32. The Steam–Carbon Complex.

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Experiments were made on the interaction of steam and carbon to determine whether the formation and persistence of a complex could be demonstrated. By contact and evacuation at 300°, fixation of steam was shown to occur, and, by further heating to 1050° and evacuation in stages, complete decomposition of the complex so formed into hydrogen and oxides of carbon was effected. In the earlier stages of the decomposition the hydrogen obtained was less than the equivalent of the oxygen combined as oxides of carbon, but the balance was restored at higher temperatures. Other experiments with hydrogen instead of steam furnished an explanation of this peculiarity. The results were affected by the form of carbon used.

THE understanding of the process by which solid carbon is gasified in combination with oxygen has been the object of many experimental investigations and the subject of much controversy, but a definite advance was made when Rhead and Wheeler demonstrated the formation and persistence of what they termed a physicochemical complex C_xO_y which liberated the oxides of carbon by its decomposition on heating. The gasification of carbon in steam, also a process of fundamental theoretical and practical importance, has similarly been a matter of controversy, so we decided to test whether in this case also a fixation of steam by the carbon occurred. The experimental method followed was substantially the same as that used by Rhead and Wheeler, except in so far as the use of steam instead of oxygen made modifications necessary.

The steam was supplied in known quantity to carbon in the reaction bulb (see Fig. 1) by bursting in it a small sealed tube filled with a known weight of water. The course of reaction was followed in two ways:

(1) In " evacuation " experiments, by heating the carbon in contact with steam at a chosen initial temperature until a steady condition had been attained, evacuating the vessel completely at that temperature and analysing the gas so removed, then heating the residue

TABLE I.

Interaction of charcoal and steam at different initial temperatures.

(Weight of wood charcoal in bulb = 30·8 g.)

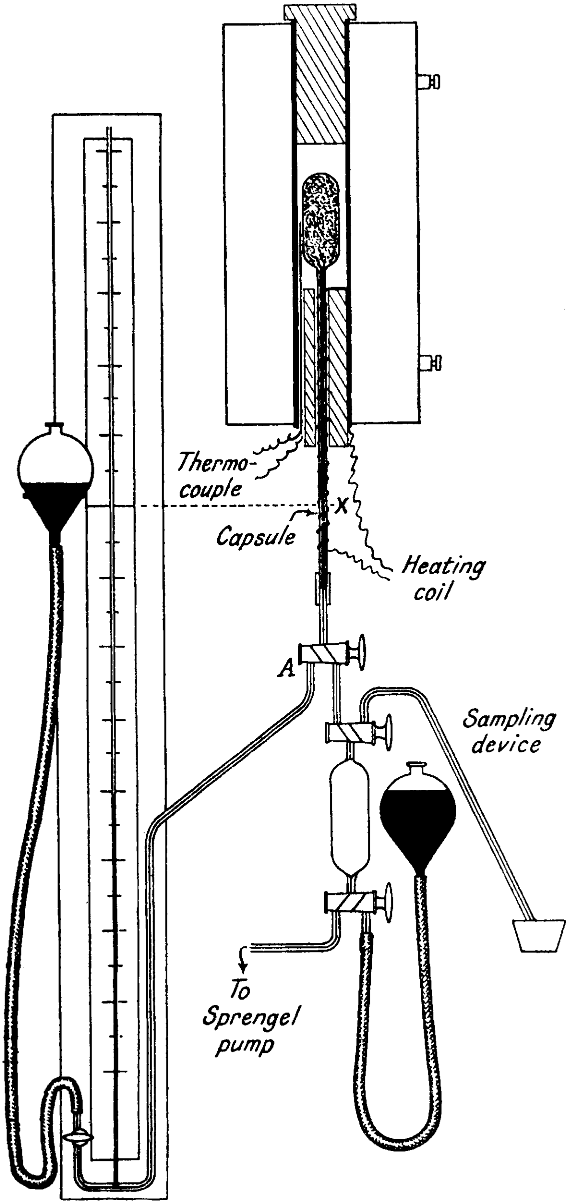
Initial temp.	Steam admitted.		Temp. of evacuation.	Gas evacuated.					
	G.	C.c. at N.T.P.		Vol., c.c. at N.T.P.	Analysis, %.			$CO+2CO_2$, c.c. at N.T.P.*	H_2, c.c. at N.T.P.
					CO_2.	CO.	H_2.		
300°	0·0386	48·0	300°	nil	—	—	—	—	—
			580	2·9	22	40	35	2·3	1·0
			920	20·8	0·7	45·3	52·4	9·7	10·9
			1050	16·6	0·2	47·5	50·0	7·9	8·3
								19·9	20·2
500	0·0424	52·7	500	8·6	62·6	13·1	21·9	11·9	1·9
			700	8·2	3·4	12·3	82·1	1·6	6·7
			920	32·7	1·8	39·9	57·1	14·3	18·7
								27·8	27·3
700	0·0484	60·2	700	44·0	24·9	21·0	52·5	31·1	23·1
			930	36·0	0·7	33·8	62·5	12·0	20·0
			1050	20·9	0·1	48·2	50·0	10·0	10·4
								53·1	53·5
930	0·0216	26·9	930	27·8	0·4	48·2	49·7	13·6	13·8
			1050	21·6	—	48·1	50·0	10·4	10·8
								24·0	24·8

