

48. *The Primary Gaseous Products of Carbonisation.*

By K. BOLTON, J. E. CULLINGWORTH, B. P. GHOSH, AND JOHN W. COBB.

Substances differing widely in constitution and oxygen content were subjected to fractional carbonisation up to 1100°. Liquid products were evolved up to 600°. X-Ray powder photographs were made of the solid residues from cellulose and glycine. These disclosed an early breakdown of the original structure, followed by a repatterning of the carbon atoms in a hexagonal graphitic network visible at 400—500°, and more distinct from 800° upwards. The specific gravities of the same residues rose rapidly up to 800°, much more slowly afterwards. The primary gaseous products were specially studied, and their formation from the solids and from simple aromatic hydrocarbons compared. In the initial decompositions the gaseous products displayed wide quantitative differences, but afterwards were fundamentally similar, being evolved in the succession methane, hydrogen, carbon monoxide, and believed to arise from $\cdot\text{CH}_3$, $\cdot\text{H}$, and $\cdot\text{OH}$ groups (attached to the hexagonal network) by molecular condensations of the type $\text{R}_1\cdot\text{CH}_3 + \text{R}_2\text{H} \longrightarrow \text{R}_1\text{R}_2 + \text{CH}_4$. The maximum methane evolution was at 500—600°, and that of hydrogen and carbon monoxide at 700—800°. The single hexagonal carbon ring of benzene was apparently broken by rise of temperature with comparative ease, but the solid hexagonal carbon network was unbreakable by that means.

The hydroxyl group was held to form steam and become responsible for the formation of carbon monoxide as water gas by the gasification of nuclear carbon from the hexagonal network. The ideas that the free evolution of hydrogen from coal at 700—800° was (1) the property of one kind of constituent or (2) due to secondary decompositions, were both found untenable.

THE term "carbonisation" is used to denote the process of decomposition by rise of temperature which converts a carbon compound into a solid residue richer in carbon and approximating more closely to carbon itself as the temperature is higher and the time of heating more prolonged. In a typical applic-

* The polycyclic hydrocarbons are really amphoteric. We have seen that they can act as donors (forming positive ions) or as acceptors, as is well known from the compounds of naphthalene, anthracene, and phenanthrene with metallic sodium or potassium. We have found that even such highly symmetrical hydrocarbons as coronene ($\text{C}_{24}\text{H}_{12}$) can form deeply coloured compounds with these metals quite easily, where they are most probably present as negative ions.

† Unpublished results. This compound is formed by shaking the solution of the nitro-compound in ether with the finely divided alkali metal.

ation of the process to a solid, chemical breakdown begins before simple volatilisation of the substance carbonised, and proceeds by a succession of decompositions to yield solid, liquid, and gaseous products. The experimental analysis of the process demands that, as far as possible, (1) the substance shall be homogeneous, *e.g.*, a definite chemical compound, (2) the temperature shall be raised gradually and maintained at each level until the decomposition at that level is complete, and (3) the volatile products shall be removed so quickly at each temperature level from the region of decomposition that further secondary decomposition is minimised. In such an industrial process as the carbonisation of coal, no one of these conditions is even approximately satisfied, so that, although chemical and thermal studies of large-scale carbonisation, treating coals of many kinds in different ways, have been usefully made, they have not given and cannot give the data for such an analysis of the essential features of the carbonisation process as is now desired. The method of fractional carbonisation has not been followed in such large-scale experiments because it is not practicable to secure gas-tightness of the apparatus over the long periods of time necessary for even approximate completion of reaction at each of a succession of chosen temperatures, and even if that were done the size of the apparatus and charge would facilitate secondary decompositions in the primary products. Numerous laboratory investigations, particularly those of the late R. V. Wheeler and his collaborators, have amplified our information by small-scale work including some fractional and vacuum carbonisation, but they have dealt usually with coal and the lower temperature phenomena, and so have served to bring out the peculiarities and differences in a narrow range of substances rather than the resemblances which, as will be seen, emerge in a wider survey having more regard to higher temperatures. Moreover, the method of experiment followed, particularly for high temperatures, has commonly been not to fractionate but to take a number of separate charges of the substance under test to different temperatures, noting the difference in result.

This method cannot serve the purpose of a fractional carbonisation. The products from such an experiment at any temperature will be a mixture of primary products at that temperature, surviving primary products from lower temperatures, and secondary products from all the decomposed primaries. It is difficult to draw conclusions from any such experiment, and the results by two investigators will disagree unless all their conditions of operation are identical. For instance, although such work by Wheeler *et al.* (J., 1910, **97**, 1917, etc.) led them to conclude that there was a critical point in the decomposition of coal (attributed by them to its ulmin constituents) about 700°, marked by a greatly increased evolution of hydrogen, and that of Vignon (*Compt. rend.*, 1912, **153**, 1514) was confirmatory, yet Porter and Taylor (*Proc. Amer. Gas Inst.*, 1914, **9**, i, 234), on the basis of their own experiments, regarded the increased hydrogen evolution at 700–800° as due rather to secondary decomposition of tars and gases than to a breakdown of the coal substance as a whole—leaving the position in an obscurity which has not been removed (cf. Bone and Himus, "Coal: Its Constitution . . ." p. 161, 1936).

It may be reasonably expected that in carbonisation, as the temperature rises, the almost infinite variety of stable molecular constitutions and aggregations which are possible at room temperature will give place, under the stress of increasing molecular agitation, to more stable structures richer in carbon, following lines of decomposition converging to carbon itself and shedding volatile products, liquid and finally gaseous, in the process.

In the work now described, the gaseous products have been singled out for examination. The substances carbonised represented a wide range of chemical constitution and complexity. They were: cellulose, bakelite, glycine, petroleum coke, anthracite, and New Hucknall and Charlston Wallsend coals.

EXPERIMENTAL.

The method of experiment was the same throughout. The substance was heated in stages of 100° in a vacuum, and the gas formed at each stage was collected, measured, and analysed. On plotting the volume of the gaseous products obtained, it was found that the emission of a particular gas was not confined to one temperature stage, but that a stage of maximum emission (or at times more than one maximum) was usually well marked, so that the succession of decompositions could be clearly traced. The ideal was to complete the gas evolution at one temperature stage before proceeding to the next, but that was not feasible, and long-continued emissions were regarded as complete when the rate fell below 1 c.c. per hour.

