

CXLI.—*The Thermal Decomposition of Methane.*
Part I. Decomposition in Silica Bulbs.

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THE static experiments upon the decomposition of methane described in this paper form part of an investigation of the secondary reactions of coal carbonisation in gas retorts which is proceeding in the laboratories of the Gas Light and Coke Co. At an early date it is hoped to publish the results obtained by the streaming method to which reference is made, and then to discuss the bearing of the work upon industrial practice in gas manufacture.

Although much attention is at present being paid to the synthesis of higher hydrocarbons (Fischer, *Brenn. Chem.*, 1928, 9, 309; Wheeler and Wood, *Fuel*, 1928, 7, 535) from methane, the literature gives very little information with regard to the rate of decomposition of the gas. With certain catalysts the reaction appears to be a straightforward unimolecular one (Schwab and Pietsch, *Z. physikal. Chem.*, 1926, 121, 189), whereas on other surfaces the order is uncertain (Bone and Coward, *J.*, 1908, 93, 1197). Our experiments have been chiefly confined to surfaces of silica, coke, and retort graphite, and have shown that under these conditions the decomposition is by no means so simple as might be expected, for between 900° and 1200° the initial velocity of decomposition is very great but later becomes so strongly retarded that for all practical purposes a condition of false equilibrium, far removed from the theoretical, is set up.

EXPERIMENTAL.

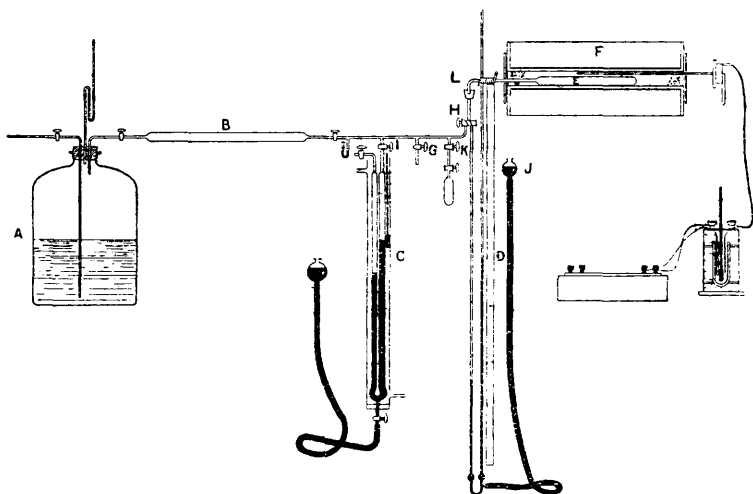
Fig. 1 shows the apparatus used. It consists of a reservoir for methane A, a phosphoric oxide drying tube B, a measuring burette C, a manometer D, and a clear silica bulb E, heated to the required temperature in the double-wound nichrome furnace F. The temperature of the bulb over its whole length could be kept constant within 1—2°.

To carry out a run, dry methane was first passed into C, the bulb evacuated *via* tap G, tap H closed, tap I opened, and the volume of methane in C read. Tap H was opened and methane allowed to enter the bulb. Tap H was then turned through 180° and the mercury raised by means of the reservoir J to the constant-volume mark L, above the ground joint. Readings could then be taken at intervals showing the increase of pressure resulting from the dissociation. A first reading could be obtained within a minute of the entry of gas into the bulb. The initial pressure P_0 was calculated from the amount of methane admitted and the volume of the bulb,

previously determined by calibration with nitrogen. Before the second reading in C was taken, the capillary in tap H was filled with mercury. At the end of the run a sample of the resulting gas could be taken *via* taps K and H.

Temperatures were accurately controlled by means of a platinum-platinum-rhodium thermocouple with its cold junction in ice. The capacity of the bulbs varied from 130 to 150 c.c. The results are corrected where necessary for hydrogen diffusion, which was, however, negligible at 900° and still very small at 1000° and 1100°, owing to the thickness of the silica used. Agreement between pressure measurements and gas analysis was usually within 1%.

FIG. 1.



