

Transactions (*continued*).

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“On the Combined Action of Heat and Pressure upon the Paraffins.” By T. E. THORPE and JOHN YOUNG, of the Andersonian University, Glasgow. Communicated by Prof. H. E. Roscoe, F.R.S. Received June 5, 1872\*.

1. In a preliminary communication read before the Royal Society on March 9th, 1871†, we described the combined effect of heat and pressure upon the solid paraffins. We showed that when these substances are exposed to a high temperature in a closed vessel they are almost completely resolved, with the evolution of but little gas, into hydrocarbons, which remain liquid at the ordinary temperature. This transformation may be easily effected on the small scale. A few grms. of ordinary paraffin are sealed up in a piece of strong combustion-tubing bent in the form of the letter **V**: the tube is securely surrounded by stout wire gauze, and the limb containing the paraffin is gently heated along its entire length in a gas combustion-furnace. If the heat is properly regulated, the paraffin rapidly distils over and solidifies in the cold portion of the tube. The gas-flames are then turned down, the tube reversed, and the paraffin again distilled. After a very few repetitions of this process the paraffin acquires the consistency of butter, and the warmth

\* Read June 20, 1872. See abstract, vol. xx. p. 488.

† Proc. Roy. Soc. vol. xix. p. 370.

of the hand is sufficient to liquefy it, and after about a dozen distillations it remains permanently liquid. Although there is no difficulty in thus ultimately effecting the resolution of the solid paraffin into liquid products, the rapidity of the transformation seems to be dependent upon conditions which we cannot yet say we have satisfactorily determined. On one occasion, after all the paraffin had been distilled over and had solidified in the colder limb of the tube, the empty portion in contact with the flame became softened and blew out, when instantly, on the removal of the pressure, the solid matter became liquid, and slightly effervesced as if gas had been condensed in the substance by the pressure to which it had been subjected. It seems to be absolutely necessary that the paraffin should be thus distilled over and condensed; by merely heating it in the tube in such a manner that the condensed vapours flow back again upon the heated portion, the liquefaction of the paraffin is never accomplished. About 6 grms. of a pure paraffin, melting at  $41^{\circ}5$  C. (see section 12), were heated in a sealed tube to about  $200^{\circ}$  for twelve hours, but the melting-point remained unchanged. The same portion of paraffin was then transferred to a **V**-tube surrounded by wire gauze, and distilled backwards and forwards in the combustion-furnace. After six distillations it was rendered completely liquid. The total quantity of liquid obtained was about 6 cub. centims. On gently warming it, bubbles of gas were evolved, and the liquid was in full ebullition at  $40^{\circ}$ , but only about one sixth came over below  $100^{\circ}$ ; about  $2\frac{1}{2}$  cub. centims. distilled between  $100^{\circ}$  and  $200^{\circ}$ , and nearly the whole of the remainder below  $300^{\circ}$ ; the small quantity remaining solidified when the bulb was plunged into cold water.

2. It appears that only paraffins boiling at an extremely high temperature, and those usually solid under ordinary conditions, are thus susceptible of decomposition. The readiness with which they yield liquid hydrocarbons appears to depend upon the complexity of their constitution. We have not determined with certainty the limits of the decomposition; but we find that the paraffin (and olefine) boiling at about  $255^{\circ}$  (see section 11) may be repeatedly distilled backwards and forwards in a sealed **V**-tube without suffering the slightest change. 6–7 grms. of the mixture of hydrocarbons were distilled backwards and forwards twenty-one times; but on opening the tube no gas was evolved, and the boiling-point ( $252^{\circ}$ – $255^{\circ}$  uncorrected) remained unaltered. A further proof of its unalterability on repeated distillation under pressure is afforded by its reaction with bromine (see section 5).

I. 9.38 grms. of the mixed hydrocarbons before distillation required 2.95 grms. of bromine before the liquid became permanently reddened; 100 parts by weight would require 31.4.

II. 8.605 grms. hydrocarbon before distillation required 2.672 grms. of bromine, or 100 grms. would require 31 of bromine. Mean amount of bromine needed 31.2 per cent.

III. 5.13 grms. of the hydrocarbon after repeated distillation (21 times) required 1.54 grm. of bromine, or 100 grms. would require 30 grms.

3. In the hope of throwing some light upon the constitution of the solid paraffins, we have repeated this process of transformation into liquid products upon a large scale. The paraffin employed was obtained from shale; it melted at  $46^{\circ}$  and solidified at  $43^{\circ}$ , and had a specific gravity of 0.906 at  $13^{\circ}$ , when solidified under an extra pressure of 0.75 millim. of mercury\*.

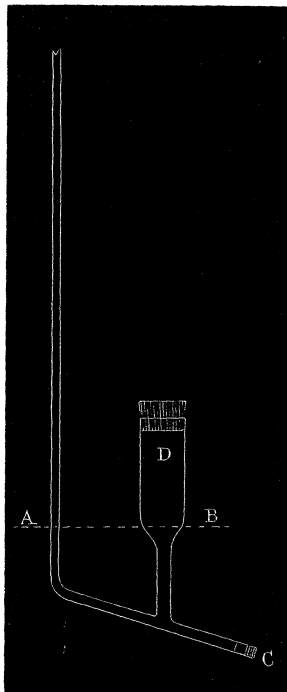
It was burnt with copper oxide in a stream of oxygen, with the following results:—

