X.—*The decomposition, and genesis of hydrocarbons at high tempera-tures. I. The products of the manufacture of gas from petroleum.*

By HENRY E. ARMSTRONG and A. K. MILLER.

1. A PRELIMINARY account of our work was given to the Society in June of last year (*Chem. News*, **49**, 285), a somewhat lengthy descrip-tion of the manufacture of gas from oil, as practised in this country, having been previously communicated by Dr. Armstrong to the Society of Chemical Industry in a paper read before their London Section in April, and printed in their Journal for September, 1884 (pp. 462—468).

2. The investigation was commenced several years ago, and was

carried on almost uninterruptedly during 1884 and the first half of 1885, but the products are so numerous and their separation and identification is attended with such difficulty, that the progress made is far from satisfactory. Nevertheless, a stage has been reached at which it appears desirable to record the results, as they are in part highly suggestive and will lead to new inquiries being undertaken; besides which the methods at our disposal are scarcely sufficient to enable us to unravel the very tangled skein which the investigation presents. An abstract of the present paper is given in the number of the *Abstracts of the Proceedings of the Chemical Society* for June 18th, 1885.

3. The products of the manufacture of oil-gas are historically of great interest, as their examination led Faraday, in 1825, to his momentous discovery of "Bicarburet of Hydrogen," now known as benzene.* Another new compound described in the same paper was obtained from the most volatile portion of the condensed liquor from the oil-gas receivers. According to Faraday's analysis, it contained carbon and hydrogen in the same proportions as olefiant gas, but was of double the density. This is the composition of *butylene*, the discovery of which has therefore always been attributed to Faraday; we shall have occasion later on to consider whether the evidence he adduces is sufficient to warrant this conclusion.

Faraday's memoir affords a considerable amount of information which we think justifies the inference that the oil-gas of the present day differs but little from that then made, although the oils now used are derived from shale and petroleum and it was then customary to use fish or vegetable oil.

4. We have not been able to ascertain that any attempt has been made to add to our knowledge of the chemistry of the subject since Faraday's investigation was published, notwithstanding the attention paid within recent years to the manufacture of oil-gas, excepting that Greville Williams appears to have commenced the examination of the bye-products of its manufacture not long after Dr. Armstrong had begun to study them (*Chem. News*, 1884, p. 197; see also *Jour. Soc. Chem. Ind.*, 1884, p. 462).

5. In describing our work we propose to disregard the order in which the various constituents were separated or identified; our main object being to throw light on the nature of the changes resulting from the decomposition of petroleum hydrocarbons at high temperatures, it will be desirable to give a connected account of the observations relating to each of the series of hydrocarbons which occur in one or other of the products examined, viz., the compressed gas itself;

* "On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat:" a paper read June 16th, 1825, by M. Faraday, F.R.S., &c., *Phil. Trans.*, 1825, 440—466.

the liquid deposited during compression of the gas, either in a chamber attached to the compressing pump or in the reservoir in which the gas is stored; and the tar which is deposited from the crude gas prior to compression. In this paper, however, we shall deal only with that portion of the gas which is absorbed by bromine and with the steam-distillable portion of the tar.

I. *Benzenoid hydrocarbons.*

6. The liquid deposited during compression of the gas is wholly volatile in steam when recently obtained, and consists of hydrocarbons capable of being polymerised by sulphuric acid, benzenes and a relatively very small proportion of hydrocarbons unattackable by sulphuric acid; the last-mentioned constituents are present in larger quantity in the steam distillate from the tar.

7. On mixing either liquid with moderately dilute sulphuric acid (2 vols. acid 1 vol. water) much heat is developed, and by its action the unsaturated hydrocarbons are for the most part converted into compounds which are not distillable in steam; in order to effect as complete a conversion as possible, it is desirable when the action appears to be at an end to separate the acid from the oil and to treat the latter with stronger acid—4 : 1. In dealing with small quantities a glass stoppered bottle is used; but for large quantities it is well to use a copper can with a tightly fitting metal plug: there is then no danger of the vessel bursting, and it is much easier to quickly cool the mixture. The acid should be added in small quantity at first, and care should be taken in agitating; in working with large quantities it is desirable to steam-distil as soon as the treatment with 2 : 1 acid is at an end, and to well mix the distillate with the stronger acid, as owing to the viscid character of the product it becomes very difficult to complete the conversion of the unsaturated hydrocarbons into polymerides.

The steam distillate finally obtained has a peculiar characteristic unpleasant odour, due apparently to the presence of volatile products of the action of the acid.

8. A large quantity of benzene may be directly crystallised out from the product so obtained from the liquid deposited from the gas during compression in the manner first described by Faraday and made popular many years later by Mansfield. We have employed a very simple apparatus for the purpose, consisting of a cylindrical vessel, closed only at the bottom, 12 inches high and 4·5 inches in diameter, made of brass $\frac{1}{16}$ of an inch thick; into this fits fairly closely a similar cylinder, the bottom of which has numerous fine holes bored through it. The larger cylinder is placed in a wooden pail or tub, surrounded

with a good freezing mixture, and the hydrocarbon is then poured into it; the walls of the cylinder soon become coated with crystals, which are detached by means of a stout metal rod, and this is frequently used in stirring the contents of the cylinder. When crystallisation is complete, the smaller cylinder is pushed down upon the crystalline pulp, the pail is placed between the jaws of an ordinary long carpenters' cramp, a block of wood is placed across the mouth of the inner cylinder, and pressure is gradually applied by turning the screw of the cramp. The expressed liquid is syphoned off as it rises into the interior of the cylinder. Pressure having been applied to a sufficient extent and during a sufficient length of time, the screw is released, the ram withdrawn, the cylinder lifted out of the freezing mixture, and the small amount of liquid floating on the solid cake is poured out; the benzene is then caused to melt by lowering into it a tube fitted up after the manner of a wash-bottle, through which steam is being passed.