* *I.e.*, combined oxygen in CO and CO_2 calculated to equivalent hydrogen, or steam.

in successive stages to higher temperatures, evacuating and analysing the gas at each stage.

(2) In " pressure " experiments, by heating the carbon with steam as before at a definite temperature, usually 300°, until a steady pressure had been attained, then (without evacuation) raising the temperature gradually and noting the accompanying changes in pressure, which were compared with the changes to be expected if no reaction or fixation had occurred. A parallel experiment with argon in known volume instead of steam measured the free space in the carbon-charged bulb.

FIG. 1.



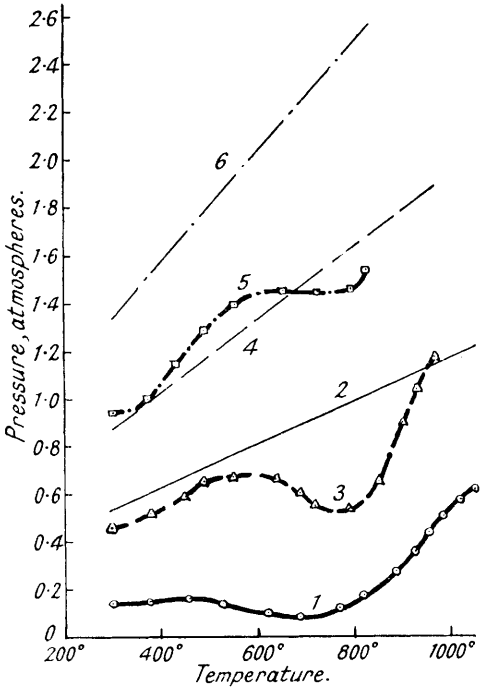
Other experiments were made with carbon monoxide or dioxide or hydrogen instead of steam, in order to indicate any complexities in interpretation of the results with steam which might arise from these gaseous products of reaction.

The results obtained in a typical evacuation experiment in which steam interacted with purified wood charcoal at 300° are given in Table I. At 300° no permanent gas could be evacuated from the bulb after interaction, but when the solid residue was heated to 580° some permanent gas was pumped off, and much larger quantities on raising the temperature to 920° and 1050°, with evacuation at each stage.

The total oxides of carbon from these successive evacuations contained combined oxygen equivalent to the hydrogen. Moreover the volume of water so represented was the same as the " missing volume " indicated in pressure experiments after steam had been allowed to interact to equilibrium with the carbon at 300° (Table II and Fig. 2). It follows

FIG. 2.

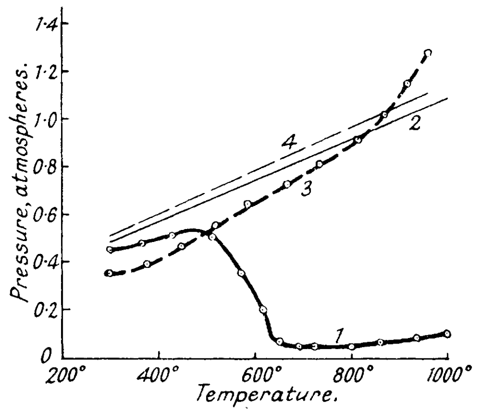
Pressure curves for wood charcoal.