Apparatus.—A vitreous silica tube, as used in the Gray-King high-temperature assay of coal, rounded at one end and stoppered at the other, with a small side tube near the stoppered end projecting downward, was heated in an electrical resistance furnace. The 5 (or 10) g. charge was packed at the rounded end and lay entirely in the constant-temperature region of the furnace. Nearly all the remaining free space of the tube was filled by several vitrified Morgan fire-clay blocks; the under surface of each block but the one next to the charge was grooved, and the furnace was sloped towards the exit tube. In this way a minimum time of contact before leaving the heated tube was secured for the gases, and any liquid condensing in the cooler exit end was drained away quickly, so that secondary decompositions were prevented as far as possible. (Preliminary trials showed that with widely different rates of carbonisation only the same very thin dark

film formed on the tube.) The exit tube dipped straight into an air condenser in which liquid collected; this was followed by a bubbler containing glycerol and water or, if any ammonia was present, dilute sulphuric acid. Gas then passed to a mercury-sealed holder, and by means of a Sprengel pump the pressure was kept below 10—20 mm. of mercury, except during short periods of rapid emission.

In carrying out an experiment, the gas-tightness of the apparatus having been tested by leaving it overnight under vacuum, the temperature was raised at the rate of 100° per hour and halted at each 100° for the emission of gas at that temperature. The result reported for any temperature relates to the gas emitted in reaching that temperature from one 100° lower and in maintaining it at that temperature until emission could be regarded as complete. Some experiments occupied several weeks, and in such cases a little in-leakage of air was responsible for nitrogen and oxygen totalling, on the average, 1.6% in the gas collected, but analyses are reported "nitrogen and oxygen free" unless otherwise described. The carbonisation was usually carried up to 1200° or 1300°, but there was a liability to increased leakage at 1200°, so results are tabulated only up to 1100°, although many obtained at the higher temperatures gave no obvious reason for suspicion.

Gas analyses were carried out in the Bone and Wheeler apparatus. Unsaturated hydrocarbons were determined by absorption in a half-saturated solution of bromine in water, hydrogen and carbon monoxide by passage over copper oxide at 280° and washing with sodium hydroxide solution, and paraffins by after-combustion over copper oxide at a red heat. Any oxygen resulting from slight dissociation of the copper oxide was removed by washing with alkaline pyrogallol after absorption of the carbon dioxide resulting from the combustion.

Results.—These are presented in the tables, which give the volumes of gas (in c.c. at N.T.P.) evolved per g. of substance carbonised, and are illustrated in the figure.

Cellulose, (C₆H₁₀O₅)_n.—Whatman filter-paper clippings were used. Previous work had paid more special attention to liquid and solid products. Lebeau carried out a fractional carbonisation at 100° intervals but for only one hour at each temperature, so his results, although generally similar to ours, are only roughly comparable.

Progress of carbonisation on 10 g. up to 1100°. Total time, 1199 hrs.; 860 hrs. from 700° upwards. Maxima of gas emission at 300° and 800° (rapid emission noted at 280°). Heavy evolution of reddish-brown liquid at 300°. No liquid products above 600°. Of 0.49 g. of oxygen in 1 g. of cellulose, 0.10 g. was evolved as carbon monoxide and 0.09 g. as dioxide, *i.e.*, 39% as oxides of carbon. The gas evolved in the first 24 hrs. at 1100° contained H, 59.7; CO, 40.3%; and that in the remaining 238 hours H, 52.3; CO, 47.7%. The approach to water gas is noteworthy (see Discussion below).

	Cellulose, (C ₆ H ₁₀ O ₅) _n .										Total up to 1100°.	Vol. %.
	Temperature.											
	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.			
CO ₂	38.0	11.5	4.2	1.9	2.2	2.4	0.2	—	—	60.4	15.2	
C _n H _m (unsatd.) ...	0.9	1.2	0.3	—	—	—	—	—	—	2.4	0.6	
H ₂	0.1	0.9	6.4	17.6	27.7	36.6	29.2	28.0	19.7	166.2	41.9	
CO	17.4	15.9	10.0	5.4	8.9	22.6	22.0	22.4	16.8	141.4	35.5	
C _n H _{2n+2}	0.4	6.5	8.9	6.5	2.9	0.8	0.2	—	—	26.2	6.8	
Total.....	56.8	36.0	29.8	31.4	41.7	62.4	51.6	50.4	36.5	396.6	100.0	
Value of <i>n</i> in C _n H _{2n+2}	1.5	1.3	1.1	1.0	1.0	1.0	1.0					

Solid residues. Those used for a specific-gravity determination and X-ray examination were obtained as follows: For that at any one temperature *t*°, cellulose was heated at 100° per hour to *t* — 100°, held at that temperature for 24 hours, heated to *t*° in one hour, and held at *t*° for 24 hours. Prolonged exposure was thus secured, and gas samples drawn at each temperature, compared with those from the fractional carbonisation, indicated the same reactions, but volumes were somewhat smaller. The specific gravity results obtained were:

Temp.	15°.	200°.	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.	1200°.
<i>d</i>	1.60	1.61	1.41	1.38	1.42	1.59	1.70	1.82	1.82	1.86	1.86	1.85

The rapid increase between 600° and 800° and the slow increase afterwards are notable.

Bakelite.—The sample used, presented by British Bakelite Ltd., was a light yellow, powdered resin with a strong phenolic odour; it was described as prepared from a mixture of phenol and formaldehyde, with ammonia as catalyst. On gentle heating it did not fuse but gave some liquid with the odour of phenol. (The special property of formaldehyde resin is that it polymerises on heating, hardens and becomes very insoluble.) In ultimate analysis it resembled a coal, rich in hydrogen and oxygen.

Progress of carbonisation on 5 g. up to 1000°. Total time, 785 hrs.; 662 hrs. from 700° upwards. Maximum gas emission at 800°. First analysed gas emission, very slow and in small volume, at 400°. Liquid products in some quantity at 100° and 200°, none above 600°. 1 G. of bakelite as carbonised contained 0.162 g. of oxygen, of which 0.105 g. was evolved as carbon monoxide and 0.010 g. as dioxide, *i.e.*, 71% as oxides of carbon. Fractional analysis was made of gas evolved in periods at the higher temperatures:

	In rise 700—800°.	First 30 mins. at 800°.	Remainder at 800°.	Similar remainder at 1000°.
H ₂ , %	77.9	82.8	58.3	58.1
CO, %	18.0	15.2	40.2	40.9
CO ₂ , %	3.3	1.5	0.2	0.2
CH ₄ , %	0.8	0.5	1.3	0.8

Results from the other samples corresponded.

Bakelite.

