XXXV.—*On the most Volatile Constituents of American Petroleum.* By EDMUND RONALDS, Ph.D.

(Read 15th February 1864.)

Crude American petroleum evolves, at ordinary temperatures, a quantity of combustible gas, which takes fire on contact with flame, and, when mixed in certain proportions with air, produces an explosive mixture. It is in consequence of this property that it has been thought necessary to pass a very stringent law, known as the Petroleum Bill, with a view of preventing accidents from the incautious storing and handling of the oil.

The more volatile liquid products obtained by distilling the crude oil are still more highly charged with combustible vapour, which, when these liquids are again distilled, escapes condensation even by the most powerful freezing mixtures.

The liquid constituents of petroleum have now been carefully studied by Messrs PELOUZE and CAHOURS, and some of them also by Mr SCHORLEMMER. These eminent chemists have shown that the oil consists essentially of a mixture of the homologues of marsh gas, having the general formula,

$$C_nH_{2n+1}, H.$$

It was during the collection of the more volatile of this series of compounds with a view to their analysis, in which object I have now been forestalled, that my attention was drawn to the large quantities of incondensible gas which escaped at each successive fractionation, and it appeared desirable to ascertain whether the gaseous ingredients of the oil belonged also to the same series, or were accompanied by other hydrocarbons. With this object in view, and still waiting the arrival of some specimens of oil collected and secured in hermetically sealed vessels, direct from the oil wells, I was enabled by the kind permission of Mr SHAND of Stirling, to collect the gas which floated over the surface of the crude oil in the barrels in which it is imported into this country. I also obtained from the same manufacturer some of the very first products of the stills employed in refining the petroleum o n amanufacturing scale.

The gas floating over the surface of Pennsylvanian oil was collected at a temperature of — 1° C., and was observed to contain combustible ingredients. It took fire instantly on being brought into contact with flame, burning with a very faint, bluish light, but without explosion. From Canadian petroleum, which is of much thicker consistence, no combustible gas was obtained at that temperature.

The gas was collected over water by simply removing the original wooden bung of the casks and inserting immediately a cork bung furnished with a tube, for the delivery of the gas, and a long shanked funnel tube, through which liquid petroleum was poured.

Thus obtained the gas was of course a mixture of air and hydrocarbon; it was not affected by fuming oil of vitriol, nor was bromine water discoloured by it. It was hence inferred that no perceptible quantities of the olefiant series were present, and the temperature of collection is sufficient guarantee for the absence of any known members of the benzole series.

The gas was treated over mercury, with solid potash and pyrogallate of potash successively, when it yielded—

1·27 per cent. of carbonic acid, and
6·58 „ „ oxygen.

The residue, analysed eudiometrically, gave the following results:—

Gas collected from the surface of Pennsylvanian Petroleum at a temperature of —1°C., freed from Carbonic Acid by Potash and from Oxygen by Pyrogallic Acid.

	Observed Volume.	Pressure m.	Temperature Cent.	Corrected vol. at 0° C.+1 m. pressure.
Gas, ...	133·1	0·3099	9°·	39·934
Do. + air, ...	392·8	0·5666	9·	215·47
Do. + do. + oxygen, ...	465·6	0·6391	8·2	288·92
After explosion, ...	421·3	0·5940	10·	245·09
After absorption of CO_2, ...	383·4	0·5515	8·	205·23
After addition of hydrogen, . . .	474·3	0·6395	3·8	299·15
After explosion, ...	346·5	0·5062	4·	172·86

Deducting the nitrogen, or 23·4 vols. = 54 per cent. of the original gas, we have here a relation of hydro-carbon to condensation and carbonic acid, as—

16·534 : 43·83 : 39·86
or, 100 : 265 : 241.

The oxygen consumed amounts to 67·16 vols., or 4·06 times the volume of the hydrocarbon. The members of the olefiant and benzole series being absent, it may fairly be inferred that the hydrocarbon resembles in constitution the liquids with which it is associated; and if this be the case, the gas must be a mixture of the hydrides of ethyl and propyl, the former of which requires a relation of hydrocarbon to condensation and carbonic acid, as—

1 : 2·5 : 2

while the hydride of propyl requires a relation of 1 : 3 : 3. By calculation from the numbers above, it can be shown that the gas analysed must have consisted of a mixture of these gases in nearly equal proportions, or of—

C_2H_6, Hydride of Ethyl	7·94
C_3H_8, Hydride of Propyl	8·01

—the correctness of which is confirmed by the amount of oxygen consumed being about the mean of the quantities required for the combustion of these hydrides separately.