1 = 0·0216 *G. of steam* : "*actual*" *pressures.*
2 = ,, ,, ,, "*theoretical*" *pressures.*
3 = 0·0358 *G. of steam* : "*actual*" *pressures.*
4 = ,, ,, ,, "*theoretical*" *pressures.*
5 = 0·0546 *G. of steam* : "*actual*" *pressures.*
6 = ,, ,, ,, "*theoretical*" *pressures.*
(*Wt. of carbon* = 30·8 *g.; vol. of free space* = 106 *c.c.*)

FIG. 3.

Pressure curves for hydrogen and carbon dioxide.



1 = 24·8 *c.c. of* H_2 : "*actual*" *pressures.*
2 = ,, ,, ,, "*theoretical*" *pressures.*
3 = 25·9 *c.c. of* CO_2 : "*actual*" *pressures.*
4 = ,, ,, ,, "*theoretical*" *pressures.*
(*Wt. of carbon* = 30·8 *g.; vol. of free space* = 106 *c.c.*)

TABLE II.

Pressure loss on interaction of steam and charcoal at 300°.

(Weight of wood charcoal in bulb = 30·8 g. ; vol. of free space = 106 c.c.)

Expt. No.	Temp. of introduction of steam.	Amount of steam admitted. G.	C.c. at N.T.P.	Pressure in the bulb after interaction, atm.	Vol. of steam equivalent to this pressure, c.c. at N.T.P.	" Missing " volume, c.c. at N.T.P.*
1	300°	0·0216	26·9	0·140	7·1	19·8
2	300	0·0358	44·5	0·471	23·8	20·7
3	300	0·0546	68·0	0·938	47·4	20·6

* *I.e.*, col. 4 – col. 6.

that the steam which had been fixed at 300° was gradually and completely liberated at 1050° as hydrogen and oxides of carbon. (In the gaseous products of decomposition by heat of the complexes formed by interaction at different initial temperatures, the quantity of carbon dioxide obtained was always small and practically confined to the lower temperatures and the first stage of decomposition in each case.) The equivalence between the combined oxygen in the oxides of carbon evacuated *up to* 1050° and the free hydrogen held also in the gas evacuated *at* 1050°, which in a number of experiments was very nearly of the " ideal water-gas " composition, $CO + H_2$. At lower temperatures, however, there was no such equivalence. In passing from 300° to 1050°, during the first half of the rise (approximately), the gas evacuated contained much more combined oxygen than the equivalent of the accompanying hydrogen; then came a stage in which the balance was quantitatively restored by the evacuation of gas containing more hydrogen than was equivalent to this combined oxygen, and in the final stage the gas contained combined oxygen equivalent to the hydrogen. (The analyses of this series of gases, 300—1050°, included examination for methane, but none was found.) This phenomenon was emphasised in an experiment in which interaction of steam and carbon at 700° was followed by cooling to 340°; evacuation at that temperature gave oxides of carbon with no hydrogen, although again the balance was restored by further heating and evacuation.

The Behaviour of Hydrogen and Other Gases.—As bearing on the question so raised, the behaviour of hydrogen (and carbon dioxide) was investigated by the pressure-curve method (Fig. 3). In contact with carbon a little hydrogen was absorbed at 300°, and as the temperature was raised the pressure fell rapidly from 500° to a minimum at about 750° and then rose again slowly. After reaching 1000° the temperature was allowed to fall gradually, whereupon the pressure diminished, reaching zero at 750° and remaining so down to 300°. On again raising the temperature to 930°, nearly all the hydrogen was withdrawn by 24 hours' evacuation. No such abnormality was indicated by carbon dioxide, and in experiments with hydrogen and the two oxides of carbon in turn, in which contact at 300° was followed by evacuation at that temperature, practically all the gas was withdrawn.

This behaviour of hydrogen with carbon explains the peculiarities noted above in the decomposition of the carbon-fixed steam. Broom and Travers (*Proc. Roy. Soc.*, 1932, *A*, **135**, 512; Broom, *Trans. Faraday Soc.*, 1938, **34**, 580) have observed similar phenomena in a much more extensive study of hydrogen and carbon, and particularly that hydrogen reacted very differently towards carbon above and below about 600—700°. Key and Cobb (*J. Soc. Chem. Ind.*, 1930, **49**, 439 T) also recorded an unexplained, marked screening effect exercised by hydrogen when it was used as a carrier gas for steam in their experiments on the reaction of coke with steam and carbon dioxide.

