an inclination of 45°. The window could, as a rule, be safely used up to 200 atmospheres, and the remainder of the furnace was capable of withstanding a pressure of 1000 atmospheres.

The carbon used at *C* consisted of amorphous retort carbon in the form of tubes about 12 cm. long and either 20 mm. external and 15 mm. internal diameter or 15 mm. external and 9 mm. internal diameter.

In some experiments rods of (Acheson) graphite were used, 12 cm. long and 9 mm. diameter.

With amorphous carbon, after mounting in the furnace, a partial purification was obtained by giving a preliminary heating to about 1400° in hydrogen at about 50 atmospheres pressure, and then liberating and renewing the gas. As mentioned above, the quantity

of combined hydrogen present as impurity was always well below the large amount of methane subsequently synthesised.

The capacity of the furnace was about 750 c.c. In experiments at 100 atmospheres, where, say, 10 per cent. of methane was formed, this would involve the synthesis of about  $7\frac{1}{2}$  litres (at N.T.P.) of this hydrocarbon.

On account of the corrosion of the carbon, it was not as a rule possible to use the same carbon in more than one experiment. In the course of a large amount of work where carbon rods and tubes have been heated electrically at atmospheric pressure under different conditions, it has been found that the heating of the carbon always takes place with great uniformity throughout the whole length when the amorphous variety is used. This is on account of the negative temperature-coefficient of resistance. With graphite, however, the temperature falls a little near the cold ends of support.

*Analysis of Gases.*—The gas obtained in these experiments, which contained from 1 to 20 per cent. methane, was analysed in the Sodeau apparatus. After complete removal of carbon monoxide and any unsaturated hydrocarbons, a fractional combustion of the hydrogen by means of oxygen in presence of palladium-black was usually applied (compare Pring and Fairlie, *Trans.*, 1911, **99**, 1796). The saturated hydrocarbon could then be estimated and identified by the relation found between the contraction after exploding with oxygen, and the volume absorbed by potassium hydroxide solution. In all these cases methane was, at all temperatures, found to be the only saturated hydrocarbon produced.

In an experiment carried out at  $1275^{\circ}$ , an examination was made for traces of ethylene by circulating a large quantity of the gas (25 litres) through a tube cooled in liquid air. Most of the methane was thus condensed, together with the whole of any ethylene present. This liquid was then allowed to evaporate slowly, and the last portion was passed through a tube containing carefully purified cocoanut charcoal. A further fractional separation was here carried out (compare *ibid.*, p. 1802), and the last portion of 50 c.c. on analysis was found to contain 0.51 c.c. ethylene, or 0.002 per cent. of the total gas. As the amount of methane formed was 21 per cent., the ratio of ethylene to the latter is lower than that found at atmospheric pressure (*ibid.*, p. 1806), but the method of fractionation used could only serve for a rough measure of the actual quantity of ethylene present.

On account of the difficulty of accurately estimating nitrogen, the following method was adopted. In experiments in Part I, the hydrogen on being analysed several times was found to give a mean

value of 2.0 per cent. for the nitrogen content. In Part II the hydrogen used was commercial electrolytic, and was found to contain 0.2 per cent. nitrogen as the mean result of several analyses. These mean values were taken in considering the results of subsequent experiments.

*Change of Pressure.*—The formation of methane, proceeding according to the equation  $C + 2H_2 = CH_4$ , is accompanied by a contraction of volume equivalent to the volume of methane formed. In these experiments this was equivalent to a change of pressure. Consequently, by reading the pressure indicated by the gauge, the course of the reaction could usually be followed, and the attainment of equilibrium recognised. With the first type of pressure furnace (Part I) it was not possible to keep the enclosure quite gas-tight when used for long intervals on account of the gradual heating of the electrodes by the heavy currents used. This softened the packing in the stuffing-boxes, and caused leakage. With the second type of furnace this trouble was obviated by the use of the water-cooled electrodes. In this case, however, a considerable time was necessary for the mean temperature of the enclosure to become constant on account of the large quantity of metal present. In many experiments samples of gas were withdrawn during the heating at different intervals, and analysed, in order to ascertain when equilibrium had been reached.