If the mother-liquor from the crystals be fractionally distilled, and the portions boiling near to 80° be then treated as above described, a further considerable quantity of crystalline benzene may easily be obtained.

In like manner the lowest fractions of the product obtained on agitating the steam distillate from the tar with acid, &c., also yield benzene.

The benzene thus separated is by no means pure, and should be treated with alkaline permanganate, bromine, or sulphuric acid, fractionally distilled, and again crystallised.

9. As much of the benzene as possible having been removed, the residue is now extracted with hot concentrated sulphuric acid, and the benzenes are recovered from the solution by hydrolysis (*Chem. Soc. Trans.*, 1884, 148).

The acid should be placed together with the hydrocarbon in a vessel which can be closed—a stoppered bottle if a moderate quantity is to be treated, or a copper can if the quantity be large. To ensure intimate contact, the vessel is then very vigorously shaken. In the first instance cold acid may be used, as heat is developed by the dissolution of the more easily attacked hydrocarbons; afterwards the mixture of acid and hydrocarbon should be heated to 60—70°. An insufficient quantity of acid is used in the first treatment, and the unattacked hydrocarbon is afterwards shaken with fresh acid; finally it is violently shaken with weakly fuming acid in order to remove all the benzene. Care must be taken in doing this, as the action of the fuming acid usually gives rise to the production of gas—sulphur dioxide.

10. The residual unattacked hydrocarbon is then mixed with a little

alkali and steam-distilled; the product is a brilliant colourless liquid, having the pleasant sweet odour characteristic of a pure paraffin.

11. On hydrolysing the crude mixture of sulphonic acids, after the whole of the benzenoid hydrocarbons have been recovered, a considerable amount of black carbonaceous matter remains with the acid; we have always regarded this as formed from products of the polymerisation of unsaturated hydrocarbons by the dilute acid during the first treatment.

12. The method described is that which renders it possible to separate the whole of the benzenoid hydrocarbons from the original oil-gas products.   Much of the benzene, may, however, be obtained without destroying the unsaturated hydrocarbons by refrigerating the appropriate fraction of the liquid deposited on compression of the gas or of the steam distillate from the tar.   And it is scarcely necessary to point out, that either separate fractions of the original crude materials, or the crude materials as a whole, may be submitted to treatment in the above manner.

13. To separate the various constituents of the complex mixture of benzenoid hydrocarbons thus obtained, it is fractionally distilled. From the lowest fraction a considerable amount of benzene may easily be frozen out.   To separate the toluene, the fractions boiling below 115°, from which no more benzene can be obtained by refrigeration, are shaken with hot concentrated sulphuric acid: as benzene is less readily attacked than toluene, it is possible by fractional treatment with the acid to dissolve chiefly the latter, leaving a residue from which a further quantity of benzene may be crystallised out.   The mixture of sulphonic acids with sulphuric acid is poured into water, the solution neutralised with whiting paste, and the resulting calcium salts are then converted into potassium salts, &c.; the liquid when sufficiently concentrated deposits a large crop of the characteristic crystals of potassium tolueneparasulphonate, which are recrystallised and hydrolysed to recover the toluene.

14. The xylenes were separated by Jacobsen's method (*Ber.*, **10**, 1009) from the fractions boiling at 135—145°.   *Metaxylene* was identified by conversion into its characteristic trinitro-derivative; independent evidence of its presence was afforded by the production of metatoluic acid in large quantity on oxidation of the fractions collected between 135—145° of the original steam distillate from the oil-gas tar.   *Para-xylene* was obtained as sodium paraxylenesulphonate, $C_8H_9 \cdot SO_3Na \cdot H_2O$; and paratoluic acid was obtained on oxidation of the hydrocarbon separated by hydrolysis of this salt.   *Orthoxylene* was separated in the form of the highly characteristic sodium orthoxylenesulphonate, $C_8H_9 \cdot SO_3Na \cdot 5H_2O$.   The three isomeric xylenes appear to us to occur in the oil-gas product very much in the proportions in which

they ordinarily occur in coal-tar xylene, metaxylene being by far the most abundant, and paraxylene the least abundant.

15. Mesitylene and pseudocumene were separated from the fractions boiling between 155—175° by our method of fractional hydrolysis, the hydrocarbon being for this purpose dissolved in sulphuric acid, the solution diluted with water, and steam passed into it at a temperature not exceeding 100—105°. The hydrocarbon thus separated was then reconverted into sulphonic acid; the barium salt of the acid was almost pure mesitylenesulphonate, $(C_9H_{11}\cdot SO_3)_2Ba\cdot H_2O$, which is a very characteristic salt. The equally characteristic potassium salt was also prepared.

After separation of the main bulk of the mesitylene, the temperature was raised, and the whole of the hydrocarbon present separated by hydrolysis; it was then reconverted into sulphonic acid, and the latter several times recrystallised from dilute sulphuric acid, as recommended by Jacobsen (*Annalen,* **184**, 198). In this way a considerable quantity of pure pseudocumenesulphonic acid was readily obtained. The hydrocarbon separated from it had a constant boiling point, and the trinitro- and tribromo-derivative prepared from it had all the properties of these derivatives of pseudocumene.

Mesitylene and pseudocumene are, we think, also present in about the same relative proportions in oil-gas tar as in coal-tar, but it is much easier to separate them from the former on account of the absence of basic compounds.

