CCXVIII.—*The Thermal Decomposition of Methane. Part II. The Homogeneous Reaction.*

By G. C. Holliday and W. J. Gooderham.

The work described in Part I (J., 1929, 1066) has been continued, and the results set out in the present paper indicate that the initial rapid decomposition of methane, for which no satisfactory explanation has hitherto been given, takes place throughout the body of the gas irrespective of the extent of surface.

Static Experiments.—In Part I it was shown that the decomposition of methane in silica bulbs is incomplete at temperatures between 800° and 1200°, and that the final percentage decomposition at a given temperature decreases with increase of pressure. It was suggested that the reaction $CH_4 = C + 2H_2$, if a surface one, must be very strongly retarded by adsorbed hydrogen.

Attention was drawn to the fact that hitherto the reaction has been assumed, on rather scanty experimental evidence, to take place entirely on the surface, at least up to 1300°.

Bone and Coward (J., 1908, **93**, 1201, 1208) held the view that the reaction was chiefly a surface one, on the grounds that methane always gives a hard carbon and that when a porcelain tube was packed with lime the velocity of decomposition was considerably greater than that obtained in the plain tube. It is now well known that methane can give different types of carbon, and Slater (J., 1916, **109**, 160) has shown lime to be a catalyst. No previous worker, as far as we know, has investigated the reaction on different measured surfaces of the same material. The experiments described in Part I gave no information on this point, since they were carried out in bulbs of the same size. To study the effect of surface, silica bulbs of different sizes (Table I) have now been used, the decomposition being brought about as before, except that the pressure of gas admitted initially into the bulb was measured by the fall in pressure in a constant-volume reservoir and not by decrease of volume in a burette.

TABLE I.

Bulb.	Surface, cm.^{2}.	Volume, c.c.	Surface/volume.
3a	758·0	321·0	2·36
1	266·0	152·3	1·75
2	87·0	56·2	1·55
3	240·0	429·5	0·56

After being used for several experiments, bulb 3 was broken open at the capillary joint, 54 smooth clear silica rods, each 2·55 × 0·5 cm., were inserted, and the bulb was re-sealed : this is bulb 3a in the table.

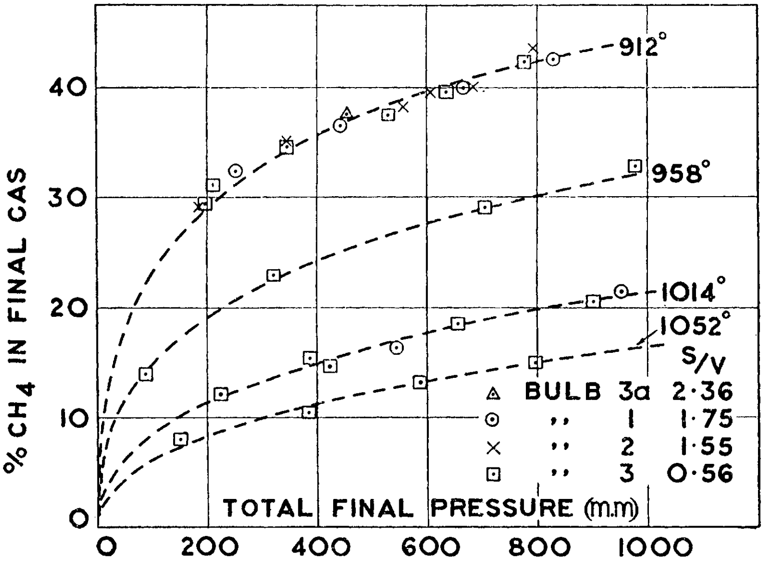
If the decomposition takes place wholly on the surface of the heated vessel, we should expect both the final amount and the velocity of decomposition to increase with increase in the ratio of surface to volume, *i.e.*, bulb 3a should give more rapid decomposition and higher " equilibrium " points than bulb 3. The results, however, showed that at the same final pressure the final concentrations of methane and hydrogen were the same in all the bulbs after one hour's heating at a given temperature. Some of the experiments in the large bulb 3 at the higher temperatures were carried out with a mixture of 70% methane and 30% hydrogen, since it was found that small amounts of polymerides, *e.g.*, naphthalene, were condensing in the cooler capillary and, by being carried into the bulb with the initial methane, sometimes caused a discrepancy between gas analysis and pressure readings. The gas analyses and the final pressure readings in the bulb, however, give the true figures for the percentage decomposition, since the concentrations of hydrogen and methane in the final gas at the same final pressure were always the same whether pure methane or the mixture had been used.