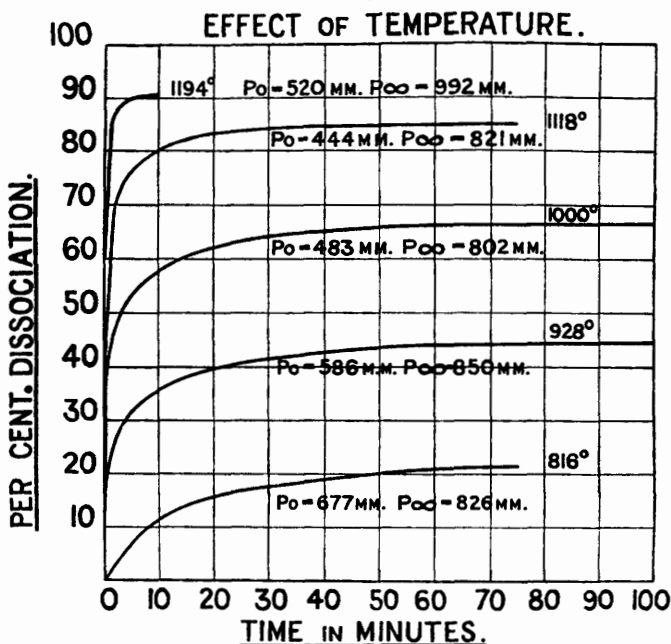
Bulbs were coated with methane carbon in all cases before the commencement of a series of runs.

Preparation of Methane.—In the early experiments methane was prepared from aluminium carbide. The crude gas was purified by passing it at a rate of 2 litres per hour successively through ammoniacal cuprous chloride, 50% sulphuric acid, 50 cms. of copper oxide contained in a tube heated to 270°, alkaline sodium hydrosulphite, and 50% potassium hydroxide. Gas of 99% purity, the remainder being chiefly nitrogen with a trace of hydrogen, can be prepared in this way. In the later experiments, cylinder methane supplied by Messrs. Insoles, Ltd., of Porth, was purified by fractionation in liquid air, and a gas of 99.9% purity obtained. Gas prepared in both ways gave precisely the same results.

Results.—Fig. 2 shows a few results obtained in a bulb of volume

129.6 c.c. and internal surface 194.8 sq. cm. It will be seen that in all cases there is a very rapid initial decomposition followed by extremely slow dissociation and that the percentages of methane remaining for all practical purposes stable after some 60 minutes are very much greater than we should expect from the true equilibrium values (see later). Two experiments at 900° show how slowly the methane is decomposing in the later stages. Beginning in each case with 660 mm., there remained after 113 minutes 41.9% and after 342 minutes 38.2% of methane, *i.e.*, less than 1% of methane

FIG. 2.



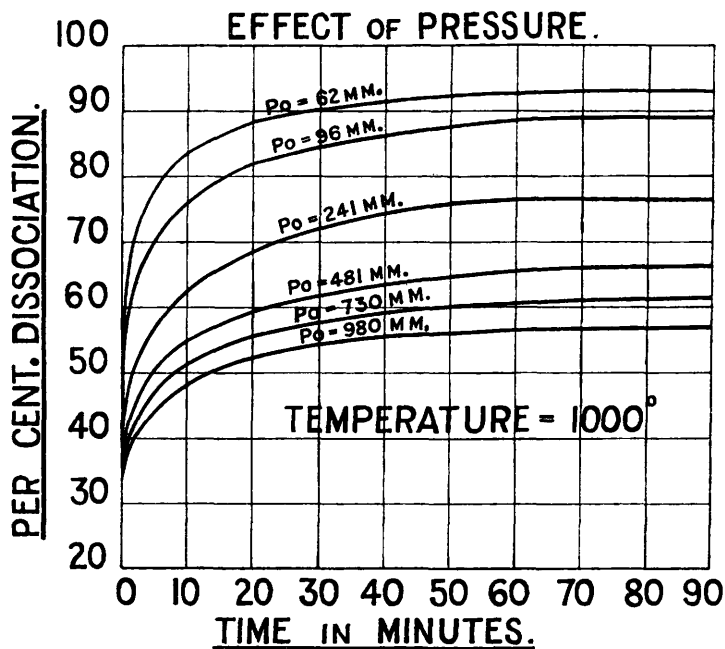
disappears per hour. Similarly at 1000° with an initial pressure of 540 mm. in each case, 1.5% of methane decomposed per hour in the later stages.