Interpretation.—The simplest explanation of the experiments described above is that at 300° a steam–carbon complex $C_x(H_2O)_y$ was formed and that, on raising the temperature, it was decomposed completely, but that the hydrogen from the decomposition was partly retained in the lower-temperature stages. It is true that normal molecular hydrogen in the free space was little affected by contact with carbon at such a low temperature as 300°, but it was easily fixed at rather higher temperatures and then remained so on reversion to lower temperatures. It is not therefore unreasonable to suppose that hydrogen, freshly liberated in the interstices of a decomposing carbon–steam complex, will be partly retained even in the first stages of heating above 300°.

Meyer (*Trans. Faraday Soc.*, 1938, **34**, 1056) concluded that the reaction of carbon with carbon dioxide or steam at low pressures and high gas velocities results in the formation of the same carbon–carbon monoxide complex (containing no hydrogen) in each case, and observations by Key (private communication) by dynamic methods on the velocity constants involved give support to that idea. The results of our static experiments at the lower temperatures would not be necessarily inconsistent with this interpretation, since any hydrogen liberated from the steam in the formation of the carbon–carbon monoxide complex would be liable to retention by carbon; but the results at higher temperatures, *e.g.*, 1050°, when hydrogen and carbon monoxide in equal volume were always obtained by the decomposition of the complex, can hardly be so explained and point to the reaction $C_x(H_2O) \longrightarrow CO + H_2 + C_{x-1}$. It is possible, however, that in this decomposition a first stage is the elimination of hydrogen with the formation of the carbon–carbon monoxide complex, and that the further decomposition of this complex is the slower of the two stages and determines the ***rate*** of the whole decomposition.

Forms of Carbon.—Most of our experiments were made with wood charcoal, reduced in ash content from 3·6 to 0·9% by boiling with dilute hydrochloric acid, and heated under vacuum at 1100° for 12—24 hours. (Preliminary tests had shown the results to be somewhat different if the charcoal were not so purified, presumably owing to the influence of alkaline ash constituents.) Previous experience had, however, demonstrated the wide quantitative differences in steam decomposition (reactivity) displayed by the cokes prepared from various coals and from the same coal with varied thermal treatment. The formation of the carbon–steam complex as determined by the form of carbon plainly called for similar systematic examination. This has not been made, but a few preliminary results are recorded. A coke was prepared from a fusible Yorkshire (Sharleston Wallsend) coal at 1000° and heated under vacuum at 1100°. In a pressure experiment after interaction of this coke at 300° with steam, followed by evacuation, no appreciable rise of pressure due to evolved gas resulted from further slow heating to 1000°. No fixation of steam had occurred. On repeating the experiment without the evacuation at 300°, the pressure curve obtained could not be held to demonstrate fixation of steam at any temperature, but did indicate clearly the fixation of some gas, probably hydrogen, in the range 500—800°.

Another experiment was made in which the coke used had been subjected to less drastic heat treatment. It was prepared at 800°, extracted by acid, and heated at 900° under vacuum for 2 days, after which it was proved that negligible quantities of gas were evolved at 750°, the highest temperature in the subsequent experiment. This was made by contact with steam at 550°, evacuating, heating gradually to 750°, and again evacuating (Table III). The results indicated a fixation of steam at 550°, and after-decomposition on rise of temperature similar to that occurring when charcoal was used.

TABLE III.

Interaction of steam and medium-temperature (800°) *coke.*

(Weight of coke in bulb = 50·5 g.)