16. The fractions 180—190° and 190—200° were separately converted into sulphonic acid, from which barium salts were prepared; the salts did not crystallise well, separating from a hot solution in an apparently amorphous state. The dry salt was highly pulverulent, and much like barium 1:2:3:5tetramethylbenzenesulphonate. The salt obtained from the 180—190° fraction was found to contain 23·97, 24·02, 23·81 per cent. of barium. Theory indicates the presence of 24·33 per cent. barium in the sulphonate of a hydrocarbon of the formula $C_{10}H_{14}$. The magnesium salt of the sulphonic acid prepared from the 180—190° fraction crystallised well in flat needles, containing 24·6 per cent. water and 5·21 per cent. of magnesium; a salt of the formula $(C_{10}H_{13}\cdot SO_3)_2Mg\cdot 8H_2O$ should contain 24·24 per cent. water and 5·33 per cent. magnesium. Magnesium pseudocumenesulphonate was prepared for comparison, and was found to be a very similar salt; it contained 26·32 per cent. of water and 5·56 per cent. magnesium. A salt of the formula $2[(C_9H_{11}\cdot SO_3)_2Mg]\cdot 17H_2O$ would contain 26·61 per cent. water and 5·68 per cent. magnesium. A small quantity of hydrocarbon separated from the barium salt prepared from the 180—190° fraction boiled at 178—188°, chiefly at 180—185°. It gave a solid bromo-derivative which, after recrystalli-

sation from alcohol melted at 215°; after repeated recrystallisation the melting point rose to 232·5°. The analysis of an impure portion of this bromide gave 64·59 per cent. bromine, but only 0·09 gram of substance could be used, and probably this contained tribromopseudo-cumene ; the amount corresponding with the formula $C_{10}H_{11}Br_3$ is 64·69 per cent. bromine.

In the barium salt prepared from the 190—200° fraction 23·12 and 23·36 per cent. of barium was found ; a salt of the formula $(C_{11}H_{15}\cdot SO_3)_2Ba$ should contain 23·36 per cent. barium.

These facts leave little doubt that at least one benzene higher in the series than trimethylbenzene is contained in the oil-gas product. Probably isodurene is present, but unfortunately the amount at our disposal was insufficient to enable us to prove this.*

17. A large quantity of naphthalene separates from the fractions collected above 200°. After its removal a comparatively small amount of hydrocarbon is left. Benzene being present in such large amount in the oil-gas product, it appeared not unlikely that diphenyl would also occur in them. Notwithstanding persistent efforts to isolate this hydrocarbon, however, we have entirely failed to discover it in the portions boiling between 250—260°. Hitherto, indeed, we have been unable to determine the nature of any of the benzenoid hydrocarbons of higher boiling point than naphthalene ; the quantity obtained is very small, and it is impossible to separate a pure substance by distillation.

II. *Hydrocarbons of the C_nH_{2n-2} Series.*

18. The separation and identification of the unsaturated hydro-carbons other than those of the benzenoid series is compassed with diffi-culty. By determining the amounts of bromine required to saturate the various fractions, it was in the first instance ascertained that not only olefines, but less saturated hydrocarbons were present. Moreover, that there were no true acetylenes among these, that is, hydrocarbons of the form $CH\cdot C\cdot C_nH_{2n+1}$, at once appeared from the fact that ammoniacal cuprous and argentic solutions were without appreciable action upon the liquid condensed from the oil-gas. This conclusion was confirmed by the observation made both at the Mansion House Station Works of the Metropolitan District Railway Company and at the Stratford Works of the Great Eastern Company that the gas

* Since this paper was placed in the printer's hands, K. E. Schulze has announced (*Ber.*, **18**, 3032) the discovery of 1:2:4:5tetramethylbenzene (durene) in coal-tar. It may be added that, in a paper read at the last spring meeting of the Iron and Steel Institute, Dr. Armstrong stated that the oil from the Jameson coke oven contained benzenes different from those in ordinary coal-tar.

itself produced but a very small amount of precipitate in an ammoniacal cuprous solution.

19. On warming the crude liquid obtained from the reservoirs in which the gas is stored, distillation at once sets in, much gas being at first given off; this gas is absorbed by bromine. On steam-distilling the resulting bromide, less than two-thirds passed over as a colourless heavy oil; the residue became almost entirely solid on cooling, and from it a pure substance was readily obtained by crystallisation from alcohol.

In like manner by passing the compressed oil-gas into bromine, a liquid bromide was obtained which was for the most part easily volatile, only about 7 per cent. remaining when oil ceased to distil over; the residue partially solidified on cooling, and from it more than half its weight of a solid bromide was obtained identical with that referred to in the previous paragraph.

The bromide in question crystallised from alcohol in small, glistening plates, exhibiting under the microscope a very irregular outline; it fused at 116°, and volatilised with extreme slowness in a current of steam. The percentage of bromine in it, as determined by Volhard's method of combustion with potassium nitrate and sodium carbonate, &c., was found to be 85·99. Hence there could be little doubt that it was a tetrabromide of the formula $C_4H_6Br_4$, the percentage of bromine in which is 85·55. Judging from its properties, the bromide thus obtained is identical with the crotonylene tetrabromide prepared by Caventou from the liquid deposited on compressing coal-gas.

Theoretically, four distinct hydrocarbons of the formula C_4H_6 are possible, viz. :—

1. Ethylacetylene	$CH \cdot CEt$.
2. Dimethylacetylene	$CMe \cdot CMe$.
3. Methylallene	$CHMe \cdot C \cdot CH_2$.
4. Vinylethylene (dimethyleneethane)	$CH_2 \cdot CH \cdot CH \cdot CH_2$.