I. 0.2980 grm. paraffin gave 0.9293 grm. carbon dioxide and 0.3980 grm. water.

II. An unknown quantity gave 1.4245 grm. carbon dioxide and 0.6060 grm. water.

	I.	II.	Mean.
Carbon .....	85.05	85.23	85.14
Hydrogen .....	14.84	14.77	14.81
	<hr/> 99.89	<hr/> 100.00	<hr/> 99.95

\* Considerable discordances exist in the statements by various observers of the specific gravities of the solid paraffins. These differences are doubtless due more to the difficulty of obtaining the bodies perfectly homogeneous after melting than to any great variations in their true specific gravity. When a piece of ordinary paraffin is examined, it is seen to be made up of an infinite number of small cavities; and however carefully it may be cooled after melting, the interstices are invariably present. From this circumstance it is obvious that any attempt to determine the real specific gravity of this body would give too low a result. By solidifying the paraffin under pressure, the formation of the cavities may be, to a great extent, obviated. We have effected the solidification in the apparatus figured in the margin. Mercury was first poured into the tube up to the level A B, the bottom end of the tube being securely plugged by a cork C. The wider portion D of the tube was then filled with the melted paraffin, and a well-fitting caoutchouc cork fastened down by wire into the opening, care being taken to exclude all bubbles of air. Mercury was now quickly poured into the longer limb of the tube until it stood about 0.8 m. above the level of the metal in the wider tube, and under the pressure of this mercury the paraffin was allowed to solidify slowly. By withdrawing the cork C, the mercury could flow out, and on warming the sides of the tube the plug of paraffin was easily detached. Thus solidified, the body was almost entirely free from cavities, and portions perfectly homogeneous were easily found; these had a specific gravity of 0.906 at  $13^{\circ}$ .



These numbers agree perfectly with those obtained by Anderson many years ago\* from analysis of a paraffin identical in origin and melting-point ( $45^{\circ}5$ ) with that employed by us. Dr. Anderson found for the substance the composition :—

Carbon .....	85.1
Hydrogen .....	15.1
	<hr/>
	100.2

A sample of paraffin from peat, melting at  $46^{\circ}7$ , gave :—

	I.	II.	Mean.
Carbon .....	84.95	85.23	85.09
Hydrogen .....	15.05	15.16	15.10
	<hr/>	<hr/>	<hr/>
	100.00	100.39	100.19

In the process of conversion we replaced the bent glass tube above described by an apparatus consisting of two cast-iron mercury bottles connected together by a bent iron pipe, in which were fixed a stopcock and pressure-gauge. One of the bottles was charged with the paraffin, and was heated over an ordinary coal fire, the heat being so regulated that a pressure of 20 to 25 lbs. was maintained in the apparatus throughout the operation. The volatilized products distilled over into the second bottle, which acted as a condenser. In about four or five hours the operation was concluded, and the distillate had the appearance of a magma of oil, and of apparently unaltered paraffin. This mixture melted at a comparatively low temperature, the warmth of the hand being sufficient to render it completely liquid.

Three and a half kilograms of the paraffin yielded about 4 litres of liquid hydrocarbons. On distillation the mixture commenced to boil at  $18^{\circ}$ , but the quantity coming over below  $100^{\circ}$  was comparatively small; by far the greater portion boiled between  $200^{\circ}$  and  $300^{\circ}$ . A preliminary separation showed that the 4 litres were approximately made up of hydrocarbons boiling :—

	litres.
I. Below $100^{\circ}$ .....	0.3
II. From $100$ – $200^{\circ}$ .....	1.0
III. From $200$ – $300^{\circ}$ .....	2.7
	<hr/>
	4.0

A considerable quantity of substance, which could not be distilled within the range of the mercurial thermometer, remained in the retort, and solidified on cooling (see section 12). Each of the portions was then submitted to a systematic fractional distillation.

\* Rep. Brit. Assoc. 1846.

4. *Fraction boiling below 100°*.—After repeated distillations over sodium this portion was almost completely resolved into three fractions, boiling constantly at (1) 32–38°, (2) 65–70°, and (3) 94–97°. The quantity of liquid boiling below 30° did not amount to 5 cub. centims. Although the distillation was conducted in winter, and freezing-mixtures of snow and salt were employed for the condensation, the greater portion of the product boiling at 32–38° came over at about 35°; this boiling-point would indicate that the liquid is probably either *quintane* or *amylene*, or a mixture of these hydrocarbons. In order to decide the point, the distillate was treated with bromine. The liquid was violently attacked, and each drop of bromine combined with the hydrocarbon with a hissing noise; so energetic was the reaction, that, in order to moderate it, it was necessary to immerse the hydrocarbon in a freezing-mixture. When proper care was taken to cool the liquid, scarcely a trace of hydrobromic acid was evolved. In order to prevent the possible formation of higher brominated products, the addition of the bromine was from time to time interrupted, and the liquid submitted to distillation; it invariably commenced to boil at about 32°, and the distillation was maintained until the thermometer stood at 50°. The distillate was again treated with bromine in the cold, and again distilled, the process being repeated until it was without visible action upon the hydrocarbon,—that is, until the liquid was permanently reddened. It was then washed with dilute potash solution, and rectified over sodium; it boiled constantly at 35–37°; the liquid was evidently *quintane*, and in all probability normal *quintane*, the boiling-point of which is given by Schorlemmer at 37–39°, and by Warren at 37°. The amount was far too small to attempt the preparation of any derivatives from it. The brominated portion boiling above 50° was then distilled; the thermometer rose rapidly to 180°, and the whole of the liquid came over below 200°. After renewed distillation the liquid was found to boil constantly, but with slight decomposition, at 184–188°; this compound is *amylene dibromide*, the boiling-point of which, according to Wurtz, is in the neighbourhood of 180°.