	Temperature.								Total up to 1000°.	Vol. %
	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1000°.		
CO ₂	0.4	0.8	1.3	3.3	0.8	0.3	0.2	7.1	1.4	
C _n H _m	0.1	0.3	0.4	—	—	—	—	0.8	0.2	
CO	0.5	4.8	11.7	14.8	40.6	38.1	36.7	147.2	28.5	
H ₂	1.0	17.8	57.3	63.6	71.5	59.9	54.0	325.1	62.9	
C _n H _{2n+2}	1.1	11.6	17.4	3.0	1.4	1.2	0.7	36.4	7.0	
Total	3.1	35.3	88.1	84.7	114.3	99.5	91.6	516.6	100.0	
Value of <i>n</i> in C _n H _{2n+2}	1.4	1.0	1.0	1.0	1.0	1.0	1.0			

In another fractional carbonisation of bakelite, the time at any one temperature stage was limited to 24 hours. The same reactions were indicated, but the volumes of hydrogen and carbon monoxide collected from 700° upwards were roughly halved.

Glycine.—Progress of carbonisation on 5 g. up to 1100°. Time, 951 hrs.; 665 hrs. from 700° upwards. Initial gas evolution noted at 245°, maxima collected at 300° and 800°. Slight smell of cyanogen. Mist at 200°, liquid from 300° to 500° and possibly 600°. 1 G. of glycine contained 0.43 g. of oxygen of which 0.07 g. was evolved as carbon monoxide and 0.12 g. as dioxide, *i.e.*, 44% as oxides of carbon.

Glycine, NH₂·CH₂·CO₂H.

	Temperature.										Total up to 1100°.	Vol. %
	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.	1100°.		
CO ₂	41.4	28.9	5.3	1.8	1.9	2.2	1.0	0.2	0.1	82.8	24.0	
C _n H _m	0.3	0.3	0.3	0.1	0.0	—	—	—	—	1.0	0.3	
CO	1.8	5.6	8.9	6.2	10.0	17.3	14.6	16.3	16.0	96.7	28.0	
H ₂	0.1	0.4	5.3	16.8	23.9	30.5	23.1	17.7	16.6	134.4	38.0	
C _n H _{2n+2}	0.5	0.5	7.2	4.1	1.8	1.1	0.2	0.1	0.1	15.6	4.5	
N ₂	—	0.1	0.5	0.5	1.2	3.1	4.3	2.9	1.9	14.5	4.2	
Total	44.1	35.8	27.5	29.5	38.8	54.2	43.2	37.2	34.7	345.0	100.0	
Value of <i>n</i> in C _n H _{2n+2}	1.1	1.1	1.1	1.0	1.0	1.0	1.0	1.0	1.0			

The close approximation to water gas in the composition of the 1100° fraction is again noteworthy (*cf.* Cellulose).

Yields of ammonia. Ammonia was not determined in these experiments but of 0.187 g. of nitrogen contained in the glycine 0.018 g. (by diff.) was evolved as free nitrogen. In a fractional carbonisation made by A. C. Monkhouse (1922, Leeds, unpublished), rather less than 50% of the nitrogen of glycine was obtained as ammonia up to 600° and a further 38% between 600° and 1000°, of which 12% was free nitrogen, 7.4% remaining in the coke. In another of our fractional carbonisations of glycine carried to 1300°, 19.6% of coke was obtained containing 3.64% of nitrogen, *i.e.*, 3.8% of the original nitrogen. It was evident that ammonia had been evolved in stages, the partial evolution at any one temperature being accompanied by the formation of a solid residue which evolved no more ammonia or nitrogen at that temperature but decomposed further at a higher temperature. There was no one temperature characteristic of ammonia evolution. Previously reported work on the thermal decomposition of glycine had been carried out at low temperatures and indicated dehydration, fusion without decomposition, and decarboxylation as primary results (*e.g.*, Balbiano, *Ber.*, 1900, 33, 2324).

Petroleum Coke.—This was supplied by the Anglo-Iranian Oil Co. and resulted, according to Dr. A. E. Dunstan, "from the cracking of distillate oils at pressures round about 650/750 lbs. and at temperatures round about 450°." The coke contained some oils and, before use in the fractional carbonisation, was extracted with ether, then with carbon disulphide, and again with ether, any solvent being finally driven off by heating at 105° in an air-oven. It then contained C, 94.7; H, 3.3%.

Progress of carbonisation of 5 g. up to 1100°. Time, 72 hrs.; 50 hrs. from 700° upwards. Gas evolved negligible below 500°. This substance displayed peculiarities in the carbonisation, probably connected with the high pressure of preparation. The first small gas fraction was collected at 500° and contained nearly all the carbon dioxide evolved in the carbonisation and some nitrogen and oxygen. In another experiment, when this fraction was collected in two equal portions, the whole of the nitrogen and free oxygen were found in the first portion. These were presumably derived from air adsorbed under the high pressure of preparation, but the proportions, 25.2 and 2.5%, respectively, suggested that some of the oxygen had gone into combination. The liberation of gas generally was slow, and that of methane more widespread in temperature than with the

other substances carbonised, showing a maximum at 700°. Evolution of hydrogen was still incomplete at 1300°, and a much more prolonged carbonisation would probably have been justified.

The outstanding feature of the carbonisation was the pronounced increase in evolution of hydrogen from 700° onwards. In this respect the behaviour of petroleum coke was the same as that of cellulose and all the other materials carbonised. The only rapid evolution of gas with petroleum coke occurred during the first hour at 700° and 800°

Petroleum coke.

	Temperature.								Total up to 1100°.	Vol. %.
	500°.	600°.	700°.	800°.	900°.	1000°	1100°.			
CO ₂	2.2	0.2	—	—	—	0.1	—	—	2.5	1.5
C _n H _m	0.4	0.2	1.0	0.6	0.4	0.1	0.0	—	2.7	1.6
CO	1.2	0.3	0.6	—	—	0.7	0.5	—	3.3	2.0
H ₂	5.5	12.7	42.9	29.2	27.5	10.7	7.9	—	136.4	81.7
C _n H _{2n+2}	3.1	4.0	6.9	5.5	1.8	0.4	0.4	—	22.1	13.2
Total	*12.4	17.4	51.4	35.3	29.7	12.0	8.8	—	167.0	100.0
Value of <i>n</i> in C _n H _{2n+2}	1.2	1.1	1.0	1.0	1.0	1.0	1.0	—		

* Also N₂, 1.7; O₂, 0.2%.

Anthracite.—This contained O₂, 2.0; H₂, 3.2%.

Progress of carbonisation to 1100°. Time, 63 hrs.; 46 hrs. from 700° upwards. First decomposition noted at 500° as shown by evolution of gas and also of a small quantity of liquid which was noticeable up to 600°. Gas evolution rapid at beginning of each heating at 700—1100°, and slow evolution continued at 1200—1300°. The volume of hydrogen emitted rose rapidly at 700° and continued large at 800° and 900°. Most of the small oxygen content appeared as carbon monoxide, suggesting previous molecular condensation (see Discussion); of 0.020 g. of oxygen contained in 1 g., 0.013 g. was evolved as this oxide and 0.005 g. as dioxide, *i.e.*, 90% as oxides of carbon.