Ethylacetylene is excluded, as our hydrocarbon is not a true acetylene; the hydrocarbon obtained by Caventou from crude butylene bromide gave a tetrabromide which volatilised somewhat readily in the air, and from Almedingen's experiments there is every reason to suppose that this hydrocarbon was dimethylacetylene (*Ber.*, **14**, 2073). By distilling erythrol with formic acid, Heninger obtained a hydrocarbon of the formula C_4H_6 yielding a bromide similar to that prepared by ourselves and apparently identical with that obtained by Caventou by the decomposition of fusel oil at a red heat and from coal-gas: as this hydrocarbon is formed from erythrol it may almost certainly be regarded as dimethyleneethane or vinylethylene. On inspection of the four formulæ it will be obvious that a study of the

oxidation-products is calculated to afford the required proof : vinyl-ethylene should not yield acetic acid, which would, however, be a product of the oxidation of both dimethylacetylene and methylallene ; and ethylacetylene forms propionic acid.

20. To obtain the hydrocarbon for oxidation, we have employed a method which we believe will in the future be of great service in the investigation of unsaturated hydrocarbons. The usual practice is to withdraw the bromine from the bromides of these hydrocarbons by means of sodium, but there are numerous objections to this method : in many cases the change takes place only with difficulty and at a high temperature ; in others secondary products are formed owing to the high temperature locally developed ; and the sodium usually becomes coated with a protecting layer of bromide. It occurred to us that Gladstone and Tribe's zinc-copper couple might be used with advantage, they having already shown that ethylene and propylene bromides are readily deprived of their bromine by its action in pre-sence of alcohol (*Chem. Soc. J.*, 1874, 406). The results have entirely surpassed our expectations ; as in all cases hitherto examined we have obtained a practically theoretical yield of hydrocarbon by merely warming the bromide with alcohol and the couple. Moreover, the hydrocarbon thus recovered has always been found to be identical with that used in preparing the bromide—that is, it again yields the same bromide. Unfortunately this method was not made use of until nearly the close of our experiments ; had we known of it earlier, we feel sure that we should have been in a position to throw far more light on the nature of the products of the oil-gas manufacture. We may add that it is our intention fully to inquire into the application of this method to the separation of unsaturated hydrocarbons from their compounds with halogens.

21. The oxidation of the hydrocarbon separated from the bromide $C_4H_6Br_4$ by the action of the zinc-copper couple was effected by displacing part of a 2 per cent. solution of potassium perman-ganate from a bottle full of it by means of the gas from 50 grams of the bromide—the gas having been collected over water in a holder and left for some time in contact with the water to remove alcohol-vapour. The permanganate was vigorously shaken to bring it into contact with the gas, and the oxidation being completed, sulphuric acid was added and the volatile acid removed by steam-distillation. The distillate was neutralised by the addition of about 1·6 gram of sodium carbonate ; the neutral liquid having been con-centrated, the required amount of silver nitrate was added, and the solution boiled : an amount of silver was precipitated practically equivalent to the silver nitrate used, and no trace of acetate could be detected in the filtrate.

As formic acid is its oxidation-product, there can be no doubt that the hydrocarbon of the formula C_4H_6 from oil-gas is dimethylene-ethane or vinylethylene, $CH_2 \cdot CH \cdot CH \cdot CH_2$.

22. On steam-distilling the bromides prepared from the fractions of the original liquid from the oil-gas reservoir collected within a few degrees on either side of 40°, dark-coloured viscid residues were obtained in which crystals gradually formed. It was easy to separate these mechanically, and to purify them by recrystallisation from alcohol. The pure substance crystallised in long, thin, narrow, well-defined prisms, melting at 115°. Analysis gave results agreeing with the formula $C_5H_8Br_4$; thus:—
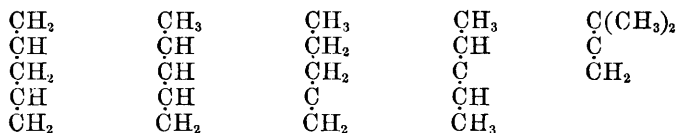
Subs. 0·1982		AgBr 0·3828	Bromine	per cent.		82·19
,,	0·2210	,,	0·4284	,,	,,	82·49
,,	·0·2441	,,	0·4734	,,	,,	82·53
,,	0·2544	,,	0·4935	,,	,,	82·55
,,	0·2083	,,	0·4021	,,	,,	82·15
,,	0·2278	H_2O	0·0471	Hydrogen	,,	2·30
,,	0·2612	,,	0·0544	,,	,,	2·31
,,	0·2278	CO_2	0·1322	Carbon	,,	15·82
,,	0·2612	,,	0·1526	,,	,,	15·93

		Percentages.	Mean results.
C_5	59·85	15·47	15·87
H_8	8·00	2·07	2·30
Br_4..........	319·04	82·46	82·38
	386·89	100·00	100·55

23. The hydrocarbon was separated from this bromide by warming it with the zinc-copper couple and alcohol; the amount obtained was almost the theoretical. After several days' digestion with calcium chloride in a sealed tube it was distilled; it boiled almost constantly at about 45°, leaving a few drops of a syrupy residue which exploded when heated on platinum, in this respect behaving somewhat like isoprene. It had the peculiar alliaceous odour so characteristic of the crude liquid deposited from oil-gas. It was reconverted into the original tetrabromide on careful treatment with bromine. It was readily oxidised by a 4 per cent. solution of potassium permanganate : more than half of the volatile acid produced was formic acid, the rest being *pure* acetic acid.
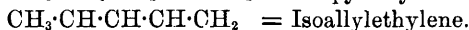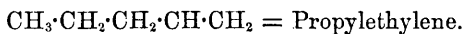
Five hydrocarbons of the formula C_5H_8 are at present known : propylacetylene, isopropylacetylene, ethylmethylacetylene, piperylene and isoprene ; ours appears to be a sixth. The first three of these are excluded from consideration on account of their behaviour on

oxidation ; moreover, our hydrocarbon is not a true acetylene, and
cannot, therefore, be either propyl- or isopropyl-acetylene. Piperylene,
according to Hofmann (*Ber.*, **14**, 665), forms a tetrabromide crystal-
lising from alcohol in glistening *plates*. Isoprene yields a liquid
bromide. Eight modifications in all are possible of a hydrocarbon of
the formula C_5H_8; three of these are derived from acetylene ; the
formulæ of the remaining five are as follows :—