0.6515 grm. bromide gave 1.0125 grm. Ag Br and 0.0235 grm. reduced silver.

	Calculated.	Found.
Br . . . . .	69.5	68.8

5. The fraction boiling between 65° and 70°, which was at least fifty times greater than that boiling at 32–38°, was then treated with bromine; the bromine was absorbed with the same avidity as in the preceding case; and it was equally necessary to cool the hydrocarbon in order to moderate the reaction. As soon as the liquid appeared permanently reddened, it was distilled. The portion boiling below 80° was no longer *instantly* attacked by bromine; it was accordingly free from the accompanying

olefine. The distillate was then treated with aqueous potash to remove the free bromine, and when colourless the hydrocarbon was decanted, dried, and distilled over sodium; it boiled almost entirely between 65° and 70°, by far the greater portion coming over at 67–68°. It was analyzed with the following results:—

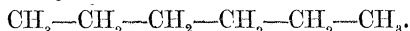
0·1440 grm. hydrocarbon gave 0·2095 grm. water; the carbon determination was lost.

	Calculated.	Found.
C <sub>6</sub> .....	83·72	—
H <sub>14</sub> .....	16·28	16·16
	<hr/> 100·00	

Two determinations of its specific gravity made by means of different bottles gave:—

- (1) 0·6620 at 19°·5, and
- (2) 0·6641 at 18°.

Compared with water at the same temperature, Pelouze and Cahours found 0·669 at 16° for the hexane boiling at 68° obtained from American petroleum. Hexane from suberic acid, boiling at 69°·5, according to Dale, has a specific gravity of 0·6617 at 17°·5; this agrees with that of β hexane obtained from mannite, viz. 0·6645 at 16°·5. Schorlemmer found 0·678 at 15°·5 for the hydride from cannell coal, which agrees perfectly with that obtained by Williams for the same hydride prepared from boghead coal, viz. 0·6745 at 18°. On the other hand, Schorlemmer has found that the hexane prepared from mannite is probably identical with that obtained for secondary hexyl iodide by the action of zinc and hydrochloric acid, and with the dipropyl obtained from primary hexyl iodide, for which he found the specific gravity 0·6630 at 17°; and these are probably identical with the hexane of Pelouze and Cahours obtained from petroleum, and with the hydride found by Schorlemmer in cannell oil, all being normal hydrocarbons with the constitution



The brominated hydrocarbon left in the flask after removing the hexane was then distilled: it commenced to boil at about 190°; the thermometer gradually rose to 195°, and nearly the whole of the liquid distilled over below 205°. As the compound showed signs of decomposition on boiling, hydrobromic acid being continuously evolved during the distillation, a considerable amount of tarry matter remaining in the flask, it was impossible to fractionate it further. It was purified, however, by distillation in a current of steam; it was nearly colourless, and on analysis yielded numbers agreeing with the formula C<sub>6</sub>H<sub>12</sub>Br<sub>2</sub>.

0·8950 grm. of the bromide gave 1·3570 grm. silver bromide and 0·0090 grm. reduced silver.

	Calculated.	Found.
Br .....	65·57	65·28
		R 2

The following are the data obtained in the determination of its specific gravity:—

Weight of bottle .....	1.6807 grm.
Bottle + water at 20° .....	7.2942 grms.
Bottle + bromide at 20° .....	10.6440 „

from which 1.5967 is obtained as the specific gravity of hexylene dibromide at 20° compared with water at the same temperature.

A second determination with a smaller quantity gave 1.5975 at 18°. Pelouze and Cahours found the boiling-point of this body to be 192–198°, and its specific gravity 1.582 at 19°. These numbers are certainly too low; the bromide had probably been slightly decomposed by distillation.

We have attempted to determine the relative amounts of hydride and olefine in the fraction boiling at 65–68° by means of the reaction with bromine.

The hydrocarbon was weighed out in a small distillation-flask, and well cooled by a mixture of ice and salt; bromine was then slowly added, and in minute drops, by means of the little apparatus seen in the figure—a small caoutchouc ball about 5 cub. centims. in diameter, which can be compressed by the plate movable along the rods by means of the milled head-screw. The mode of working the instrument is obvious; by means of it the bromine can be easily transferred from the bottle in which it is preserved to the hydrocarbon, and the amount added can be regulated with great nicety. The bromine was added until the liquid was permanently reddened, when the flask was again weighed to determine the amount of bromine employed. 13.30 grms. of the mixed hydrocarbons boiling at 65–70° required 13.16 grms. bromine before the red colour was persistent. This amount of bromine is equivalent to 6.9 grms. of hexylene, and  $13.3 - 6.9 = 6.4$  as the amount of hexane present. The mixture was now distilled, and all passing over below 110° (at which point the liquid in the flask commenced to blacken) collected in a weighed test-tube. The weight of the distillate was 6.18 grms. From these numbers it would appear that the product boiling at 65–68° is a mixture of hexane and hexylene in about equal proportions.