Effect of Pressure.—Some preliminary experiments at 900° showed that the lower the initial pressure the greater is the final amount of dissociation. A series of careful experiments at 1000° was then carried out and Fig. 3 shows the results obtained when the initial pressure varied from 60 to 980 mm. The curves again have the appearance of true dissociation equilibria, *i.e.*, higher dissociation at lower pressures.

Effect of Added Hydrogen.—Experiment showed that hydrogen

added initially behaves in the same way as that produced by dissociation, whether it is mixed initially with the methane or introduced previously into the bulb. If the initial mixture corresponds to some point on the first part of the curve, the rate is exactly the same as if dissociation of pure methane had already reached a point corresponding to the initial mixture. If more than the "equilibrium" amount of hydrogen is present initially the curve is practically a straight line and the methane decomposes extremely

FIG. 3.



slowly (Fig. 4). It will be noted, however, that no synthesis back to the "equilibrium" value occurs with excess of hydrogen.

Effect of Other Gases.—Nitrogen and carbon monoxide have no effect on the rate or on the final amount of dissociation if the initial partial pressure of methane is the same. At a constant total pressure, however, they act as diluents and, by reducing the partial pressure of methane, increase the percentage decomposition.

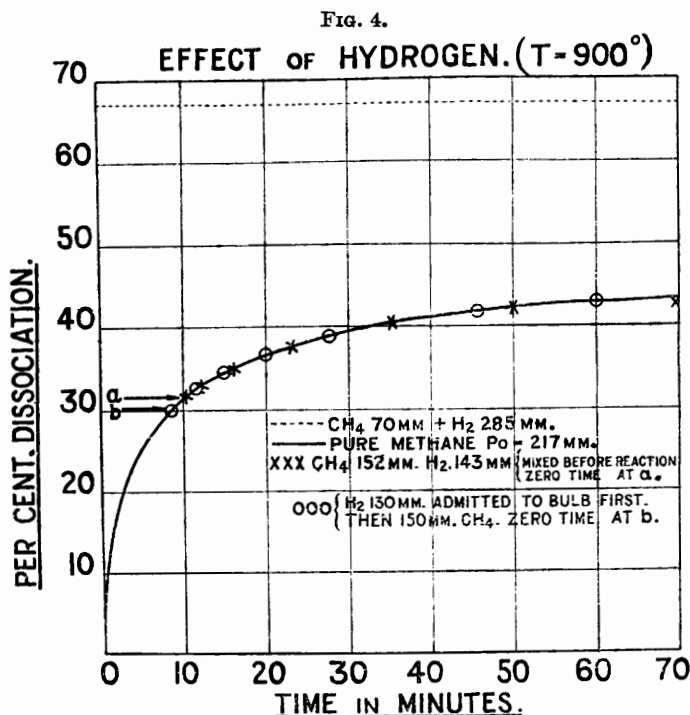
Discussion.

All the experimental results suggest a reaction approaching an equilibrium which, however, bears no relation to the true reversible equilibrium in the presence of special catalysts. Saunders's

equation (*J. Physical Chem.*, 1924, 28, 1151) for the true equilibrium of methane and hydrogen in contact with graphite, *viz.*,

$$\log K_p = 4008/T - 1.75 \log T + 0.00063T - 0.7,$$

agrees fairly well with the results obtained by Pring and Fairlie (*J.*, 1912, 101, 91). The true equilibrium amounts of methane, calculated from this equation for the temperatures and final pressures shown in Fig. 2, are given in Table I (E_{CH_4} , col. 3). The



actual amounts of methane, e_{CH_4} , remaining in the experiments are shown in col. 4, and it will be seen that they are very much greater than the true equilibrium values.