The results of all successful experiments which were carried out are tabulated below in the order of temperature. All those at pressures below 100 atmospheres were conducted in the first type of furnace, as described in Part I (p. 93), and those at pressures of 100 atmospheres and above in the second type (Part II, p. 96).

It is seen in all cases that where amorphous carbon was used an amount of methane was given which gradually fell on continuing the heating, and finally approached a stationary value, the same as that given in the first place with graphite.

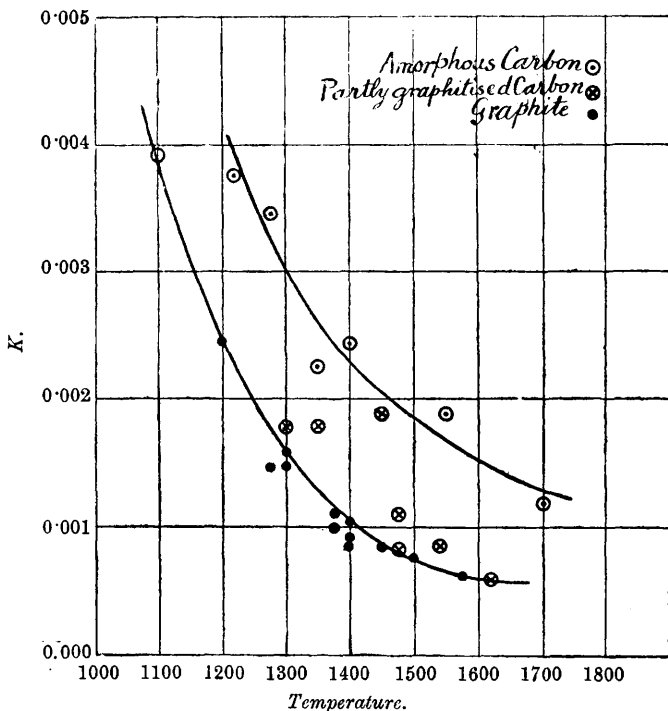
This fall in the quantity of methane always took place *pari passu* with the gradual change of amorphous carbon into graphite, and was more rapid the higher the temperature.

When the carbon was purified by heating in chlorine for a few hours at 1400° to 1500°, it was observed to have undergone a partial transformation into graphite, and when use was made of this the quantities of methane were always intermediate between those obtained with unpurified amorphous carbon and graphite. The presence of platinum or palladium on the surface of the carbon, on the other hand, did not appear to accelerate the change into graphite.



In table I below are given the values for amorphous carbon, which in some cases was impure, and in others had been partly purified in chlorine at a temperature too low to cause any appreciable change into graphite. In table II are given the experiments done with graphite. This was either Acheson graphite or else carbon which had previously been heated for a long interval at a high temperature in hydrogen, or else had been purified at a high

FIG. 3.



temperature in chlorine so as to cause transformation into graphite. The carbon in all these cases was practically pure.

In table III are given the experiments with carbon which, by previous heating or purification, had become partly transformed into graphite. The results are also plotted in the form of curves (Fig. 3), where the ordinates denote the equilibrium constants, and the abscissæ the temperatures.

The values obtained in experiments at temperatures above about 1700° do not represent equilibrium quantities, as the methane in these cases is formed chiefly by the reaction of ethylene and

acetylene in the cooler parts of the vessel. The results at these higher temperatures are consequently not plotted in the figure.

TABLE I.