6. The fraction boiling at 94–97° was next treated with bromine in the cold until the liquid was reddened. The termination of the reaction was not so easily seen in this case; the mixture blackened slightly, and more hydrobromic acid was evolved, although the hydrocarbon was carefully cooled by ice and salt. The brominated mixture on distillation commenced to boil about 95°, and it was heated to 130°, when the liquid in the flask commenced to decompose; at this point, therefore, the distillation was interrupted. The following are the details of a quantitative determination:—

Weight of mixed hydrocarbons . . . . .	14.21	grms.
Weight of bromine added . . . . .	12.9	„
Equivalent to heptylene . . . . .	7.9	„
Equivalent to heptane . . . . .	6.3	„
Amount of heptane actually obtained . .	6.15	„

From this experiment it would appear that the amount of olefine is slightly greater than that of the hydride in the fraction boiling at 94–97°; but, from the circumstances of the experiment, we have reason to believe that the amount of heptylene thus indicated is slightly above the truth. It was difficult to determine the final point of the reaction; the hydride was not altogether unacted on by the bromine, and small quantities of hydrobromic acid were continuously disengaged during the process; these circumstances would tend to increase the weight of bromine used, and consequently the apparent weight of the olefine present. In extending our research to the determination of the constitution of these hydrocarbons, we have had occasion to repeat this experiment on a far larger scale and under more favourable conditions.

900 grms. of the mixed heptane and heptylene required 716 grms. of bromine; this would be equivalent to 439 grms. of heptylene. 900 grms. of a mixture of heptane and heptylene in equivalent proportions would contain 444 grms. of heptylene.

The heptylene bromide could not be redistilled under the ordinary atmospheric pressure without decomposition; it commenced to blacken at about 150°, and dense fumes of hydrobromic acid were evolved. When distilled in a current of steam, it was obtained nearly colourless.

It cannot be preserved, however, without slight decomposition; when exposed to light, it slowly darkens in colour and evolves hydrobromic acid gas.

It was analyzed with the following results:—

0.7470 grm. gave 1.0210 grm. Ag Br and 0.035 grm. reduced silver.

	Calculated for $C_7H_{14}Br_2$	Found.
Br. . . . .	62.01	61.66

The specific gravity of this compound was found to be 1.5146 at 18°5, water at the same temperature being taken as unity.

The heptane, after washing with dilute potash solution, drying, and rectification over sodium, boiled constantly at 97–99°. Its specific gravity was found from two experiments to be (1) 0.6910 at 19°, and (2) 0.6915 at 18°. Warren and Storer found for the same hydrocarbon from Menhadden oil the specific gravity of 0.6942 at 17°5.

Burnt with copper oxide in a stream of oxygen, it yielded the following numbers:—

I. 0.1695 grm. hydride gave 0.5240 grm. carbon dioxide and 0.2460 grm. water.

II. 0.2638 grm. hydride gave 0.8119 grm. carbon dioxide and 0.3733 grm. water.

III. An unknown quantity gave 0.5015 grm. carbon dioxide and 0.2318 grm. water.

	Calculated.	Found.		
		I.	II.	III.
C <sub>7</sub> .....	84.00	84.29	83.94	84.14
H <sub>16</sub> .....	16.00	16.13	15.73	15.86
	<hr/> 100.00	<hr/> 100.42	<hr/> 99.67	<hr/> 100.00

These six bodies, quintane and amylene, hexane and hexylene, heptane and heptylene, are the only liquids we have been able to isolate from the fraction boiling below 100°. Careful search was made for the other hydrocarbons, particularly for benzol and for the hexylene of Caventou, boiling about 80°, but without success. The fractions intermediate between 70° and 90° could be resolved by repeated distillations into products boiling at 65–70° and 90–100°. The amount coming over in the neighbourhood of 80° was very small; in fact the entire quantity eventually obtained between 70° and 90° amounted to only a few grams. About a gram of the small portion boiling at 80–82° was treated with strong nitric acid; the liquid was very slowly acted upon, and when treated with alcohol, zinc, and hydrochloric acid, after washing and solution in ether, it failed to give the characteristic reaction for aniline; nor on treating the remainder of the hydrocarbon with excess of bromine, and allowing the mixture to evaporate, could any solid bromide (C<sub>6</sub>H<sub>10</sub>Br<sub>4</sub>) be obtained. Hence we infer the absence of members of the C<sub>n</sub>H<sub>2n-2</sub> and C<sub>n</sub>H<sub>2n-6</sub> groups in the liquid hydrocarbons obtained by the decomposition of solid paraffins.

7. *Fraction boiling between 100° and 200°*.—As this portion amounted to about a litre, it was thought worth while to attempt a more rigorous separation of the hydrocarbons than is possible by the ordinary method of fractionation; for this purpose a small condensing arrangement on Warren's principle was constructed, and by means of it the hydrocarbons were separated at first at intervals of 10°, afterwards into portions boiling between 5°, and eventually into portions boiling between 2°. The hydrocarbons were distilled over sodium, and the temperature of the worm was maintained about 20° lower than that of the vapour in the flask. A considerable quantity of liquid was obtained boiling below 100°; and this could be resolved into hexane and hexylene, heptane and heptylene. The amount of liquid eventually obtained between 100° and 120° was very small.