$\overset{.}{C}H_2$	$\overset{.}{C}H_3$	$\overset{.}{C}H_3$	$\overset{.}{C}H_3$	$\overset{.}{C}(CH_3)_2$
$\overset{.}{C}H$	$\overset{.}{C}H$	$\overset{.}{C}H_2$	$\overset{.}{C}H$	$\overset{.}{C}$
$\overset{.}{C}H_2$	$\overset{.}{C}H$	$\overset{.}{C}H_2$	$\overset{.}{C}$	$\overset{.}{C}H_2$
$\overset{.}{C}H$	$\overset{.}{C}H$	$\overset{.}{C}$	$\overset{.}{C}H$	
$\overset{.}{C}H_2$	$\overset{.}{C}H_2$	$\overset{.}{C}H_2$	$\overset{.}{C}H_3$	
Allylethylene.	Isoallylethylene.	Ethylallene.	Symmetrical dimethyl- allene.	Unsymmetrical dimethylallene.

Piperylene, according to Ladenburg (*Ber.*, **16**, 2059) is allylethylene ;
and that this is not the composition of our hydrocarbon may be
inferred from the fact that it yields acetic acid on oxidation. Ethyl-
allene is also excluded as it would furnish propionic acid on oxidation.
But three formulæ remain therefore, and we incline to select that of
isoallylethylene on account of the simple relation which this hydro-
carbon bears to normal amylene, from which probably our hydro-
carbon is immediately derived :—

$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH \cdot CH_2 = \text{Propylethylene.}$$
$$CH_3 \cdot CH \cdot CH \cdot CH \cdot CH_2 \ = \text{Isoallylethylene.}$$

If our argument be correct, isoprene must be either symmetrical or
unsymmetrical *dimethylallene;* taking into consideration all that is
known of the terpenes—to which it is so intimately related—the latter
is the more probable. We are now engaged in the study of the hydro-
carbons of the formula C_5H_8 in the hope of solving this problem,
which is one of considerable importance in connection with the ques-
tion of the constitution of the hydrocarbons of the formula $C_{10}H_{16}$.

24. A faulty determination of bromine, made by Volhard's method,
led us, in the first instance, to regard the bromide just described
as identical with Schorlemmer's so-called hexoylene tetrabromide,
$C_6H_{10}Br_4$, whose description of this compound tallies very closely
with that which we have given of our tetrabromide. Schorlemmer
prepared his substance from a fraction boiling at about 80° of the
more volatile products of the distillation of boghead cannel ; to this
he added bromine in excess, and after removing the greater part of
the admixed benzene by distillation, he heated the bromide with
sodium to regenerate the hydrocarbon ; this was again brominated.

The product was an oil from which the solid gradually crystallised out. It may be mentioned that Schorlemmer bases the formula $C_6H_{10}Br_4$ on a single determination of bromine in only 0·1970 gram of substance. In the hope, therefore, of obtaining hexoylene we very carefully fractioned out a portion boiling at about 80—82° from our crude material, and this was brominated; on steam-distilling the product much benzene passed over, then an oily bromide heavier than water, a moderately limpid dark-brown oil remaining; no crystals whatever separated from this, and it was therefore submitted to the action of the zinc-copper couple in presence of alcohol. The re-generated hydrocarbon was again brominated and steam-distilled; very little came over. A minute quantity of solid was, however, deposited in the condenser. The experiment was repeated with a considerable quantity of the fractions collected at 70—80°: after adding excess of bromine, the product was steam-distilled until exhausted; traces of a solid were again obtained. On extracting the residue with alcohol comparatively little dissolved and no crystals could be obtained from the alcoholic extract: the final residue was a carbonaceous mass. The solid referred to crystallised from alcohol in small, hard, well-formed, short prisms melting at 185°; the quantity obtained was too small even for an analysis.

25. In all cases, on steam-distilling the crude bromides from the various fractions, decomposition was observed to take place more or less; and the non-volatile residue from all but the lowest fractions was more or less carbonaceous, and alcohol extracted but very little oily matter, leaving a friable residue. The bromides which are thus decomposed are probably derived from hydrocarbons of the C_nH_{2n-2} series—or in part perhaps from less saturated hydrocarbons—such as Schorlemmer has shown to be present in cannel oils. The polymer-ides obtained by means of sulphuric acid were precisely of the character of those described by Schorlemmer (*Annalen*, 1866, **139**, 244).

III. *Hydrocarbons of the Olefine group.*

26. Indication of the presence of these hydrocarbons is afforded by the behaviour with bromine especially of the lowest fractions of the " hydrocarbon " deposited during compression of oil-gas; these frac-tions, if free from benzene, are entirely converted into polymerides and soluble bodies on treatment with sulphuric acid : they therefore con-sist of unsaturated hydrocarbons, but the amount of bromine which they will absorb is far less than would be the case if they contained only hydrocarbons less rich in hydrogen than the olefines.

To isolate the pure olefines from mixtures such as those with which

we have had to deal, no ordinary method will suffice ; had we become aware that the zinc-copper couple was applicable to the separation of unsaturated hydrocarbons from their bromides at an early stage instead of almost at the close of this portion of the investigation, it would undoubtedly have been possible to isolate the olefines ; but as it was we were obliged to content ourselves with the proof that olefines were present, and with an indirect determination of their nature.