*Amorphous Carbon. First Time of Use.*

Nature of carbon.	Temperature.	Pressure Time. (atms.).	Percentage composition.			$K = \frac{p\text{-CH}_4}{p\text{-(H}_2\text{)}^2}$		
			CO.	CH <sub>4</sub> .	C <sub>2</sub> H <sub>2</sub> .		C <sub>2</sub> H <sub>4</sub> .	
Purified. Pt. coated	1100°	0	—	4.10	—	—		
		2½ hrs.	20	1.1	6.35	—	0.00390	
Impure. Pt. coated	1220	0	—	4.1	—	—		
		3 „	18	1.4	5.6	—	0.00376	
Partly purified.....	1275	3 „	100	0.25	21.5	—	0.00359	
Impure. Pt. coated	1350	1 hr.	166	0.6	18.5	—	0.00173	
		2½ hrs.	153	0.7	20.9	—	0.00224	
Purified. Pt. coated	1400	0	—	4.35	—	—		
		1½ „	18	0.92	3.86	—	0.00245	
Same carbon as above (To show effect of progressive graphi- tisation) .....	1400	1½ „	19	1.0	2.35	—	0.00138	
		3 „	18.5	1.4	1.98	—	0.00120	
		4½ „	17.5	3.3	1.28	—	0.00084	
Impure .....	1550	0	—	4.65	—	—		
		1½ „	21	1.5	3.49	—	0.00188	
„ .....	1620	20 mins.	20	3.7	1.0	—	0.00058	
„ Pt. coated	1700	1 hr.	15	7.5	1.4	nil	0.00120	
„ .....	1775	4 hrs.	117	1.6	9.0	0.1	—	
„ .....	1950	7 mins.	24.5	3.4	2.4	0.29	0.44	—
„ .....	2050	7 „	23	2.8	2.8	0.74	1.10	—
Purified.....	2100	0	—	5.5	—	—	—	
		15 „	25	5.5	2.6	0.25	?	—

TABLE II.

*Graphite.*

Nature of graphite.	Temperature.	Pressure Time. (atms.).	Percentage composition of gas.		$K = \frac{p\text{-CH}_4}{p\text{-(H}_2\text{)}^2}$	
			CO.	CH <sub>4</sub> .		
Acheson .....	1200°	2½ hrs.	105	0.0	17.5	0.00244
Carbon graphitised by heating. Pt. coated.	1275	0	—	—	2.38	—
		25 mins.	37	1.6	4.23	0.00133
		1½ hrs.	32	2.4	4.02	0.00147
Carbon graphitised by heating. Pd. coated.	1300	½ hr.	37	0.6	4.69	0.00120
		1 „	35.5	1.0	4.55	0.00146
Acheson .....	1300	1 „	117	0.0	11.2	0.00126
Carbon graphitised by heating .....	1375	2½ hrs.	106	0.0	12.6	0.00158
		1 hr.	28	1.4	2.5	0.00100
Acheson .....	1375	3 hrs.	115	0.2	10.6	0.00117
Graphitised by heating. Pd. coated.	1400	0	—	—	2.4	—
		¼ hr.	46	0.1	3.90	0.000945
Graphitised by heating. Pt. coated.	1400	1½ hrs.	46	0.2	4.29	0.00103
		0	—	—	1.6	—
Same carbon as above ...	1400	1½ „	50	1.8	3.99	0.00089
		0	—	—	1.6	—
„ .....	1400	½ hr.	55	0.5	4.24	0.00080
		1½ hrs.	48	1.0	3.71	0.00089

TABLE II (continued).

Nature of graphite.	Tem- perature.	Time.	Pressure (atms.).	Percentage com- position of gas.		$K = \frac{p\text{-CH}_4}{p\text{-(H}_2\text{)}^2}$
				CO.	CH <sub>2</sub> .	
Carbon graphitised by heating. Pt. coated.	1450	0	—	—	2.3	—
		20 mins.	47	2.0	3.39	0.000843
		1 hr.	44	2.4	3.01	0.000746
Carbon graphitised by heating. Pt. coated.	1500	0	—	—	1.8	—
		½ „	55	0.8	3.96	0.00080
		1 „	52	1.2	3.62	0.00077
Carbon graphitised by heating. Pt. coated.	1575	0	—	—	—	—
		12 mins.	52	0.7	2.94	0.00063
		1½ hrs.	44	1.0	2.46	0.00062

TABLE III.