About 120 grms. of liquid were found to boil constantly between 122° and 125°. Bromine was eagerly absorbed by this fraction, indicating

the probable presence of octylene, the boiling-point of which is given by Bouis at 125°, and by Pelouze and Cahours at 118–120°. The reaction with bromine yielded the following data:—

Amount of hydrocarbon taken . . . . .	41·0	grms.
Amount of bromine needed . . . . .	34·0	„
Equivalent of octylene . . . . .	24·1	„

On the addition of bromine the hydrocarbon darkened rapidly in colour, and a small quantity of tarry matter collected at the bottom of the flask. As it was impossible to distil the mixture under the ordinary atmospheric pressure, the bromide being decomposed by a very slight elevation of temperature, it was treated with alcoholic potash, and distilled *per ascensum* for some hours until a few drops thrown into water floated upon its surface. Water was then added, the lighted portion separated, dried, and fractionated. The largest amount came over between 120° and 140°, the next fraction from 140–160° being much smaller in quantity, whilst scarcely any liquid distilled over between 160° and 180°. After this point the thermometer became more stationary, and a fraction almost as large as that at 120–140° came over between 180° and 200°. This, on renewed distillation, boiled at 185–190°; it had a feeble garlic smell, and was heavier than water. Analysis showed that it had approximately the composition  $C_8H_{15}Br$ .

I. 0·4755 grm. bromide gave 0·4165 grm. silver bromide and 0·0180 grm. reduced silver.

II. 0·4600 grm. bromide gave 0·4100 grm. silver bromide and 0·0150 grm. reduced silver.

	Calculated.	Found.	
		I.	II.
Br . . . . .	41·8	40·1	40·7

According to Rubien\*, by whom this compound was first described, its boiling-point is 185°.

The fraction boiling between 120° and 140° on repeated distillation was separated into octane, boiling at 122–125°, and a liquid of an alliaceous odour boiling constantly at 130–135°, which absorbed bromine with avidity. This in all probability was caprylidene, the boiling-point of which has already been found by Rubien (*loc. cit.*) to be 133–134°; its formation was doubtless due to the prolonged action of the alcoholic potash on the  $C_8H_{15}Br$ .

*Action of chlorine on mixed hydrocarbons boiling at 122–125°.*—34 grms. of the hydrocarbons were weighed out into a small distillation-flask, immersed in a mixture of ice and salt, and a gentle stream of chlorine sent through the liquid in the dark. The chlorine was rapidly absorbed, and for the first hour but little hydrochloric acid was disengaged; during

\* Ann. Ch. Pharm. vol. cxiii. p. 294.

the second hour and to the close of the operation, the evolution of this gas increased largely, and the mixture darkened considerably.

The chlorinated liquid was then distilled in a current of steam; as soon as the distillate appeared to be heavier than water the receiver was changed, and the heavy liquid separated, dried, and distilled. It commenced to boil at about 220°, but showed no constant boiling-point; but the greater portion came over between 230° and 240°. At this high temperature the product suffered rapid decomposition. The portion boiling at 230–240° was redistilled in a current of steam. After drying over calcium chloride it was nearly colourless, heavier than water, and of a pleasant aromatic odour. Analysis showed that it was *octylene dichloride*. 0.2760 grm. chloride gave 0.4225 grm. silver chloride and 0.0100 grm. reduced silver.

	Calculated.	Found.
Cl .....	38.80	39.09

The portions of octane obtained after treatment with chlorine and with bromine were then mixed and repeatedly distilled over sodium. The mixed liquid commenced to boil at 118°, and about two fifths came over below 122°, the remainder distilling between 122° and 125°. Both fractions were immediately reddened by bromine vapour. The 122–125° fraction was analyzed with the following results:—

0.2970 grm. hydrocarbon gave 0.9170 carbon dioxide and 0.4095 grm. water.

	Calculated.	Found.
C <sub>8</sub> .....	84.22	84.20
H <sub>18</sub> .....	15.78	15.32
	<hr/> 100.00	<hr/> 99.52

The specific gravity of this fraction was found to be 0.7207 at 15°·5; the fraction 118–122° had the specific gravity 0.7165 at 15°·6. Zincke found 0.7124 at 16° for normal octane\*.

Schorlemmer's dinitrilyl, which boils at 123–125°, has the specific gravity 0.7032 at 17°†.

*Action of nitrogen tetroxide upon the mixed octane and octylene boiling at 122–125°.*—Many years ago Guthrie described a solid crystalline compound of amylene and nitrogen tetroxide, C<sub>5</sub>H<sub>10</sub>(NO<sub>2</sub>)<sub>2</sub>. So easily is this compound formed that the reaction of the gas upon amylene constitutes a very good test for the presence of the olefine, and comparatively small quantities of amylene may, by means of nitrogen tetroxide, be discovered and separated from considerable quantities of quintane.

We have studied the reaction of nitrogen tetroxide upon a mixture of octane and octylene in the hope of discovering an easier method of separating the two hydrocarbons. No solid nitro-compound, however, was

\* Ann. Chem. Pharm. vol. clxi.

† Ibid. p. 281.

obtained. On passing the gas into a mixture of the hydrocarbons it was rapidly absorbed, and a heavy oil separated out; this had an odour resembling that of castor-oil; but the substance could only be preserved in the freezing-mixture, and on distillation, even in steam, it was immediately decomposed.