Anthracite.

	Temperature.								Total up to 1100°.	Vol. %.
	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.		
CO ₂		0.7	1.0	1.3	0.2	0.2	0.1	0.1	3.6	1.4
C _n H _m		0.0	0.3	—	—	—	—	—	0.3	0.1
CO		0.4	1.6	5.7	4.4	2.4	2.4	2.0	18.9	7.4
H ₂		1.2	17.5	66.0	50.5	41.6	13.2	12.7	202.7	79.4
C _n H _{2n+2}		2.0	13.0	7.6	3.5	1.4	0.4	0.3	28.2	11.0
N ₂ (diff.)		0.0	0.1	—	0.2	1.1	0.1	0.2	1.7	0.7
Total	(0.4)	4.3	33.5	80.6	58.8	46.7	16.2	15.3	255.4	100.0
Value of <i>n</i> in C _n H _{2n+2}		1.0	1.0	1.0	1.0	1.0	1.0	1.0		

Of the products, 88.9% were solid, 7.6% gaseous, and (by diff.) 3.5% liquid.

New Hucknall Coal.—This was a bituminous, fusible; coking coal containing C, 77.4; H, 5.6; S, 1.6; N, 1.3; ash, 3.8; O (by diff.), 10.3%.

Progress of carbonisation to 1100°. Time, 78 hrs.; 40 hrs. from 700° upwards. First decomposition (gas and trace of tar) noted at 400°. Rapid gas evolution first noted at beginning of heating at 500° (methane at maximum), then again at 700° (hydrogen at maximum) onwards. Slow evolution continued at 1200° and 1300°. Of 0.103 g. of oxygen contained in 1 g. of coal, 0.055 g. was evolved as carbon dioxide and 0.023 as dioxide, *i.e.*, 76% as oxides of carbon.

New Hucknall coal.

	Temperature.									Total up to 1100°.	Vol. %.
	300°.	400°.	500°.	600°.	700°.	800°.	900°.	1000°.	1100°.		
CO ₂		1.8	1.9	1.6	4.3	2.8	2.8	0.4	0.1	15.7	4.0
C _n H _m		0.2	1.0	0.5	1.1	—	—	—	—	2.8	0.7
CO		1.1	6.2	5.4	11.5	13.7	19.9	11.2	8.3	77.3	19.6
H ₂		0.1	6.2	17.3	57.2	49.9	41.9	26.3	17.9	216.8	54.8
C _n H _{2n+2}		4.1	29.6	16.2	12.8	5.8	1.9	0.5	0.3	71.2	18.0
N ₂ (diff.)		0.1	0.4	0.3	2.5	3.1	2.1	1.6	1.4	11.5	2.9
Total	(1.4)	7.4	45.3	41.3	89.4	75.3	68.6	40.0	28.0	395.3	100.0
Value of <i>n</i> in C _n H _{2n+2}		1.7	1.4	1.1	1.1	1.0	1.0	1.0	1.0		

Of the products, 61.5% were solid, 21.4% gaseous, and (by diff.) 17.1% liquid. In a much more rapid carbonisation (2½ hours) of 30 lbs. of this coal (moisture, 5.0%) to 976° on a semi-commercial scale in a horizontal cronite retort on the Corbet-Woodall experimental plant at the University of Leeds, the results were: coke, 65.5; gas, 17.6; tar and pitch, 6.1; liquor, 10.7%. The gas contained much more unsaturated hydrocarbons, 4.9%, and much less carbon monoxide, 11.3%, than in our fractional carbonisation where the high carbon monoxide resulted from a slow and long-continued reaction and the volatile matter was not subjected to decomposing influences.

Sharlston Wallsend Coal.—This was also carbonised, for comparison; it contained C, 82.9; H, 5.4; S, 0.9; N, 1.3; ash, 0.9; O (by diff.), 8.6%. Like New Hucknall coal, it was a fusible, bituminous, coking coal and the results of the carbonisation, being very similar, are not reported. There was, however, one striking difference. Of 0.086 g. of oxygen contained in 1 g. of coal, 0.011 g. was evolved as carbon monoxide and 0.006 as dioxide. Thus, although this coal contained nearly as much oxygen as the New Hucknall, only about one-fifth as much was evolved as oxides of carbon. The explanation lies presumably in the greater molecular condensation which the New Hucknall coal had already undergone in formation, so that, on heating, a much larger proportion of the oxygen was left in the form of firmly attached hydroxyl groups surviving to react with hydrogen and carbon (see Discussion) in the higher temperature range to produce carbon monoxide. Bakelite had disclosed the same phenomenon.