The method followed consisted in oxidising the various fractions by agitation in a stoppered bottle with a cold 4 per cent. solution of potassium permanganate. In selecting this method of treatment we were guided by the knowledge that the normal olefines—those of the type $C_nH_{2n+1}\overset{\cdot}{C}H\cdot CH_2$—are converted by oxidation into acids of the acetic series of the type $C_nH_{2n+1}COOH$, the CH_2 group being eliminated as formic acid ; only true acetylenes—i.e., hydrocarbons of the formula $C_nH_{2n+1}C\cdot CH$—yield similar products, and, as these were known to be absent from our crude material, the production of the corresponding acid from a fraction of about the boiling point of any particular normal olefine would be conclusive proof of the presence of that olefine. Thus the normal amylene fraction should yield butyric acid, the normal hexylene fraction valeric acid, &c.

The appropriate fractions having been oxidised, sulphuric acid was added, and the volatile acid separated by steam-distillation ; the distillate was neutralised with sodium carbonate, concentrated, and then fractionally precipitated with silver nitrate ; the silver precipitates were fractionally extracted with water, the solutions well boiled to decompose formate, and the dissolved salts crystallised out and analysed. When a silver salt of constant composition was obtained, it was converted into the calcium salt, as the lower normal primary acids of the acetic series all furnish characteristic calcium salts.

27. The amylene, hexylene, and heptylene fractions treated in this way gave respectively normal butyric, normal valeric, and normal caproic acids.

The higher fractions were similarly treated, but repeated experiments failed to yield any indication whatever of the presence of olefines higher than heptylene : formic and acetic were the only volatile paraffinoid acids produced—these being associated with the oxidation-products of the benzenoid hydrocarbons present in the fractions examined.

A very careful study of all the various fractions obtained has convinced us that besides the three normal primary olefines above mentioned, no other hydrocarbons of the C_nH_{2n} series, or indeed of any other paraffinoid series, can be present, except such as yield acetic and formic acids on oxidation ; and we have no reason to suspect that any olefines other than those mentioned are present in the liquid

products from the manufacture of oil-gas : our opinion being that the acetic acid obtained was derived from hydrocarbons less saturated than the olefines.

28. We have already referred to the presence of the hydrocarbon C_4H_6 in the compressed oil-gas (§ 19), and to the manner in which it was separated from the crude mixture of bromides obtained on passing the gas into bromine. On distilling the steam-distillate from this mixture of bromides some hydrogen bromide was evolved, but after a few distillations the constituent yielding this gas was practically all decomposed. By far the largest amount of the bromide separated by fractional distillation had about the boiling point of ethylene bromide, and a considerable quantity of this compound was crystallised out from this portion of the distillate by refrigeration.

29. The next largest fraction had about the boiling point of methylethylene (propylene) bromide, and we have no doubt that it mainly consisted of this compound, as acetic acid was obtained in large quantity by direct oxidation of this fraction with permanganate.

30. Ethylene and propylene having thus been detected in the oil-gas, and normal amylene, hexylene and heptylene in the liquid deposited from it, it was to be expected that normal butylene was also present. A quantity of about 4000 grams of bromides from the gas gave, however, but a relatively small quantity boiling at a higher temperature than propylene bromide, and as it was impossible to separate a pure product by distillation, the various fractions were directly oxidised with permanganate. The quantities used were :—

59 grams boiling at			$148—153°$
42	,,	,,	$153—158$
14	,,	,,	$158—164$
51	,,	,,	above $164°$.

The acid distillate was treated with lead oxide in the manner recommended by Linnemann (*Annalen*, **160**, 222), in order to separate propionic acid, but this acid could not be detected ; in fact, only acetic and formic acids were formed.

We have before mentioned that a considerable quantity of bromides was obtained by passing into bromine the gas given off when we began to distil the liquid deposited from oil-gas on compression, and that at least two-thirds of this was volatilised on steam-distillation, the residue consisting mainly of crotonylene tetrabromide ; it is possible that the portion of the mixture of bromides volatile with watervapour contained butylene bromide, but most unfortunately the whole of this material was lost in the fire which occurred in the laboratory of the London Institution during the course of the investigation.

As butylene has a much lower boiling point than crotonylene, we

should certainly expect to find its bromide among those obtained from oil-gas itself, as a considerable quantity of crotonylene tetrabromide is present; our failure to detect it has led us to consider the evidence advanced by Faraday upon which the discovery of butylene among the oil-gas products is attributed to him, and we are of opinion that it is by no means conclusive.   His words are as follows:—

"If a portion of the original liquid be warmed by the hand, or otherwise, and the vapour which passes off be passed through a tube at 0° (Fahr.), very little condensed vapour will go on to the mercurial trough, but there will be found after a time a portion of fluid in the tube distinguished by the following properties.   Though a liquid at 0°, it upon slight elevation of temperature begins to boil, and before it has attained 32° is all resolved into vapour or gas.   .   .   .   The sp. gr. of the portion I obtained was between 27 and 28, hydrogen being 1.   .   .   .   .   When cooled to 0° it condensed again, and inclosed in this state in a tube of known capacity and hermetically sealed up, the bulk of a given weight of the substance at common temperatures was ascertained.   This compared with water gave the sp. gr. of the liquid as 0·627 at 54°.   .   .   .   .   Alcohol dissolves it in large quantity.   .   .   .   .   Sulphuric acid condenses the gas in very large quantity: 1 volume of the acid condensing above 100 volumes of the vapour.   .   .   .   .   Great heat is produced during the action; no sulphurous acid is formed; the acid is much blackened, has a peculiar odour, and upon dilution generally becomes turbid, but no gas is evolved.   A permanent compound of the acid with carbon and hydrogen is produced, and enters as before mentioned into combination with bases. A mixture of 2 volumes of this vapour with 14 volumes of pure oxygen was made, and a portion detonated in a eudiometer-tube; 8·8 volumes of the mixture diminished by the spark to 5·7 volumes, and these by solution of potash to 1·4 volumes, which were oxygen.   Hence 7·4 volumes had been consumed, consisting of:—