8. The next well-defined fraction of the original liquid boiling between  $100^{\circ}$  and  $200^{\circ}$  distilled constantly at  $145-148^{\circ}$ . It was remarked that as this fraction increased in bulk, and the neighbouring ones became more free from octane and octylene, they gradually acquired a very characteristic and unpleasant smell, quite different from the fraction boiling at  $122-125^{\circ}$ . A portion of the mixed hydrocarbons was treated with bromine in the cold. The same darkening was observed as in the case of the  $122-125^{\circ}$  fraction; but it was by no means so marked as in that instance, and there was no difficulty in perceiving when a decided excess of bromine had been added. The following are the details of the experiment:—

Hydrocarbon employed . . . . .	18.95 grms.
Bromine needed . . . . .	12.8 „
Equivalent to nonylene . . . . .	10.0 „

As it was impossible to distil off the hydride, even in a current of steam, without at the same time decomposing the bromine compound, the liquid was treated with alcoholic potash and distilled upwards for some time. Water was then added, the dark brown oil separated, dried, and distilled; it commenced to boil at  $150^{\circ}$ , and fractions were collected between every  $10^{\circ}$ . The largest fractions came over at  $160-170^{\circ}$  and  $200-218^{\circ}$ .

The portion boiling between  $200-218^{\circ}$  on repeated distillation boiled almost entirely between  $208^{\circ}$  and  $212^{\circ}$ , and had approximately the composition  $C_9H_{17}Br$ .

0.4165 grm. bromide gave 0.3370 grm. silver bromide and 0.0105 grm. reduced silver.

	Calculated.	Found.
Br . . . . .	39.0	36.3

The quantity obtained was too small to admit of purification.

A second portion of the liquid, boiling between  $145^{\circ}$  and  $148^{\circ}$ , was treated with fuming sulphuric acid. A considerable rise of temperature was observed, so that it was necessary to cool the mixture in order to prevent, as far as possible, the polymerizing action of the strong acid. The supernatant oil was then decanted, washed with dilute soda solution, dried, and distilled over sodium. About half the liquid came over below  $170^{\circ}$ , after which the thermometer rose very rapidly to above  $340^{\circ}$ , when the distillation was stopped. On cooling, the dense oily liquid in the retort solidified. The fraction boiling below  $170^{\circ}$  was redistilled over sodium; it boiled almost entirely between  $145^{\circ}$  and  $150^{\circ}$ . It was then mixed with the hydride obtained after treatment with bromine (see preceding section), and the mixed liquids were again distilled over sodium. The boiling-point

was unchanged, the greater portion of the liquid distilling at 147–148° This liquid is nonane, as the following analysis shows:—

0.1970 grm. hydride gave 0.6080 grm. carbon dioxide and 0.2820 grm. water.

	Calculated.	Found.
C <sub>9</sub> .....	84.37	84.16
H <sub>20</sub> .....	15.63	15.92
	<hr/> 100.00	<hr/> 100.08

A determination of its vapour-density afforded the following data:—

Balloon with air .....	13.8050 grms.
Temperature of air .....	13.7° C.
Balloon with vapour .....	14.0525 grms.
Temperature on sealing .....	209°
Residual air .....	0
Capacity of balloon .....	116.8 cub. centims.

Vapour-density calculated for C <sub>9</sub> H <sub>20</sub> (H=1).	Found.
64.0	66.2

Its specific gravity was 0.7279 at 15°·5, compared with water at the same temperature.

It should be remarked that no liquid boiling at about 145–148° was discovered by Pelouze and Cahours in American petroleum. The nouyl hydride isolated by these chemists had the boiling-point 136–138°. We have assured ourselves that there is no liquid boiling at about this temperature in the products obtained from solid paraffin.

The boiling-point of the nonane isolated by us agrees perfectly with that calculated on the assumption that the differences in the boiling-points of the simpler members of the C<sub>n</sub>H<sub>2n+2</sub> become continually less by 4°, until the well-known difference of 19° is obtained. (Schorlemmer.)

Calculated boiling-point of C<sub>9</sub>H<sub>20</sub> 146°      Found 147–148°

*Action of chlorine upon nonane.*—About 15–20 grms. of the purified hydrocarbon were heated in a small flask fitted to an upright condenser, and a current of well-dried chlorine was sent through the liquid. The apparatus was placed in direct sunlight. The action appeared to commence immediately, the liquid darkened slightly in colour, and a large quantity of hydrochloric acid was evolved. The chlorine on passing into the heated liquid appeared to burn, a flash of light appearing at the end of the delivery-tube as each successive bubble of gas passed into the hydrocarbon. In order to prevent as far as possible the formation of high chlorinated products, the passage of the chlorine was occasionally interrupted and the liquid distilled; the portion boiling below 200° was set aside, and that which came over below this point was submitted to the

further action of the chlorine. Ultimately the greater portion of the liquid was found to boil between  $200^{\circ}$  and  $230^{\circ}$ , about  $\frac{2}{3}$  boiling above this point. By repeated distillation the former portion was divided into two portions—one boiling at  $190$ – $198^{\circ}$ , and the other boiling constantly at  $240$ – $245^{\circ}$ . The first fraction on analysis gave numbers agreeing with the composition of nonyl chloride.

I. 0.6670 grm. chloride gave 0.5937 grm. silver chloride and 0.0100 grm. metallic silver.

II. 0.5195 grm. chloride gave 0.4930 grm. silver chloride and 0.0080 grm. metallic silver.

	Calculated.	Found.	
		I.	II.
Cl .....	21.9	22.5	22.8

The specific gravity of the nonyl chloride was found to be 0.8962 at  $14^{\circ}$ . Pelouze and Cahours found the so-called pelargyle chloride to boil at  $196^{\circ}$ ; its specific gravity was 0.899 at  $16^{\circ}$ . It is highly probable, however, in spite of the concordance of these results, that the liquid obtained by us was a mixture of primary and secondary chlorides; and the same remark is probably applicable to the product obtained by Pelouze and Cahours. The fraction boiling at about  $245^{\circ}$  was in all probability  $C_9H_{18}Cl_2$ , produced by the further action of the chlorine upon the hydride; the quantity, however, was insufficient to purify it for analysis.