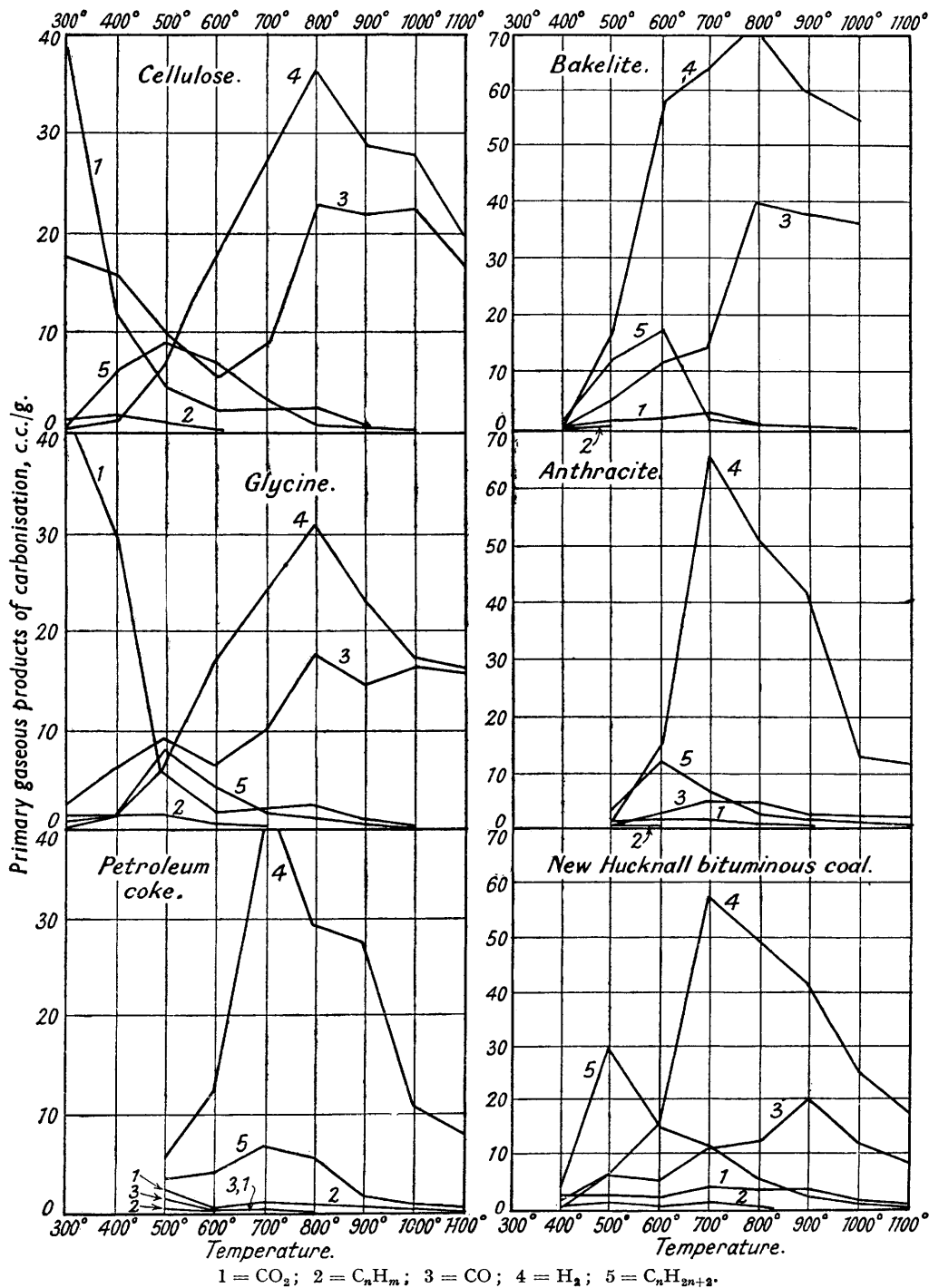
DISCUSSION.

A striking feature of the results detailed above and displayed in the tables and the figure is the general similarity in the nature and temperature sequence of the primary gaseous products of decomposition from substances of widely different composition and complexity. In every case the decomposition occurred in two phases. In the first, lasting up to 600°, the gaseous products were accompanied by liquids which were not examined but obviously varied widely and by their removal were largely responsible for the progress towards a common type of solid residue; in the gaseous products methane was prominent in every case, with a maximum emission at 500–600°. In the second phase, from 700° upwards, there were no liquid products but always a dominating emission of hydrogen, accompanied by widely differing quantities of carbon monoxide, both persisting at the highest temperatures of these experiments although in greatly diminished quantity. In the first phase, the emission of gas at each temperature could be completed (*i.e.*, reduced to <1 c.c./hr.) in a reasonable time of heating. In the second phase, the emission of hydrogen (and carbon monoxide) increased rapidly at 700°, and although it fell away to a slow rate on continued heating at that temperature, its cessation could at times not be secured even after many days. The same was experienced on raising the temperature further to 800°, so that the choice between 700° and 800° as the temperature of maximum emission was somewhat arbitrary.

X-Ray Evidence.—The gas emission may be considered in relation to the changes in the solid residues disclosed by an X-ray examination made for us by Dr. W. T. Astbury and Dr. E. Green (Ph.D. Thesis, Leeds, 1938). Cellulose residues from 200° to 1200° at 100° intervals, and glycine residues at 400° and 1200° were examined. Below 200° cellulose showed no change, but at 300° the rings in the X-ray photograph of unheated cellulose had given place to a general diffuseness, which indicated a break-down of the original structure. Some aromatisation has been detected chemically below this temperature (Smith and Howard, *J. Amer. Chem. Soc.*, 1937, 59, 234). At 400° a carbon re-patterning was already in evidence, and at 500° the appearance of the two most characteristic rings as given by graphite denoted the formation of a hexagonal network of carbon atoms in parallel sheets. The rings were somewhat diffuse at this stage, such as would be given by very minute or imperfectly formed crystals, and the diffuseness persisted at higher temperatures. At 800° it was greatly lessened, but even at 1200° was still there. The sharpness of the rings shown on a comparison photograph from graphite was lacking. Moreover, as observed by others, at the first appearance of the carbon network the spacing between the sheets was slightly larger than in graphite. Although much more extensive surveys on crystallite growths during carbonisation have been made by Riley and others with similar results, yet it was desirable for our purpose to demonstrate by this examination what had occurred to the solid residues in their prolonged heating when decomposition had reached approximate finality at the successive stages of temperature. A carbonisation rate of 5°/min., with 10 mins. at the final temperature, had been found by Blayden, Riley, and Taylor to provide sufficient time for maximum crystallite growth (*J. Amer. Chem. Soc.*, 1940, 62, 180; *J.*, 1939, 67).

Perhaps the most striking indications were those of the lower-temperature residues, *viz.*, that the disruption of the original compound under thermal shock, in evidence at 300°, had been followed so quickly at 400° and 500° by rearrangement of carbon atoms in a hexagonal network so fundamentally resistant that the increasing thermal shocks of higher temperatures only resulted in its further growth and stabilisation. The formation of such a carbon network would be effected no doubt in different ways according to the constitution of the original compound decomposed. Thus the fusion of glycine at a low temperature would confer a much greater degree of molecular mobility and facilitate the rearrangement of carbon atoms in the new and more stable formation. In some other substances, such as the coals, the existence of six-membered carbon rings in some quantity at the outset, as demonstrated chemically by Fischer and Schrader, Francis and Wheeler, and more convincingly and quantitatively by Bone *et al.* (*Proc. Roy. Soc.*, 1927, A, 110, 537, etc.), would assist in providing nuclear centres for the growth of the carbon network, again facilitated if the coal were fusible. But the progress in every case examined is towards an ultimate residue of graphitic carbon by the splitting away of a variety of larger

molecular groups, up to 600°, which volatilised and condensed to liquids on cooling, and of gases in an orderly succession up to the highest temperature used in the fractional carbonisation. This succession has been our special study.