The results definitely showed that the variation in the surface/

volume ratios had no effect on the end point, and Fig. 1 summarises the values obtained. The final percentage of methane is plotted against the total final pressure ($p_{H_2} + p_{CH_4}$). In examining these new data it was found that the constant $C = p_{CH_4}/p^2_{H_2}$ mentioned in Part I, did not represent the results accurately enough at the lower temperatures and pressures but that a new constant $C' = p^2_{CH_4}/p^3_{H_2}$ gave close agreement at all temperatures and pressures studied.

The broken lines are calculated from the constants $1{\cdot}17 \times 10^{-3}$ at 912°, $3{\cdot}36 \times 10^{-4}$ at 958°, $9{\cdot}38 \times 10^{-5}$ at 1014°, and $4{\cdot}61 \times 10^{-5}$ at 1052° (the partial pressures being expressed in mm.), and show the close agreement with the experimental data. Further, log C, when plotted against temperature, gives a straight line, so the analogy with true equilibria still holds good. The significance of the constant C' is discussed later.

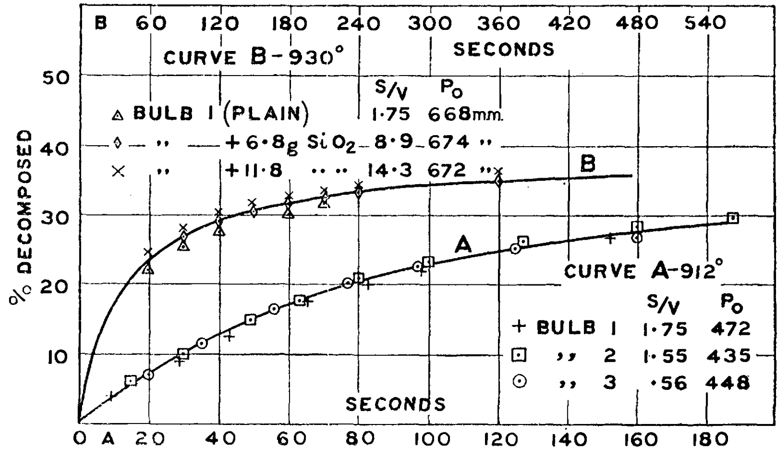
Fig. 1.



Effect on Initial Velocity.—Curve A, Fig. 2, shows the results obtained in three different bulbs (Nos. 1, 2, and 3) at 912° with approximately the same initial pressures, *viz.*, 472, 435, and 448 mm. respectively. The effect of increased surface appears to be negligible. Similar results were obtained with initial pressures of 130, 350, and 600 mm.

Curve B, Fig. 2, represents results obtained at 930° with a plain bulb (No. 1), and also with the same bulb packed with 6·8 g. and with 11·8 g. of silica powder. The powder was ground to pass through an 80 and remain on a 100 mesh I.M.M. sieve, and the surface was calculated on the assumption that the granules were small spheres: this, no doubt, greatly underestimates the area exposed, apart from the possibility that the sharp edges might be more active than smooth silica. The calculated figures for the ratio surface/volume in the three cases were 1·75, 8·9, and 14·3, but these differences had little effect on the initial rate although the curves rise more steeply with the larger surfaces during the later part of the reaction (not shown). It should be noted that with the small weights of silica used in these experiments a negligible amount of hydrogen would dissolve in the powder (see Part I).

FIG. 2.



This was shown to be the case, since the final gas analyses and pressure readings agreed exactly, and this would not be so if hydrogen had been appreciably dissolved.

These later experiments therefore prove that a four-fold variation in surface/volume ratio does not affect the initial velocity or end-point, and with silica powder an eight-fold variation does not affect the initial velocity but gives greater final decomposition with larger surface. The results suggest the presence of both a homogeneous and a surface reaction. In order to elucidate this further, experiments were carried out in a streaming apparatus.