*Partly Graphitised Carbon.*

Nature of carbon.	Tem- perature.	Time.	Pressure (atms.).	Percentage com- position of gas.		$K = \frac{p\text{-CH}_4}{p\text{-(H}_2\text{)}^2}$
				CO.	CH <sub>4</sub> .	
Purified .....	1300°	1½ hrs.	7	7.3	1.0	0.00178
Impure. Pt. coated.....	1350	2 „	11.5	5.75	1.71	0.00178
Purified. „ .....	1450	1¼ „	136	0.3	17.1	0.00186
Impure. „ .....	1475	1¼ „	177	0.3	16.7	0.00187
		4½ „	155	0.3	11.9	0.00101
Impure.....	1475	1¼ „	200	0.05	13.1	0.00087
		3¼ „	200	0.25	12.4	0.00083
Impure.....	1540	1½ „	183	0.05	12.0	0.000860

*Results and Conclusions.*

The reaction between carbon and hydrogen resulting in the formation of methane was found to proceed with increased velocity at high gaseous pressures. Using carbon in the form of a compact rod or tube, and either in presence or absence of a catalyst, the equilibrium stage was reached in about two hours, when the temperature was 1200—1300°, and the pressure 30 to 50 atmospheres. Above 1400°, equilibrium was reached in about fifteen minutes under the same conditions. At 200 atmospheres the reaction was still more rapid.

These results indicate the probability that carbon in a fine state of division would at still higher pressures combine with hydrogen with extreme rapidity, as the reaction is exothermic. In this way, the preparation of methane might most conveniently be carried out on a large scale. No saturated hydrocarbon but methane is formed at any temperature between 1100° and 2100° or pressure up to 200 atmospheres. The relative amount of methane produced increased with the pressure to the extent demanded by the law of mass action as applied to the reaction  $C + 2H_2 = CH_4$ . According to

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this, the value  $\frac{p\text{-CH}_4}{p\text{-(H}_2\text{)}^2}$  should be constant at any given temperature.

In all experiments at pressures varying from 10 to 200 atmospheres, a value which was constant within the limits of experimental error was always obtained for this ratio at any particular temperature and when the same modification of carbon was used.

In some experiments where an amount of methane in excess of this value was added to the gas beforehand, decomposition took place until the same final value was obtained. Consequently, this represents the true equilibrium constant.

The amount of methane which at atmospheric pressure is in equilibrium with hydrogen and graphite is at 1200° equal to 0.24 per cent., and at 1500°, 0.07 per cent. For amorphous carbon the "metastable equilibrium" values are 0.36 per cent. at 1200° and 0.21 per cent. at 1500°.

The values for amorphous carbon are not so definite as those for graphite on account of the gradual transformation which the former undergoes into the latter at the temperatures used in these experiments.

The results definitely show, however, that the change of free energy in the transformation of carbon into graphite increases rapidly in the range of temperature between 1200° and 1600°.

It follows from this by the application of Kirchhoff's law relating to heats of reaction and specific heats, that the mean specific heat of amorphous carbon must be much higher than that of graphite between 0° and 1200°, and that this difference increases with the temperature. This shows that the values obtained for the specific heat of carbon by Kunz (*Ann. Physik*, 1904, [iv], 14, 327) and of graphite by Weber (*Ber.*, 1872, 5, 303) are relatively not applicable at these temperatures. According to these values, in which the specific heat of graphite is at all temperatures above 100° higher than amorphous carbon, it would follow from Kirchhoff's law that the latter modification of carbon is at all temperatures more stable than the former. Hence, the specific heat of carbon must increase with temperature more rapidly than that of graphite.

The values for the equilibrium constants obtained in this work will probably serve for a more accurate determination of the relative specific heats of carbon and graphite, and of carbon, hydrogen, and methane at these high temperatures, than is possible by any direct method of measurements.

This calculation is possible from the formula of van't Hoff showing the relation between the equilibrium constant, temperature, and heat of reaction, and by applying the law of Kirchhoff.

The formation of traces of ethylene has been observed at a

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temperature as low as  $1275^{\circ}$  (0.002 per cent. of the total gas when the pressure was 100 atmospheres). This quantity could not exert any noticeable effect on the methane yield, which in this particular experiment amounted to 21.5 per cent.

At temperatures between  $1800^{\circ}$  and  $2100^{\circ}$ , no appreciable effect was exerted by high pressures on the yield of acetylene and ethylene when the results are compared with those obtained in earlier work (*loc. cit.*) at atmospheric pressure.

We are indebted to Dr. R. S. Hutton for his kind assistance in the early stages of this work. Part of the expense incidental to the construction of the pressure furnace has been borne by a grant from the Research Fund of the Royal Society.

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