TABLE I.

Temp.	Total pressure (mm.) after 60 mins.	E_{CH_4} (mm.).	e_{CH_4} (mm.).
816°	819.2	19.0	534.8
928	845.3	9.3	326.7
1000	799.3	5.6	166.7
1118	820.6	3.2	66.4
1194	(992)*	3.4	48.0

* After 10 minutes.

It is clear that the decomposition is not a simple unimolecular reaction, proceeding simply to the true final equilibrium point. The apparent equilibria are due possibly to two causes: (1) The solid deposited by methane may not be pure carbon but a high hydrocarbon with a greater vapour pressure than carbon, in which case the equilibrium concentrations of methane would be higher (compare equilibrium of carbon monoxide, carbon, and iron oxide with different forms of carbon; Schenk and Heller, *Ber.*, 1905, **38**, 2139). (2) The reaction is being very strongly retarded by selective adsorption.

Since synthesis from hydrogen and the solid deposited by previous decomposition of methane could not be effected to the extent required by the "equilibrium" value, and since the "equilibrium" values vary with the extent of the surface (unpublished results), the first explanation is not valid. The second, however, appears to be the true one. Hinshelwood ("Kinetics of Chemical Change in Gaseous Systems," p. 158; *J.*, 1925, **127**, 1114) has given examples of retardation, and shows that the lower the initial pressure the greater the velocity of reaction (compare nitrous oxide and ammonia). Our experiments show that the retardation in the case of methane is extremely strong and is almost certainly due to the preferential adsorption of hydrogen, which finally protects the surface so efficiently that further decomposition of methane is practically prevented.

A glance at the velocity curves shows that at most of the temperatures used the greater part of the reaction is over before the first reading can be taken. Thus it is not yet possible to determine the order of the reaction or the complete velocity equation, which will probably involve hydrogen as a retarding factor to some power of its concentration. Experiments are in progress on the course of the rapid reaction at low pressures, and it is hoped that these will throw light on the present results.

Whatever the final form of the velocity equation, the similarity between the "equilibrium" values and true equilibria is remarkable. In fact, if the concentrations of hydrogen and methane remaining after one hour are regarded as true equilibrium values, the results shown in Fig. 3 give a fairly good constant for the expression $p_{\text{CH}_4}/p_{\text{H}_2}^2 = C$, which means that the amount of initial decomposition on a given surface for any pressure of methane can be calculated from one result. If P_0 is the initial pressure of methane, and P_∞ the total pressure after 1 hour, then the values of C at a temperature of 1000° (Table II) are seen to be approximately constant over the range 60—980 mm. for P_0 .

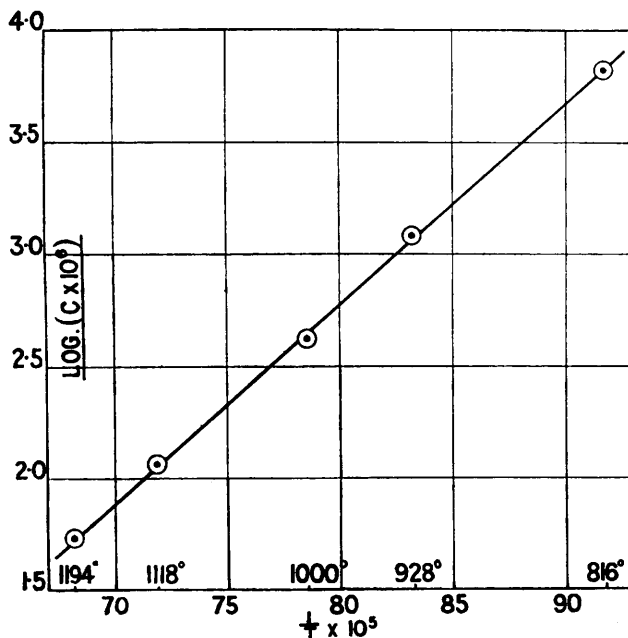
Further, if C is found for the results at different temperatures

TABLE II.