Streaming Experiments.—A number of tubes ranging from 2 mm. to 63 mm. in diameter both packed and unpacked were used. As in the static experiments described in Part I, the reaction rate in all cases becomes negligible in the later stages before the true methane equilibrium is reached. The end-points, however, vary with the surface employed but bear no simple relationship to it. Though the effect of surface on the later stages of the reaction is not yet clear, the presence of a homogeneous reaction is definitely shown by the results obtained during the initial decomposition. This is evident from the Table II, where the time of heating for 32% decomposition at 1000° is seen to be practically constant although the surface/volume ratio varies from 0·8 to 93·0.

TABLE II.

		Heated zone.				
Type of tube or packing.	Intl. diam., mm.	Length, cm.	Surface, cm.^{2}.	Vol., cm.^{3}.	S/V.	Time (secs.) for 32% decomp.
20—30-Mesh silica	20·0	15	2139	23·0	93·0	12½
20—30-Mesh silica	20·0	7	896	11·7	76·6	12½
10—20-Mesh silica	5·0	14·5	79·5	1·47	54·1	11
3—6-Mesh silica	20·0	15·0	908	25·9	31·4	13
2 Quill silica tubes	5·0	14·5	61·6	2·12	29·1	13
6—10-Mesh silica	20·0	14·5	511	23·7	21·6	12
6—10-Mesh retort carbon	20·0	14·5	497	24·3	20·4	10
Spiral tube	2·0	190·0	119·2	5·96	20·0	11½
Plain tube	2·0	14·5	9·36	0·465	20·0	12½
Plain tube	2·7	14·5	12·34	0·825	14·9	12½
Coiled tube	5·6	137·0	240	33·6	7·1	11
Plain tube	14·7	48·0	222·1	81·7	2·7	12½
8-mm. Sheath in centre	62·5	30·0	683	892	0·8	12

It is a further indication of a homogeneous reaction that the initial velocities at 912° and 1013° in both static and streaming experiments were the same up to 250 secs. and 12 secs., respectively, since " time " in the static method is the same as " time of heating " in the streaming method.

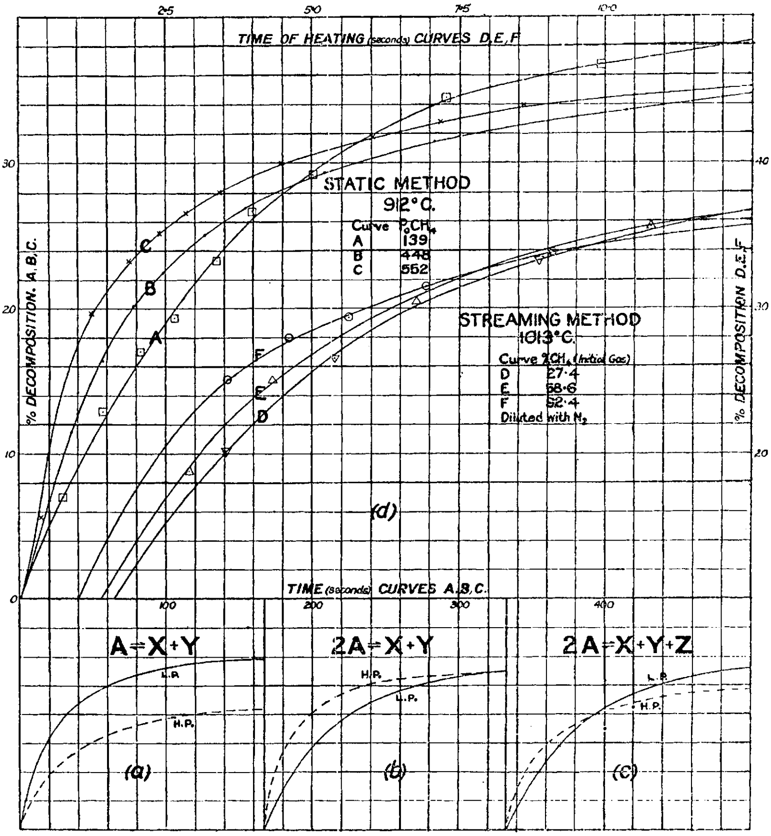
The rapid initial decomposition must be practically independent of surface, and further, any direct surface decomposition of methane to carbon and hydrogen must be extremely slow. Two important questions arise once the presence of a homogeneous reaction is assumed : Why does the reaction not proceed to the true methane equilibrium, and what is the mechanism of the decomposition? The results can be satisfactorily explained on the assumption that at least one intermediate substance is formed in the gas phase. We believe that this substance is acetylene and that the homogeneous reaction is bimolecular and represented by the equation