Vapour of substance	1·1
Oxygen	6·3
Carbonic acid formed....................	4·3
Oxygen in carbonic acid	4·3
Oxygen combining with hydrogen..........	2·0
Diminution by spark	3·1

This is nearly as if 1 volume of the vapour or gas had required 6 volumes of oxygen, had consumed 4 of them in producing 4 of carbonic acid gas, and had occupied the other 2 by 4 of hydrogen to form water.   Upon which view 4 volumes or proportionals of hydrogen = 4, are combined with 4 proportionals of carbon = 24, to form

1 volume of the vapour, the specific gravity of which would therefore be 28. Now this is but little removed from the actual specific gravity obtained by the preceding experiments; and knowing that this vapour must contain small portions of other substances in solution, there appears no reason to doubt that, if obtained pure, it would be found thus constituted. . . . . Chlorine and the vapour were therefore mixed in an exhausted retort: rapid combination took place, much heat was evolved, and a liquor produced resembling hydrochloride of carbon, or the substance obtained by the same process from olefiant gas. . . . . Further, it was composed of nearly equal volumes of the vapour and chlorine; it could not, therefore, be the same as the hydrochloride of carbon from olefiant gas, since it contains twice as much carbon and hydrogen."

Taking into account our own observations, especially the fact that we have failed to detect butylene although crotonylene was obtained in considerable quantity, we are inclined to think that Faraday was the discoverer of crotonylene rather than of butylene. It is obvious that he could not have had a pure substance for examination; the ratio of the density of his gas to that of hydrogen was between 27 and 28, and these are numbers which represent the relative density of crotonylene and butylene respectively; the results of his combustion-analysis are almost equally compatible with either formula, C_4H_6 or C_4H_8, always bearing in mind that probably both propylene and amylene were present as impurities; we are not aware that the behaviour of butylene with sulphuric acid has been studied, but it is scarcely probable that it would be so readily absorbed as Faraday describes; there remains but one fact which undoubtedly lends support to the conclusion that it was butylene, viz., that on mixing it with chlorine a chloride was formed, "composed of nearly equal volumes of the vapour and of chlorine." Our proof of the absence of butylene, it should be added, holds good only on the assumption that the butylene present is *ethylethylene*, as the two dimethylethylenes would yield acetic acid on oxidation. As, however, all the olefines which are proved to have been present are represented by the formula $C_nH_{2n+1}\cdot CH\cdot CH_2$, it does not appear probable that the butylene would form an exception, especially as the crotonylene which is so abundantly contained in oil-gas is indubitably a derivative of normal butylene.

IV. *Hydrocarbons insoluble in sulphuric acid.*

31. Our method of separating these hydrocarbons has already been described (§§ 7—10). They are contained almost exclusively in the portion boiling above 150° of the steam-distillate from oil-gas tar: for example, about 1800 c.c. of fractions boiling at 105—130° gave after

exhaustive treatment with sulphuric acid only 6 grams of insoluble hydrocarbons boiling at about 125—140°.

As far as possible, with the limited amount of material at our disposal, the attempt was made to separate the mixture into its constituents by fractional distillation; but no very decided separation was accomplished. Three fractions were analysed with the following results:—

	160—165°.	180—185°.	200—205°.
Carbon percentage	85·33	85·37	85·27
	—	85·26	85·70
	—	85·63	85·50
	—	—	85·39
Hydrogen percentage	14·80	14·74	14·32
,, ,, ...	—	14·73	—
Relative density, $\dfrac{0°}{0°}$	0·7775	0·7886	0·8050
,, ,, $\dfrac{20°}{20°}$	0·7637	0·7768	0·7980

The general mean of the eight carbon determinations is 85·43 per cent., and of the four hydrogen determinations* 14·63 per cent. These numbers are very nearly those which correspond to the formula C_nH_{2n}, viz., 85·56 per cent. carbon and 14·32 per cent. hydrogen. A paraffin of the formula $C_{10}H_{22}$ contains only 84·47 per cent. carbon and 15·53 per cent. hydrogen; while even that of the formula $C_{12}H_{26}$ contains but 84·67 per cent. carbon and 15·33 per cent. hydrogen. The conclusion that our products did not in the main consist of hydrocarbons of the C_nH_{2n+2} type is confirmed by the comparison of our determinations of relative density with the data given by Krafft (*Ber.*, **15**, 1687) for the normal paraffins:—

	B. p.	Density at 0°.	Density at 20°.
$C_{10}H_{22}$	173·0°	0·7452 gram.	0·7304 gram.
$C_{11}H_{24}$	194·5	0·7557 ,,	0·7411 ,,
$C_{12}H_{26}$	214·5	0·7655 ,,	0·7511 ,,

Our figures are in every case considerably higher, and the difference would be greater if a strict comparison were made by calculating the densities corresponding to our relative densities. We are satisfied that this is not due to the presence of benzenoid hydrocarbons, as special care was taken to remove these by treatment with fuming sulphuric and nitric acids followed by distillation from sodium.

* As a warning to those who, like myself, are in the habit of using compressed oxygen for combustions, I may mention that several hydrogen determinations were lost, owing, as was afterwards discovered, to the presence of traces of hydrogen in the oxygen.—H. E. A.

Our figures more nearly agree with those given by Markownikoff and Oglobine (*Ann. Chim. Phys.*, 1884 [6], **2**, 372) for the C_nH_{2n} hydrocarbons which they separated—probably in a state of only approximate purity—from Russian petroleum :—

	B. p.	Density at 0°.	
$C_{10}H_{20}$.	161°	0·795	gram.
$C_{11}H_{22}$.	180	0·8119	,,
$C_{12}H_{24}$.	196	0·8025	,,

Hence we are of opinion that the portion insoluble in sulphuric acid of the steam-distillate from oil-gas tar which we have examined contained both true paraffins and *pseudolefines* such as mainly compose Russian petroleum, the latter being probably the principal constituents.