9. The next well-defined fraction distilling at a constant temperature boiled at  $170$ – $172^{\circ}$ . It was treated with bromine, with the following results:—

Weight of liquid taken .....	4.80 grms.
„ Bromine needed .....	3.38 „
Equivalent to decylene .....	2.95 „

The liquid was too strongly reddened by the bromine; it was evident that too great an excess had been added. This would make the amount of olefine too large. The quantity of hydrocarbon taken was too small; the experiment should have been repeated on a larger scale. Our object, however, was to economize our material, as we could find no ready method of separating the brominated compound from the unattacked hydride without decomposition. Boiling with alcoholic potash gave a very indefinite result.

About 37 grms. of the mixed hydrocarbons were cautiously treated with nitric and sulphuric acids, and the mixture cooled to moderate the reaction. After standing about 17 hours the clear amber-coloured oil was separated, repeatedly washed, and distilled in a current of steam. When about  $\frac{1}{3}$  of the liquid had passed over, the remainder in the flask suddenly decomposed, becoming almost solid, and fumes of oxides of nitrogen were abundantly disengaged. The distillate, which floated on water, was dried and distilled; it commenced to boil at  $169^{\circ}$ , and all came over below  $175^{\circ}$ ,

after repeated distillation over sodium, until the metal was no longer attacked; it boiled constantly at 166–168°.

It was analyzed as under :—

0.2090 grm. hydride gave 0.6460 grm. carbon dioxide and 0.2950 grm. water.

	Calculated.	Found.
$C_{10}$ .....	84.45	84.30
$H_{22}$ .....	15.55	15.69
	<hr/> 100.00	<hr/> 99.99

Its specific gravity was 0.7394 at 13°.5, compared with water at the same temperature. Schorlemmer's amyl (decatyl hydride), obtained by the action of sodium on amyl iodide, boiled at 158–159°, and had the specific gravity 0.7275 at 14°. It is very probable that this hydrocarbon is not the normal hydride, but stands to the decatyl hydride boiling at 168° in the same relation that the amyl hydride boiling at 30° does to the isomer boiling at 39°, or as the ethyl amyl boiling at 90° (sp. gr. 0.6819 at 18°.5) does to the normal heptane boiling at 99° (sp. gr. 0.6915 at 18°). The normal decatyl hydride obtained by Pelouze and Cahours from petroleum had the specific gravity 0.735 at 15°; the hydride found by Greville Williams in the oil from boghead coal had the specific gravity 0.7365 at 18°.

A determination of the vapour-density of the decatyl hydride from paraffin gave the following data :—

Balloon with air .....	13.9745 grms.
Temperature of air .....	12°
Balloon with vapour .....	14.2215 grms.
Temperature on sealing .....	222°
Residual air .....	0.2 cub. centims.
Capacity of balloon .....	105.5 cub. centims.

Vapour-density calculated for $C_{10}H_{22}$ (H=1).	Found.
71	72.8

10. The next fraction of the liquid boiling below 200° distilled constantly between 192° and 197°, the greater portion of the liquid coming over at about 193–195°. The fraction boiling at 193–195° was treated with bromine, with the following results :—

(1) 7.63 grms. required	4.76 grms. bromine.
(2) 7.18                   ,,	4.09                   ,,
<hr/> Mean . . 7.405	<hr/> 4.425

The fraction boiling at 195–197° was also treated.

7.04 grms. hydrocarbon required 3.85 grms. bromine.

Assuming that the fractions are mixtures of undecane and undecylene,

4.425 grms. of bromine would be equivalent to 3.78 grms. of the olefine, leaving 3.625 grms. of the hydride, or the fraction is a mixture of undecane and undecylene in equal proportions.

A determination of the vapour-density of the 193–195° fraction gave the following data:—

Balloon with air .....	13.2640 grms.
Temperature of air .....	16°
Balloon with vapour .....	13.5470 grms.
Temperature on sealing .....	261°
Residual air .....	0.8 cub. centims.
Capacity of balloon .....	113 cub. centims.
Found....	81.1
Calculated....	77.5

11. *Fraction boiling between 200° and 300°*.—By long-continued distillation over sodium the  $2\frac{1}{2}$  litres boiling originally between these limits were resolved into the following fractions:—

- (1) 212–215°\*
- (2) 230–235° solidifies at  $-14^{\circ}.5^{\dagger}$
- (3) 252–255° „ 5°.
- (4) 273–276° „  $+2^{\circ}.0$
- (5) 290–295°

The portion boiling at 300° (in the neighbourhood of 315°) is solid at ordinary temperatures.

The following details of the bromination experiments show that the fractions were invariably mixtures of olefines and hydrides:—

Fraction 212–215°:

4.48 grms. required 2.65 grms. of bromine.

Fraction 230–235°:

4.23 grms. required 1.92 grm. of bromine.

Fraction 252–255°:

(1) 9.38 grms. required 2.95 grms. of bromine.

(2) 8.605 grms. required 2.67 grms. of bromine.

(3) 5.13 grms. required 1.54 grm. of bromine.

Fraction 273–276°.

7.39 grms. hydrocarbon required 2.04 grms. of bromine.