Primary Gaseous Products.—These were principally methane, hydrogen, and oxygen in the form of the two oxides of carbon. *Methane and hydrogen.* These may be considered together. The maximum methane emission was at 500—600°, above which it fell away rapidly and was replaced by an extensive hydrogen emission, at a maximum from 700° to 800°, falling away slowly at first, then more rapidly to

the highest temperatures used. A useful comparison can be made with the break-down of simple aromatic hydrocarbons. It was found (Dufton and Cobb, *Trans. Inst. Gas Eng.*, 1919, 137) that benzene, with nitrogen as a neutral carrier gas, underwent its first decomposition at 650° with the (reversible) formation of a single condensation product, diphenyl, and hydrogen: $2C_6H_6 \longrightarrow (C_6H_5)_2 + H_2$. At 750° the decomposition was much more extensive, with the formation of more condensation products, including diphenylbenzene and hydrogen and also, significantly, some methane, the carbon of which could only come from the incipient breakdown of the benzene nucleus. The first decomposition of toluene in nitrogen was also a condensation at nearly the same temperature (600°) as for benzene, with emission of hydrogen complicated almost at once by the formation of methane from the methyl group and of benzene. Here again the amount of condensation products, hydrogen and methane, obtained at 750° indicated rapid extension of the decomposition with the rise to that temperature. Similar experiments carried out by F. J. Dent and assistants in this laboratory [see 41st Report of the Joint Research Committee of the Institution of Gas Engineers and the University of Leeds (*Trans. Inst. Gas Eng.*, 1937)] were confirmatory and were extended to coals, coke, and lignite, with special reference to the influence of pressure and atmosphere on the formation of methane. From a comparison of the results obtained with xylene and with benzene, heated in hydrogen at 50 atm. pressure, it was deduced that in the production of methane from xylene, commencing slowly at 500° and quickening rapidly up to 800°, the methane below 675° came from "a hydrogenation of the side chains which was sensibly complete at 700°," but the rest of the methane came from nuclear carbon. With low-temperature cokes, prepared at 400–450° and heated in hydrogen under pressure, however, the rate of production of methane passed through two distinct maxima, one at 500–550° and the other at 750–800°, and it was suggested that "the first maximum was due to the hydrogenation of side chains, chain compounds, etc., and the second was caused by the hydrogenation of the basic six-membered carbon rings." With heating in nitrogen at normal atmospheric pressure, the first methane maximum was fully in evidence, although less pronounced than with high-pressure hydrogen, but the second was absent, being replaced by a hydrogen maximum in the same temperature range, 750–800°. Other fuels gave similar results.

Comparison of the behaviour of simple aromatic hydrocarbons and of the substances used in our experiments discloses interesting resemblances and differences. In the first place, the temperature, 700–800°, which brought about marked molecular condensation and consequent emission of hydrogen with benzene, toluene, and xylene, was also that of maximum hydrogen emission in all the solid substances carbonised; *i.e.*, the specific reaction $2C_6H_6 \longrightarrow (C_6H_5)_2 + H_2$, involving two single six-membered rings, and a generalised reaction $R_1H + R_2H \longrightarrow R_1R_2 + H_2$ in the solid hexagonal network of carbon atoms formed in the carbonisation, both became prominent at 700–800°. The X-ray phenomena provided evidence of this changing solid structure, as did also the changes in specific gravity during carbonisation: that of the carbonised cellulose increased rapidly in the process from 1.42 in the 500° to 1.82 in the 800° residue, but much more slowly afterwards (see p. 254). Similar results for specific gravity had been obtained from a bituminous coal and anthracite by Greenwood and Cobb (*J. Soc. Chem. Ind.*, 1922, 41, 181; Lane, Leeds Thesis, 1934) and from Durham bituminous coals by Drakeley and Wilkins (*ibid.*, 1931, 50, 331). A diminution in the electrical resistance of powdered coke from 1,000,000 units when prepared at 650° to 180 when prepared at 750°, noted in "The Solid Products of the Carbonisation of Coal" (South Metropolitan Gas Co., 1934, p. 59), is another striking indication of radical change effected in the solid structure when a temperature of 750° has been attained in carbonisation.

With methane, however, the temperature range of maximum emission from the solid substances carbonised was no longer the same as from the simple aromatic hydrocarbons, but distinctly lower. With toluene it was practically the same as the range of maximum hydrogen emission, and with xylene the formation of methane by hydrogenation under pressure appeared to be continuous for the attached groups and the nuclear carbon, but with the solid substances carbonised the maximum decomposition producing methane occurred in a lower temperature range (500–600°) than that producing hydrogen (700–800°), and there were two corresponding methane maxima on hydrogenation under pressure. The growth of the hexagonal carbon network in the solids, indicated by the X-ray examination of cellulose and glycine as occurring at temperatures well below that of the main condensation producing maximum hydrogen may well be the mark of more easily effected condensations of the type $R_1 \cdot CH_3 + R_2H \longrightarrow R_1R_2 + CH_4$ coming into play at these lower temperatures. There was plainly little survival of attached methyl groups to the higher temperature range in the substances carbonised, except with petroleum coke, from which the emission of methane was apparently more widely spread, perhaps as a consequence of this material having been prepared under high pressure (650–750 lbs./in.²).

Apart from the condensations just considered, there are, of course, the varied decompositions and

aromatisation from which a little methane and other gaseous hydrocarbons appeared from the beginning of breakdown, but it is clear that in all the substances carbonised the emission of methane at 500—600° was outstanding. The value of n in the paraffins C_nH_{2n+2} was usually 1.0; it exceeded 1.1 only for the small volumes of the initial decompositions and for the bituminous coal up to 600°; the highest value obtained was 1.7 for the small yield of gas (7.4 c.c. per g.) from the bituminous coal at 400°.

There is an important respect in which the decomposition of the solids differs from that of benzene. At 750° benzene decomposes with the production of methane in a quantity increasing with further rise in temperature, but the solids in carbonisation, after the free emission at 500—600°, yield only small and diminishing volumes of methane unless treated with hydrogen under pressure. This phenomenon seems to demand the interpretation that the single hexagonal carbon ring of benzene can be broken by rise of temperature with comparative ease, but that the solid hexagonal carbon network is unbreakable by that means. It forms the "fixed carbon" of a proximate analysis. This increased resistance conferred by consolidation of the benzene ring structure has other manifestations. Carbonised residues from anthracite, bituminous coal, lignite, peat, wood, and cellulose have been shown to be much less active with sulphuric acid when the temperature of preparation reaches 700—800° (South Metropolitan Gas Co., *op. cit.*, p. 40). This is the region of extensive molecular condensation marked by maximum hydrogen emission on heating and rapid increase in specific gravity. Similarly, in Bone's work, the benzenecarboxylic acids formed by the attack of permanganate on carbonised residues increased with the temperature of carbonisation until that had reached 600°, but then diminished, which surely meant, not that the six-membered carbon rings were diminishing in number, but that their aggregations were becoming more resistant. How far the increase in stability can go with rise in temperature and increasing consolidation of structure is seen in an extreme case from an extension of Dent's experiments on the hydrogenation under pressure of carbonised residues, to crystalline graphite, which was found to be completely inert. (Of course the degree of consolidation represented by crystalline graphite with its specific gravity of 2.25 is much greater than that attained in our experiments or in commercial carbonisation, where the maximum specific gravity reached may be taken as 1.9.)