P_0 (mm.).	P_∞ (mm.).	p_{CH_4} .	p_{H_2} .	$C \times 10^7$.
62	119.4	4.6	114.8	3491
96	181.0	11.0	170.0	3807
241	425.6	56.4	369.2	4139
481	796.1	165.9	630.2	4179
730	1171.7	288.3	883.4	3694
980	1533.7	426.3	1107.4	3477

shown in Fig. 2 and $\log C$ is plotted against temperature, a straight line is obtained (Fig. 5), again showing close analogy with a true equilibrium reaction. For a given surface, therefore, the amount

FIG. 5.



of rapid dissociation of methane at any pressure and temperature can be calculated from two results at different temperatures. There is at present no theoretical justification for the constant C , but it is likely to be of practical use.

Ethane.—The following experiment shows that methane and hydrogen resulting from the decomposition of ethane exhibit the same retardation as methane itself, and give the correct C value for the temperature and pressure of the experiment. 297 M.m. of ethane containing 3.4% of nitrogen were admitted to a bulb of very nearly the same size as that used for methane. The temperature

was 929°. The decomposition initially was extremely rapid but practically stopped when the total pressure was 663 mm. Analysis of the residual gas gave 29.8% CH₄, 68.7% H₂, and 1.5% N₂. Assuming that the methane and hydrogen are in equilibrium, and calculating *C* from their partial pressures, we find that log (*C* × 10⁶) is 2.9807, which lies very close to the same value for methane at 929°, viz., 3.05 (Fig. 5).

Experiments on Porcelain.—A porcelain bulb of approximately the same size as the silica bulbs was used for a few experiments at 1000°. In all cases the retardation was just as marked, and the "equilibrium" values almost exactly the same as those obtained on silica.

Experiment with a Nickel Catalyst.—One of the silica bulbs used in the previous runs was coated with nickel by decomposition of a solution of the nitrate and reduction in the bulb itself. At 900° the velocity of decomposition of the methane was enormously increased, no retardation taking place. Only 3% of methane remained after 18 minutes, showing that the true equilibrium point was being rapidly approached.

Effect of Surface.—Previous workers have assumed that at least up to 1300° the decomposition of methane is a purely surface reaction, but very little quantitative evidence is given. If a gas reaction and a surface reaction are occurring simultaneously, differentiation can usually be achieved by measuring velocities on surfaces of different areas, and the value of the velocity coefficient found by extrapolation to correspond to a zero value for the ratio surface : volume is the coefficient for the homogeneous reaction. An attempt was made to determine the influence of surface. A silica bulb packed with thin silica tubing and sealed into a larger silica bulb was used, the outer bulb serving as a jacket of hydrogen to prevent diffusion entirely. The results in this bulb, however, were disappointing, the analyses diverging considerably from the pressure readings. Experiments with pure hydrogen showed that the velocity of decomposition was being masked by rapid solution of hydrogen in the silica packing, the rate of which was of the same order as the decomposition itself and affected the pressure readings in the reverse direction by lowering the total pressure. The amount of hydrogen absorbed increases as the temperature is raised and is directly proportional to the total hydrogen pressure. At 900°, 6.4% of the pressure of hydrogen was absorbed by 105 g. of silica packing in a bulb in which the free space was 51.8 c.c.; at 1000°, 10.6%; and at 1100°, 16%, most of the absorption being complete in 10 minutes in all cases. It will be seen that such absorption would seriously affect the accuracy of velocity determinations carried out under the above conditions

and with the object specified; it was therefore necessary to use a streaming method to find the effect of surface, and the results obtained will be published shortly.

Summary.

(1) The decomposition of methane on silica at temperatures between 800° and 1200° has been studied.

(2) Retardation is so strong in all cases that for practical purposes a false equilibrium is obtained.

(3) Results obtained over a wide range of pressures show that values of $p_{\text{CH}_4}/p_{\text{H}_2}^2$ are constant, and the effect of temperature on the constant is exactly analogous to its effect on true equilibria.

(4) Similar results are obtained on porcelain.

(5) Ethane decomposes to give the same "equilibrium" mixture of methane and hydrogen.

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