	Amount of steam admitted.			Gas evacuated.					
Temp. of introduction of steam.	G.	C.c. at N.T.P.	Temp. of evacuation.	Vol., c.c. at N.T.P.	Analysis, %.			$CO+2CO_2$, c.c. at N.T.P.	H_2, c.c. at N.T.P.
					CO_2.	CO.	H_2.		
550°	0·0232	28·9	550°	5·8	32·4	4·1	58·0	4·0	3·4
			750	10·8	7·0	36·6	54·6	5·5	5·9
								—	—
								9·5	9·3

The form of the carbon is therefore of importance in determining the degree of steam fixation, which presumably lessens as graphitisation proceeds by the formation of comparatively large and stable molecular groupings of the $(C_6)_n$ type with a gradually diminishing number of peripheral unsatisfied affinities. Somewhat similar effects have been noted in the production of methane by the hydrogenation, under high pressure, of cokes prepared at different temperatures, by F. J. Dent, in the work of the Joint Research Committee of the Institution of Gas Engineers and the University of Leeds (Reports 41 and 43), and the methods of X-ray analysis have been applied to the elucidation of such phenomena by Riley.

EXPERIMENTAL.

Apparatus.—The apparatus is illustrated in Fig. 1. The charge of carbon was contained in a clear silica bulb, 10 cm. long and of 4 cm. internal diameter, placed vertically in an electric furnace. The stem of the bulb could be connected either to a mercury manometer or through a sampling device to a Sprengel pump. When pressure readings were being taken, the mercury was adjusted by means of the levelling bulb of the manometer to a zero mark on the stem of the silica bulb, and the pressure was read off on the scale. By this means the bulb was completely isolated while these readings were being taken, and there was no possibility of leakage of gas through rubber joints or taps.

Water was introduced into the bulb by means of a glass capsule containing a weighed quantity of water placed at a convenient position in the stem. This capsule was readily burst by heat at the appropriate time. The charge of carbon was prevented from falling down the stem by a silica rod of cross-sectional area approximately equal to half the internal cross-sectional area of the stem. This rod also supported the water capsule, and, in addition, prevented particles of glass flying to the top of the stem when the capsule burst, where they might have given trouble by fusion. To keep it above the dew point of the water introduced, the stem had a separate heating coil.

Method.—The charge of carbon, graded 8—16 I.M.M., was evacuated for 12—24 hours at 1100°. The bulb was then allowed to cool, the capsule introduced, and the bulb evacuated, reheated, and again evacuated. Mercury was then run up the stem to the zero mark, and tap *A* (Fig. 1) was closed. The bulb was allowed to cool to the working temperature desired, and when steady conditions were obtained, the capsule was burst by heating with a small blow-pipe flame. The small coil for heating the stem of the bulb was then brought into operation. The heating of mercury in the stem would introduce a small but negligible error in the pressure readings obtained.

The temperature being kept constant, the bulb was connected with the manometer, and time (several hours) allowed for equilibrium to be attained, as shown by a constant pressure reading. One of two procedures was then followed.

(a) *Pressure experiments.* The temperature was raised at the rate of 15—20°/min., and readings of temperature and pressure were recorded. They did not indicate equilibrium conditions.

(b) *Evacuation experiments.* The bulb was completely evacuated through the Sprengel pump at the temperature at which the steam was introduced. The temperature was then raised by about 200° at the rate of 15—20°/min., pressure and temperature readings of the bulb being taken during the interval. The process of *complete evacuation* was repeated at this higher temperature, and the temperature raised by another 200° as before. Successive evacuations were carried out at intervals of about 200° until 1050° was reached, whereupon the final evacuation was made. The samples of gas obtained by evacuation at different temperatures were measured and analysed.

Determination of Free Space in the Bulb.—The carbon in the bulb was evacuated completely at 1050°, and, after sealing with mercury, the temperature was allowed to fall to 300°. A suitable measured volume of argon was introduced through the sampling device, and the pressure read. The temperature was then raised at 15—20°/min., pressure and temperature readings of the bulb being taken up to 1000°. The pressure at 1000° was employed for the calculation of the free space. As a check on the amount of argon used, an evacuation was made at 1000°, and the gas was evacuated, measured, and analysed.

Blank Experiments with Empty Bulb.—In order to prove that, in the absence of carbon, steam gave a normal pressure curve with increase of temperature under the conditions existing in these experiments, an empty bulb otherwise similar to that used in later experiments was employed, the free space having been determined by argon. The bulb was evacuated, and a suitable weight of water introduced at 300°. After the pressure at 300° had been noted, a series of pressure readings was taken while the temperature was raised at 15—20°/min. up to 1000°. The curve so obtained for water vapour coincided with that calculated from the free space in the empty bulb as determined with argon.