$$2CH_4 \rightleftharpoons C_2H_2 + 3H_2 - 91{,}000 \text{ cals.}$$

Most of the acetylene formed is then rapidly decomposed on the surface to carbon and hydrogen, leading to still further decomposition of methane. The accumulation of adsorbed hydrogen later retards the decomposition of the last traces of acetylene, which are, however, sufficient to maintain the observed amounts of residual methane in equilibrium in the gas phase.

The Order of Reaction.—For the following reasons we are led to believe that the acetylene is formed by the collision of two methane molecules. Homogeneous unimolecular reactions are rare, and a bimolecular reaction is much more probable than one of a higher

Fig. 3.



L.P. = *Low pressure.*
H.P. = *High* ,,

order. The effect of pressure on the velocity of three theoretical equilibrium reactions at one temperature is shown in Fig. 3 (*a*), (*b*), and (*c*), from which it will be seen that it is only in the case of a bimolecular reaction with three or more molecules taking part in the reverse reaction (type *c*) that crossing curves would be obtained. Fig. 3 (*d*) shows that, notwithstanding the subsequent decomposition of the acetylene formed, the static and streaming results still exhibit crossing curves, thus pointing to a reaction of the type (*c*).

Heat Effect and Carbon Formation.—The methane–acetylene reaction is endothermic, whereas the subsequent decomposition of acetylene to carbon and hydrogen is exothermic. It should therefore be possible to control carbon deposition and, if the mass of gas is large, to detect these heat effects.

With fast rates of flow in a wide tube of 62·5 mm. diameter at 1000°, carbon was deposited only near the exit end of the heated zone. A sheathed thermocouple which could be passed down the middle of the tube showed that temperature rises of 7—30° occurred near the outlet with times of heating up to 50 secs., whilst the temperatures at the inlet end decreased by 14—20°. Blank experiments with hydrogen and nitrogen gave no such effects. In a tube of 5·8 cm. diameter with times of heating of 2·4, 3·8, 7·2, and 13·7 secs., the carbon deposit commenced at 35, 18, 11, and 6 cm., respectively, from the inlet end of the heated zone.

Presence of Acetylene.—Streaming experiments at 900° and 1000° have shown that, even with the slowest rates of flow, acetylene is always detectable in the outlet gases, as indicated by Schulze's reagent (*Z. angew. Chem.*, 1916, **29**, 341). The fact that the characteristic colour change is much more quickly obtained when the gases are swept from the outlet zone by means of an auxiliary stream of nitrogen, shows that unless the acetylene is rapidly cooled it is almost completely decomposed or polymerised at the intermediate temperatures. The presence of ethane and ethylene in the gas must be attributed to hydrogenation of acetylene during cooling.

Type of Carbon from Acetylene.—Experiments in both static and streaming apparatus have shown that with certain mixtures of hydrogen and acetylene the carbon deposited is of the glossy type and exactly similar to that formed when methane is decomposed. It should be noted, however, that soft types of carbon can be obtained from both methane and acetylene under other conditions.