Hydrogen was the most voluminous primary gaseous product of decomposition. In our experiments, the first gas samples collected in quantity allowing of analysis always contained a little hydrogen. As the temperature rose, the volume of hydrogen increased, more rapidly from 500° upwards, until the maximum was reached at 700—800°, after which it fell away, but the emission was never complete at 1100°. From 700° upwards, our practice of collecting gas at any one temperature until its rate of emission had fallen below 1 c.c./hr. (see p. 253) could not always be followed without an impracticable extension of the time of carbonisation, which, as it was, reached 860, 662, and 665 hrs. from 700° upwards with cellulose, bakelite, and glycine respectively. At 700° gas came away rapidly at first but, after a time, at a slow rate falling almost imperceptibly. The same occurred at 800°, and the choice between 700° and 800° as the temperature of maximum emission became rather arbitrary. This slow-continuing emission of gas was probably due partly to its location between superimposed planes of the solid hexagonal network which were closing up to form graphitic crystallites, a phenomenon studied by Riley and others (*e.g.*, J., 1936, 456).

There was, however, another even more potent cause of the continuing slow emission of gas at these higher temperatures, *viz.*, the greatly enhanced production of carbon monoxide, which began at the same temperature as that of hydrogen, 700° or a little higher. Moreover, with the more highly oxygenated substances such as cellulose and glycine, and higher temperatures, the gas evolved approximated more and more closely in composition to ideal water gas (equal vols. of hydrogen and carbon monoxide), and the same tendency displayed itself unmistakably with other substances if the gas at any one temperature was collected fractionally. For instance, with bakelite, although the gas evolved in the first $\frac{1}{2}$ hour at 800° contained 82.8% of hydrogen and 15.2% of monoxide, the remainder contained 58.3 and 40.2% respectively (with small quantities of carbon dioxide and methane). In no case, however prolonged the heating, did the gas sample contain more carbon monoxide than hydrogen. It seems that, from 700° upwards, two reactions occur side by side; at each temperature a rapid generation of hydrogen is prominent early, whereas the slower generation of water gas tends to predominate later. This continuing emission of carbon monoxide in coal carbonisation was noted by Burgess and Wheeler (J., 1911, 99, 661), who suggested the action on carbon "of any steam formed" as the cause. That supposition is fully justified by our results. Exactly what happens is not deducible with certainty, but a hypothesis consistent with the facts is that the formation of carbon monoxide (as water gas) is analogous in its mechanism to that already put forward for hydrogen and methane, and that it depends upon the formation of steam by a molecular condensation which can be most simply represented as $R_1\cdot OH + R_2H \longrightarrow R_1R_2 + H_2O$, the steam so liberated then attacking the carbon. Nuclear carbon of the hexagonal network would be so attacked, and indeed only a small quantity

of any other carbon survives to that temperature range. According to Rau and Lambris (*J. Gasbel.*, 1913, **56**, 561), on gradual heating of cellulose 600° was the highest temperature at which water was evolved, and coals behaved similarly. Above that temperature presumably any steam formed would combine with carbon. Surviving hydroxyl groups attached to the hexagonal network would provide steam in the manner suggested, and the formation of water gas would proceed from 700° upwards as indicated in our experiments.

The high-temperature evolution of oxygen in combination with carbon as carbon monoxide just considered followed, with every substance, upon a low-temperature evolution, mainly as carbon dioxide. The two stages were most plainly exhibited by glycine and cellulose, from which oxygen as carbon dioxide, along with much smaller quantities of carbon monoxide, came away quickly at 300°, diminished greatly in the medium range of temperature, and was finally evolved again in quantity as carbon monoxide from 700° upwards. With bakelite and anthracite, the low-temperature emission of oxides of carbon was negligible in comparison with that occurring from 700° upwards. For this, antecedent molecular condensations in the preparation of the bakelite and in the natural formation of the anthracite may be regarded as responsible. Determinable quantities first appeared at 400° for bakelite and 500° for anthracite. The two bituminous coals differed in behaviour though not much in oxygen content, New Hucknall (with 10.3% of oxygen) resembling bakelite in its much larger emission of carbon monoxide at high temperatures. Both coals gave only small emissions of oxides of carbon at low temperatures, commencing at 300–400°. Again a difference in antecedent molecular condensations during formation may be held responsible, leading to a greater survival of firmly attached hydroxyl groups above 700° with the New Hucknall coal.

Attention may be directed to the complex results in the very gradual process of fractional carbonisation arising from the single carboxyl group of glycine (the only possible source of oxides of carbon), results strikingly similar to those obtained from the much more complex cellulose. Another example is forthcoming in the behaviour of the single amino-group of glycine, which was found responsible in fractional carbonisation for the emission of ammonia in temperature stages and for nitrogen held in the solid residue (see above). It is plainly not permissible to connect complexity (or simplicity) of behaviour on heating with that of original constitution—a not unnecessary warning. It is always to be remembered that the gaseous products of carbonisation are not emitted from the original substance but from the solid residue as existing at the temperature of emission, and that residues from different substances have so far conformed to a common type after the first few hundred degrees of carbonisation that the composition of the gaseous products offers only a limited guidance to the original constitution.

Unsaturated hydrocarbons (C_nH_m). These formed a very small proportion of the gaseous products in fractional carbonisations but they appeared in the first analysable volume forthcoming from each substance and their emission sometimes persisted up to 600°. The volumes obtained ranged from 0.3 and 0.8 c.c./g. for anthracite and bakelite to 2.8 c.c./g. from the two bituminous coals—well under 1% of the gas in every case. (A commercial carbonisation of these coals would have given about 4% in the gas.) In laboratory carbonisations of 20 g. of Charlston Wallsend coal up to 800° at 5°/min., in apparatus generally resembling the one we used, N. R. Balmford (Leeds, Thesis, 1934) obtained gas containing 1.6% of unsaturated hydrocarbons, but when all the volatile products were passed through a short length of tube, maintained throughout at 800°, the percentage was raised to 4.5 as a result of the secondary decomposition thereby effected. The tar yield was correspondingly diminished. Moreover, it was found by Jones and Wheeler (*J.*, 1914, **105**, 141, 2562, etc.) that oils boiling below 300°, distilled from the tar obtained by the vacuum distillation of a bituminous coal at 430°, contained 40–45% of “ethylenic” unsaturated compounds, and Jones reported later (*J.*, 1915, **107**, 1106) that heating the vaporised tar at temperatures from 550° to 800° decomposed naphthenes, paraffins, and unsaturated hydrocarbons present in it, to form olefins which condensed at higher temperatures to form aromatic substances. Thus, the low yield of unsaturated hydrocarbons in our fractional carbonisation of bituminous coals is not surprising, and the same explanation presumably holds for the other substances carbonised, *viz.*, that the “ethylenic” groups when present were largely retained in the liquid products. To establish this firmly throughout would, however, require an examination of these products.