Evacuation Experiments.—In Table I the relevant numerical data have been collected for a series of experiments in which contact of steam with charcoal at a number of initial temperatures was followed by heating and evacuation in stages to trace the decomposition of the solid complex. It will be understood that the first evacuation after heating at any one of these initial temperatures extracts any gas formed at that temperature in the free space, but that the gas from subsequent evacuations is of necessity solely derived from the complex.

Pressure Experiments.—In Table II and Fig. 2 are shown the detailed results obtained in pressure experiments when different quantities of steam after reaction to equilibrium with charcoal at 300° were taken without evacuation to higher temperatures. The corresponding theoretical pressures which the steam would have exerted if unaffected by the charcoal are also calculated and plotted. The " missing volume " at 300° was found to be the same as that represented by the decomposition products from the complex in the 300° evacuation experiments, and was the same for different quantities of steam. This may be explained on the view that the " missing " steam had attached itself to unsatisfied peripheral affinities of the carbon, after which the rest of the steam was of no effect.

The behaviour of hydrogen (and of carbon dioxide) in pressure experiments is shown in

Fig. 3. The importance of fixation of hydrogen in influencing the composition of the products of decomposition of the carbon–steam complex in the evacuation experiments has been stressed. The attainment of zero pressure at 750° on cooling, continuing down to 300° (see p. 180), is not shown on the figure.

Discussion.—The foregoing work is not a general investigation of the interaction of carbon and steam, but a specific experimental enquiry into the fixation of steam by carbon at pressures near atmospheric, which it seems to establish. It is probable that a similar fixation of steam and hydrogen would occur at high pressures, but that the mode of decomposition would be different. The work carried out by F. J. Dent and others (see p. 181) is of interest in this connection, particularly with reference to the production of methane, which may have important industrial applications.

Our results and their indications may be summarised as follows :

(1) The action of steam at 300° on charcoal in a closed space resulted in the fixation of steam. No permanent gas was evacuated at 300° after attainment of equilibrium, but, on heating and evacuating in stages up to 1050°, the solid residue underwent such change that gas was withdrawn from it consisting of hydrogen and of oxides of carbon in which the combined oxygen was equivalent to the hydrogen. The volume of steam represented by this decomposition was the same as the " missing volume " represented by the fall of pressure which occurred at 300° during the exposure of the steam to the carbon. With higher initial temperatures of interaction, the results were similar, but some permanent gas was withdrawn on evacuation without further heating.

(2) The gas evacuated at 1050°, representing the final stage of decomposition, was of the " ideal water-gas " composition, 50% H_2, 50% CO. During (approximately) the first half of the temperature rise from 300° to 1050° the gas evacuated contained combined oxygen in the oxides of carbon more than equivalent to the hydrogen, then came a stage in which this was balanced by an excess of hydrogen over combined oxygen, with a final stage of equivalence and the ideal water-gas composition.

(3) The departure from equivalence of hydrogen and combined oxygen in all but the later stages of decomposition can be understood in the light of results obtained by parallel experiments made with hydrogen, instead of steam, in which the fixation of hydrogen, as relevant to this enquiry, was studied and demonstrated, so that its liberation into the free space at the time of its formation by decomposition of the carbon-fixed steam was not to be expected.

(4) The results obtained indicate the initial formation of a carbon–steam complex, $C_x(H_2O)_y$, in which $y = 1$ at the higher temperatures, in accordance with the decomposition $C_x(H_2O) \longrightarrow CO + H_2 + C_{x-1}$, complete at 1050°, and y is slightly greater than unity at the lower temperatures, allowing the formation of carbon dioxide in the first decomposition products. The gas evacuated at the temperature of interaction contained most of the carbon dioxide.

(5) From a few preliminary tests it would appear that the results depend on the form of carbon used; *e.g.*, a high-temperature coke from a fusible caking coal, prepared at 1000° and heated under vacuum at 1100°, gave no evidence of the steam fixation at 300° which occurred with wood charcoal, but a specially prepared medium-temperature (800°) coke behaved like charcoal in forming a complex at 550° with steam, which yielded hydrogen and oxides of carbon on thermal decomposition.

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