The Ratio $p^3_{\mathrm{H}_2}/p^2_{\mathrm{CH}_4}$.—It now remains to examine in the light of the theory outlined above the constant obtained in the static experiments. If the residual amounts of methane, hydrogen, and acetylene are in equilibrium in the gas phase then

$$p^3_{\mathrm{H}_2}p_{\mathrm{C}_2\mathrm{H}_2}/p^2_{\mathrm{CH}_4} = K_p.$$

If the chemical constants for methane, hydrogen, and acetylene be taken as 2·8, 1·6, and 3·2 respectively, rough values of K_p are given by the Nernst equation

$$\log_{10} K_p = -\ 91{,}000/4{\cdot}571T - 3{\cdot}5 \log T + 2{\cdot}4.$$

At 912° the value for K_p (in mm.) is 131·7. In one experiment at this temperature the pressures of hydrogen and methane remaining in the bulb were 454 and 327 mm. respectively. From these figures the calculated pressure of acetylene required to maintain the observed amounts of methane and hydrogen in gaseous equilibrium is found to be very small, *viz.*, 0·15 mm. Further, in the remaining experiments the calculated amounts of acetylene vary only between 0·14 and 0·16 mm. over the whole of the final pressure range from 200 to 800 mm. At 958°, 1014°, and 1052°, the average pressures of acetylene required by the above formula are 0·19, 0·35, and 0·55 mm. respectively, the variation with the total experimental pressures being again very small. The approximate constancy of the acetylene pressure has been experimentally proved at 1014° by estimation with Schulze's reagent after sweeping out the gas rapidly with nitrogen: the amounts of acetylene remaining after 30 mins. were found to be 0·25, 0·26, and 0·29 mm. at final pressures of 151, 371, and 964 mm. respectively. Thus, as the acetylene concentration varies only slightly, the constancy of the ratio $p^3_{H_2}/p^2_{CH_4}$ is explained on the basis of the acetylene–methane equilibrium.

It would appear also that the amount of acetylene prevented from appreciable decomposition by adsorbed hydrogen varies only slightly with the pressure of hydrogen over the range investigated. How far surface affects the amounts of residual acetylene is not yet understood.

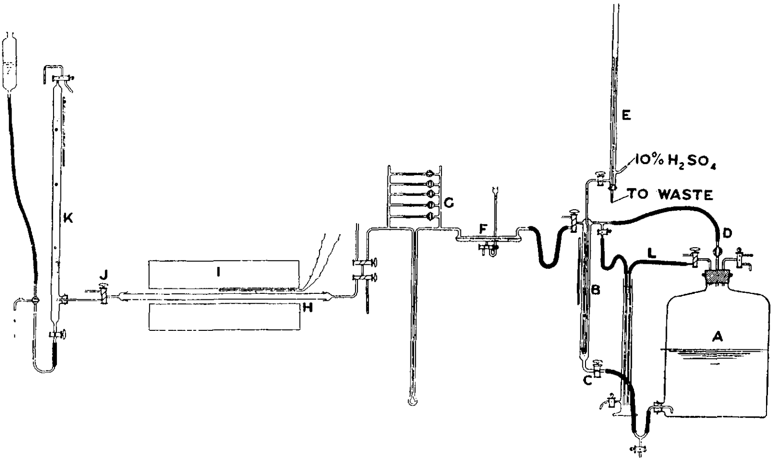
EXPERIMENTAL.

The apparatus (Fig. 4) was designed to give a steady stream of gas and to enable a series of measured volumes to be passed through the reaction tube without causing any alteration in the rate of flow.

When the temperature conditions of the furnace I were correct, an experiment was commenced by evacuating the reaction tube, filling it with methane, and allowing the gas in excess of atmospheric pressure to flow out into the burette K. Methane was then streamed at the desired constant rate from both the reservoir A and the calibrated burette B, of 50 c.c. capacity, through the sulphuric acid drier F, the flow gauge G, containing concentrated sulphuric acid, the reaction tube H, and *via* tap J to air, until the apparatus was thoroughly washed out and conditions were stabilised. Taps C and D were then closed, tap J opened to K, and the time taken for a measured quantity of methane to pass from B was noted; the resulting gas was collected simultaneously at atmospheric pressure in K without causing any change in the rate of flow. The gas collecting in K was then measured and analysed. The overflow tube L corrected any rise in pressure in A, so that when taps C and D were opened at the close of each sampling period the acid level in B fell without altering the pressure or rate of flow. During each experiment, several samples could thus be passed from B, which was flexibly fixed in order to allow for the rise in level in A. The rate was controlled by the head of 10% sulphuric acid in E and by one of the jets in the flow gauge C, which, with its five different capillaries, gave a range of steady flow of 2 c.c. to 20 litres per hour. For high rates of flow, B and K were replaced by larger vessels.