12. It has already been mentioned that, on the first distillation of the oils obtained by splitting up the  $3\frac{1}{2}$  kilogs. of paraffin, a considerable amount of substance (which could not be distilled within the range of the thermometer) remained in the retort and solidified on cooling. This substance in its crude condition melted at 31°, but on recrystallization from ether the melting-point became higher. The whole of the substance was therefore cut up into small fragments, and spread upon filter-paper

\* These boiling-points are uncorrected.

† These points of solidification are only approximative.

to remove adhering oil as far as possible, and repeatedly recrystallized from ether until the melting-point was unaltered.

It melted invariably at  $41^{\circ}\cdot 5$  and solidified at  $40^{\circ}\cdot 5$ ; it could not be distilled within the range of the mercurial thermometer.

It crystallized from ether in beautifully white satiny scales, and gave the following numbers when burnt with oxide of copper in a stream of oxygen:—

0.3035 grm. gave 0.9590 grm. carbon dioxide and 0.419 grm. water.

Carbon . . . . . 85.19

Hydrogen . . . . . 15.34

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100.53

*Action of bromine upon the solid paraffin melting at  $41^{\circ}\cdot 5$ .*—A few grams of the substance were dissolved in bisulphide of carbon, and four minute drops of bromine added; this small quantity of bromine sufficed to colour the liquid strongly. On standing from 12 to 15 hours, the colour appeared unaltered, and the solution was not decolorized after heating from  $60$ – $70^{\circ}$  for 12 hours. On heating the liquid to  $150^{\circ}$ , the colour disappeared after a few hours; and on opening the tube hydrobromic acid was evolved. About 10 drops of bromine were again added, and the liquid reheated to  $150^{\circ}$ ; but no diminution in the red colour of the solution was perceptible, although on opening the tube hydrobromic acid fumes were abundantly disengaged. This observation would appear to indicate that the hydrocarbon melting at  $41^{\circ}\cdot 5$  is a member of the  $C_n H_{2n+2}$  series.

*Action of heat upon  $41^{\circ}\cdot 5$  paraffin.*—Repeated crystallization from ether having failed to alter the melting-point of this substance, and the behaviour with bromine evidently indicating that it belonged to the marsh-gas series, we considered that it would be interesting to study the combined action of heat and pressure upon it. The details of the experiment have been already given in section 1. After six distillations it was rendered completely liquid. It began to boil at about  $40^{\circ}$ , and about one sixth came over below  $100^{\circ}$ , about one third between  $100^{\circ}$  and  $200^{\circ}$ , and the greater portion of the remainder below  $300^{\circ}$ ; the small quantity remaining in the retort solidified on cooling.

In a second experiment the action of bromine upon the liquid hydrocarbons was quantitatively determined:

Weight of liquid hydrocarbon taken . . . . . 5.73 grms.

„ bromine required before the liquid was reddened 30.7 „

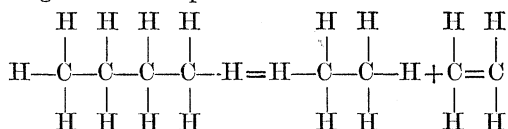
The action of the bromine was very energetic, and it was necessary to moderate the reaction by cooling the liquid.

It is evident from these experiments that the solid paraffin ( $\alpha$   $C_n H_{2n+2}$ ) had been split up by heat and pressure into a mixture of hydrides and olefines.

13. This mode of decomposition would appear to be general, at least for the higher terms of the series of normal paraffins. If these bodies be represented constitutionally by linking the carbon atoms together in a single chain,



then the simultaneous formation of hydride and olefine must be assumed to occur from the loosening of the affinities of certain of the groups of  $\text{CH}_2$ . Under the influence of heat these groups become dissociated (vibrate without the spheres of their mutual attractions), and recombine to form saturated hydrocarbons. Assuming (for the sake of simplicity) that this decomposition can occur so low down in the series as in the case of butane, it might be thus represented :—



We can offer but little direct evidence as to the exact manner of this decomposition—whether it is attended by the gradual elimination of ethylene, a hydride containing a greater number of carbon atoms being left behind, or whether the paraffin is at once split up into the hydride and an olefine containing an equal number of carbon atoms as in the above equation. Neither supposition is exactly substantiated by experiment. If the action of heat gave rise to the former mode of decomposition, we ought to obtain a large quantity of ethylene after prolonged heating, especially when the liquid portion is rich in hydrocarbons of low molecular weight; but, as we have already pointed out, the process of liquefaction is accompanied with the production of comparatively little gas. On the other hand, an examination of the amounts of bromine required to render the hydrocarbons boiling below  $200^\circ$  permanently red, shows that the proportion of hydride to olefine in the several mixtures becomes gradually larger as the molecular weight increases. It would appear, therefore, that the liquids boiling between  $200^\circ$  and  $300^\circ$  are not mixtures of hydrides and olefines in equal proportions, as are the fractions boiling at  $65\text{--}70^\circ$  and  $94\text{--}97^\circ$  &c.

It would have been doubtless interesting to have determined the relative amounts of the 12 fractions isolated from the decomposed paraffin; but when it is considered that their separation was only effected after several thousand distillations, it will be evident that the quantities obtained after such tedious treatment can afford no real indication of the amount present in the original liquid. We have, however, a distinct impression that the amounts of liquid boiling at  $94\text{--}97^\circ$  and  $122\text{--}125^\circ$  were but slightly (if at all) less than the quantities boiling at  $252\text{--}255^\circ$  and  $273\text{--}276^\circ$ .