V. *Summary and discussion of results.*

32. Thus far we have been led to recognise among the products of the manufacture of oil-gas the following hydrocarbons :—

a. Paraffins, of which traces only may be said to be present.

b. " Pseudolefines," that is, *saturated* hydrocarbons of the C_nH_{2n} series such as occur in Russian petroleum ; these also are present in relatively small amount.

c. Olefines, viz., ethylene, propylene, normal amylene, normal hexylene and normal heptylene, all higher homologues being absent. Ethylene is an important constituent of oil-gas as used, and so also apparently is propylene. The liquid deposited from the crude gas on compression is moderately rich in amylene, hexylene and heptylene.

d. " Pseudacetylenes," viz., crotonylene (dimethyleneethane), $CH_2 \cdot CH \cdot CH \cdot CH_2$, and isoallylethylene, $CH_3 \cdot CH \cdot CH \cdot CH \cdot CH_2$. The former is probably an important constituent of the gas, being of high value as an illuminant. Besides these two, both the liquid deposited on compression of the gas and the tar are rich in hydrocarbons identical with, or very closely related to, those discovered by Schorlemmer in cannel oils.

e. Benzenoid hydrocarbons, viz., benzene, toluene, the three isomeric dimethylbenzenes, the two trimethylbenzenes—pseudocumene and mesitylene—and naphthalene ; the first mentioned is a specially important constituent in point of quantity. There is reason to believe that other benzenoid hydrocarbons besides these are present, even in the portions of the tar volatile with steam.

33. We have had the opportunity of examining various samples of the oil—shale oil or crude petroleum—used at the works from which we have obtained our materials, and have satisfied ourselves that the

proportion of constituents in them volatile with water-vapour was small, and that they were of a different character from those met with in the bye-products from the manufacture; we have therefore little doubt that practically all the above-mentioned substances are produced in the course of the manufacture of the gas.

34. The paraffins are probably formed in the manner indicated by Thorpe and Young (*Proc. Roy. Soc.*, 1873, **21**, 184), although it is possible that they are in part original constituents of the oil used. It is, however, noteworthy that whereas Thorpe and Young in their investigation of the decomposition of solid paraffins by heat obtained mixtures of lower paraffins and olefines almost in equimolecular proportions from pentane upwards, our material, although rich in amylene and its next two homologues, has not been found to contain the corresponding paraffins.

35. The " pseudolefines " are also more probably products of change than original constituents. But it is to be remembered that according to Beilstein and Kurbatow (*Ber.*, **13**, 2028), American petroleum contains hydrocarbons of the C_nH_{2n} series similar to those in Russian petroleum : hence, assuming our view to be correct, the question arises whether the pseudolefines are formed by simplification of higher pseudolefines or by the removal of hydrogen from corresponding paraffins. Theoretically this question is one of considerable importance, and we are therefore making it the subject of special experimental study.

36. The presence of olefines in products of the distillation of cannel, of coal and of paraffin, has been established by various observers, but no proof of their nature had hitherto been given; it is therefore a matter of interest that those detected by us are all of the type $C_nH_{2n+1}\cdot CH\cdot CH_2$.

37. Regarding the hydrocarbons of the C_nH_{2n-2} series, it is to be noted that vinylethylene is present in much larger proportion than isoallylethylene, and hence it may be inferred that the former is a much more stable compound. Judging from the behaviour on oxidation of the remaining unsaturated hydrocarbons, which it is to be assumed are to a large extent also members of the C_nH_{2n-2} series, it appears probable that they are formed from corresponding normal paraffins by processes similar to those by which these paraffins are converted into normal olefines and by which vinylethylene and isoallylethylene are formed from the corresponding normal olefines or paraffins.

38. Since Berthelot's discovery of the formation of benzene from acetylene, the benzenoid hydrocarbons have always been regarded as built up from true acetylenes (comp. Jacobsen, *Ber.*, **10**, 853). The fact that true acetylenes are all but absent from oil-gas and the bye-products of its manufacture would lead us to doubt whether this is

so entirely the case ; and the question arises whether these hydrocarbons may not also be *directly descended from corresponding paraffins :* whether, for example, benzene may not be obtainable directly from hexane by withdrawal of hydrogen. It is sufficient to point this out, and it would be useless to further discuss the question ; but we shall endeavour to solve it by experiment.

It will suffice to have pointed out thus briefly the various problems which await experimental investigation arising out of the examination of the products of the decomposition of petroleum hydrocarbons in the manufacture of oil-gas. By continuing the examination of these products, and also by the study of the changes undergone by a material of more definite composition than the oils used for the purpose, viz., solid paraffin, we hope to obtain facts which will serve to elucidate the nature of many of the changes in hydrocarbons which occur at higher temperatures. The subject is one of very great importance, both as bearing on the discovery of rational methods of coking coal and of manufacturing illuminating gas and also hydrocarbons such as benzene, naphthalene and anthracene. It has undoubtedly also a bearing upon the question as to the origin of the complex mixtures of hydrocarbons such as constitute the different varieties of natural petroleum.

Dr. Armstrong has in his previous paper expressed his thanks to various gentlemen connected with the Great Eastern and Metropolitan District Railways for aid afforded him in carrying out this investigation. We desire on this occasion, however, to thank Mr. W. F. Pettigrew, Engineer in charge of the Great Eastern Company's oil-gas works, for his ever-ready assistance during the past year.

 City and Guilds of London Institute,
  Central Institution,
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