Ammonia. This was not determined in these fractional carbonisations, but in previous work carried out on Charlston Wallsend and a second bituminous coal and on anthracite, by carbonising them in a current of nitrogen, and keeping them for an hour at each temperature interval of 100° up to 1000°, it had been noted that the maximum ammonia emission had in each case occurred at 700–800°, *i.e.*, at the same temperature as the accompanying maximum hydrogen emission in the same experiments (Eastwood and Cobb, *Trans. Inst. Gas Eng.*, 1931, 272). The parallel was so close as to suggest a similar mechanism of reaction, as was then pointed out, such as $R_1 \cdot NH_2 + R_2 \cdot H \rightarrow R_1 R_2 + NH_3$, the amino-group being expelled with accompanying molecular condensation. Similar results were obtained

from glycine carbonised in the same way by another observer (J. E. Knight), although in that case there was a previous free emission of ammonia and carbon dioxide at 400°.

It is of interest that the bituminous coals, which in normal commercial or laboratory carbonisation fused and formed firm cokes, were only slightly coherent powders after the fractional carbonisation of our experiments. It would appear that the molecular groups responsible for fusion and the cementing of particles in normal carbonisation, had been expelled in the much slower heating, before a temperature had been reached at which they could exercise this influence. No such complication occurred with glycine, which fused completely before decomposition and yielded a firm, shrunken, porous coke on further heating.

CONCLUSIONS.

The fractional carbonisation of a solid, in the light of the foregoing experimental results and discussion, may be viewed thus: The first stage is a destruction, more or less complete, of the original molecular and crystalline pattern by the enhanced internal vibrations brought into play by the rise in temperature. With many substances, such as form a solid residue on carbonisation, there follows a repatterning of carbon atoms in a hexagonal network which is such a stable arrangement that it can resist any disintegrating tendency of further temperature rise and forms graphitic crystallites. X-Ray methods applied by Dr. W. T. Astbury showed this repatterning established at 400—500°. Its progress was accompanied by an increase in specific gravity, rapid up to 800°, much slower afterwards up to 1200°. (In such material as coal some of the carbon is in the hexagonal pattern from the beginning.) Meanwhile, other molecular groups form no part of the new stable hexagonal pattern, or are easily detached from it, and with the rise of temperature these are volatilised or decomposed, each being expelled at once, if volatile, at the temperature of its formation, or otherwise when its temperature of volatilisation has been reached. Some of these are the liquid products of carbonisation, and their expulsion, beginning early, continues up to about 600°. They are characteristic of the substance undergoing carbonisation, and by their loss the various residues assume a similarity of constitution. Some gaseous products appear early. Carbon dioxide, with some monoxide, is evolved in quantity even at 300° from such highly oxygenated substances as cellulose and glycine, with small volumes of hydrogen and paraffins and unsaturated hydrocarbons. With substances relatively poor in oxygen which have already undergone some molecular condensation, naturally or artificially, the first samples analysed in our experiments contained in small volume these same gases emitted at rather higher temperatures, 400° for coal and bakelite, 500° for anthracite and low-temperature petroleum coke. This first emission of gas in small volume may well arise largely from secondary decomposition of the larger molecules of liquid products, marking a failure to realise completely in practice the ideal fractional carbonisation. In several previous investigations of fuel, directed more especially to the initial products of decomposition, water and the oxides of carbon have been shown to be the first to leave. Our procedure with 100° intervals did not detect this.

Then follows the emission in all cases of the chief primary gaseous products, methane, hydrogen, and carbon monoxide. They may be regarded as coming from the more firmly attached $\cdot\text{CH}_3$, $\cdot\text{H}$, and $\cdot\text{OH}$ groups by molecular condensations, of the type exemplified by $\text{R}_1\text{H} + \text{CH}_3\text{R}_2 \rightarrow \text{R}_1\text{R}_2 + \text{CH}_4$, in the growing and consolidating hexagonal network. The maximum methane emission is at 500—600° and that of hydrogen and carbon monoxide at 700—800°. (The maximum ammonia production from coals at 700—800° in other experiments was probably derived similarly from attached amino-groups.) The hydroxyl group, by forming steam, becomes, on this view, responsible for the formation of carbon monoxide as water gas by the gasification of nuclear carbon from the hexagonal network. The evolution of carbon monoxide and hydrogen together seems to proceed more slowly than the direct condensation yielding hydrogen, with the result that the gas expelled at the higher temperatures from a substance rich in oxygen, and particularly that part of the gas collected after long heating at one temperature, approximates to ideal water gas in composition.

The methane has some admixture of higher paraffins, but it is slight, as indicated by the value of n in $\text{C}_n\text{H}_{2n+2}$, and most noticeable in the small volumes emitted at the beginning of carbonisation. Unsaturated hydrocarbons are produced to a very limited extent—well below 1% in the substances tested. The differences between the gaseous products of fractional and commercial carbonisation come from the overlapping of stages and incompleteness of reactions in the latter, and to a large extent from the decomposition of primary liquid products.

The experimental work described above brings out the fundamental similarity in the primary gaseous products of fractional carbonisation from a number of substances differing widely in chemical constitution, particularly when the stage of initial decomposition has been passed. With special reference to coal the results confirm Burgess and Wheeler's conclusion that there is a critical temperature of decomposition in its carbonisation, marked by greatly enhanced evolution of hydrogen, at 700—800°.

and lend no support to Porter and Taylor's contention that this phenomenon is due to secondary decomposition. They indicate clearly, however, that this is not a special property of coal, and still less of any one of its petrographical constituents. The greatly enhanced evolution of hydrogen (and carbon monoxide) at 700—800° is apparently a normal feature of molecular condensation in solid residues formed at lower temperatures in the carbonisation.

We thank the firms mentioned above for the provision of samples, Mr. H. J. Hodsman for advice and assistance throughout in the experimental work, and Dr. W. T. Astbury for the X-ray examination of carbonised residues.

FUEL DEPARTMENT, THE UNIVERSITY, LEEDS.

[Received, January 7th, 1942.]