Several double-wound nichrome furnaces, I, were made to give different lengths of heated zone constant to ± 1° with steep gradients to room temperature at the ends. Temperatures were controlled by a platinum–platinum-rhodium thermocouple with its cold junction in ice.

FIG. 4.



Gas analyses were made in a constant-volume apparatus, hydrogen being burnt on copper oxide at 290°, and methane with excess of oxygen on platinum foil in a silica tube at 950°. (In the gas samples analysed after reaction, there were always small amounts of unsaturated hydrocarbons absorbable by bromine water, varying from 0·2% to 2·2% with the fastest rates of flow.)

The methane used was 93—95% pure, the remaining gas being nitrogen.

The time of heating was calculated from the formula,

$$\text{Time of heating} = v \times 273 \times t/(T \times V)$$

where v = volume of heated zone, *i.e.*, zone constant to ± 1°;
t = time taken to pass an average volume V;
T = the absolute temperature of the heated zone;
V = an arithmetical mean of the volumes, at *N.T.P.*, of the ingoing and outgoing gases.

Discussion.

Berthelot (*Compt. rend.*, 1866, **62**, 905) first suggested that acetylene plays an important part in the decomposition of methane and our results strongly support this view. Other suggested mechanisms involving the formation of ethane, ethylene, or residues are less probable; residues such as $:CH_2$, however, may have a transitory existence, although it is not necessary to assume that they are stable. Acetylene begins to be thermodynamically stable as far as the gaseous equilibrium is concerned at about 750°, and it is noteworthy that at this temperature the uncatalysed decomposition of methane becomes measurable. Ethylene and the other hydrocarbons are not stable above 750°.

It is now well known that appreciable quantities of acetylene, benzene, naphthalene, and other polymerides are formed under certain conditions by the thermal decomposition of methane (Fischer, *Brennstoff-Chem.*, 1928, **9**, 309; Peters and Meyer, *ibid.*, 1929, **10**, 324). In the absence of surfaces capable of catalysing the direct decomposition of methane to carbon and hydrogen, the acetylene yield will depend on the difference in velocity between the reaction $2CH_4 \longrightarrow C_2H_2 + 3H_2$ and the consecutive reaction $C_2H_2 \longrightarrow 2C + H_2$. It is only at high rates of flow and at temperatures above 1000° that appreciable yields of polymerides are obtained. Under these conditions the acetylene formed is not wholly decomposed on the surface but is swept rapidly out of the zone of highest temperature and, on passing through the cooler zones, is able to escape or to polymerise. It is difficult to imagine that hydrocarbons other than acetylene could be formed in the high-temperature zone, and it must be assumed that polymerisation takes place at lower temperatures.

Wheeler and Wood (*Fuel*, 1930, **9**, 567) have published experiments in which varying surfaces have been used. We have carefully considered their results, and although we find nothing in them which contradicts our own hypothesis, it is difficult to understand the conclusions drawn by the authors. We cannot agree that the initial reaction is dependent upon surface, and a comparison of their streaming results with surface/volume ratios of 1·86 and 27 corroborates this. Further, it is stated that "all efforts to detect the presence of acetylene have failed," whereas we believe that our experiments have shown that this gas is definitely present. We cannot agree that acetylene plays a negligible rôle in the decomposition.

Summary.

(1) Static and streaming experiments with silica surfaces suggest that at and above 900° methane decomposes *via* acetylene.

(2) The acetylene is formed as a result of a homogeneous bimolecular reaction.

(3) The direct-surface decomposition of methane to carbon and hydrogen is practically negligible owing to surface retardation.

(4) The subsequent surface decomposition of acetylene to carbon and hydrogen is also retarded at a later stage by adsorbed hydrogen; the traces of acetylene remaining are sufficient to prevent further decomposition of relatively large quantities of methane owing to the establishment of a gaseous equilibrium.

THE GAS LIGHT AND COKE CO.,
LONDON.

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