Hydride of ethyl requires 3·5 times its volume of oxygen.

Hydride of propyl requires 5· times its volume of oxygen.

The gas floating over the surface of the petroleum is therefore composed of—

Carbonic acid,		1·27
Oxygen,		6·58
Nitrogen,		54·
Hydrocarbon,	$\left\{\begin{matrix} C_2H_6 \\ C_3H_8 \end{matrix}\right\}$	38·15

In this condition the gas is not explosive, and would only become so on being mixed with a large volume of air.

The most volatile liquid obtained by collecting the very first runnings from the stills employed in the process of refining petroleum has a specific gravity of 0·666. It is not sensibly affected by nitric acid, by oil of vitriol, or by bromine. When distilled, it commences to give off bubbles of gas in abundance at about 25° Cent., but after a few minutes all appearance of boiling ceases, although large quantities of gas and condensible liquid continue to pass over up to 65° or 70° Cent., and the whole liquid is evaporated below 100° Cent.

This liquid resembles very closely the kerosolene or kerosoform which an American physician of New York has introduced as an anæsthetic agent; and I am indebted to Dr SIMPSON for the opportunity of comparing it with a specimen of the latter. The specimen lent me by Dr SIMPSON was quite indifferent to the above reagents. It had a specific gravity of ·6336. It began to boil at 28° Cent., and was nearly completely volatilised at 70° Cent., so that it must have been composed almost exclusively of a mixture of the hydrides of amyl and hexyl, while the crude volatile product from the manufactory contained, in addition to these hydrides, some incondensible gaseous products, and a considerable quantity of the hydride of heptyl.

The incondensible gases dissolved in this most volatile liquid were expelled by gently warming a large quantity (about two gallons) of liquid, and passing the gases, before collecting them over water, through a long metallic worm, surrounded by a freezing mixture composed of ice and salt; the whole apparatus having been filled previously with carbonic acid to expel air.

The first two portions which were collected showed, after separating carbonic acid and oxygen, little difference in composition from that already analysed, and which had been collected from the surface of the crude oil.

I omit the details of the analyses of these two, and submit only the results, which correspond in both cases with a mixture of the hydrides of ethyl and propyl.

	Gas.		Condensation.		Carbonic Acid.
I.	8·289	:	22·947	:	19·045
	100	:	2·77	:	242
			Oxygen consumed 32·338.		
II.	7·275	:	20·70	:	17·586
	100	:	280	:	240
			Oxygen consumed 31·07		

The gas coming over a little later from the same liquid was found to approach nearer in composition to pure hydride of propyl, as is shown by the following analysis. This portion was treated with potash before being introduced into the eudiometer, but the oxygen which it contained was not separated before combustion, but was estimated in a separate experiment, and found to amount to 2·44 per cent. of the gas burned.

	Observed Volume.	Pressure.	Temperature.	Corrected vol. at 0° + 1 m. pressure.
Gas, ...	39·723	0·2817	15·1	10·604
After addition of oxygen, ...	160·	0·3939	16·	59·548
After addition of air, ...	260·128	0·4917	14·5	121·46
After explosion, ...	236·386	0·4680	16·5	104·33
After absorption, ...	204·386	0·451	15·	87·376
After admission of hydrogen, . . .	357·161	0·602	14·	204·53
After explosion, ...	231·225	0·4643	13·6	102·29

Deducting the nitrogen and the 2·44 per cent. of oxygen contained in the gas, we have here the ratio of hydrocarbon to condensation and carbonic acid, as

5·984	:	17·13	:	16·954
100	:	286	:	283

Hydride of propyl $C_3H_8=2$ vols., requires a ratio of 1 : 3 : 3.

The quantity of oxygen consumed by the hydrocarbon is 4·67 times its volume, while pure hydride of propyl would require 5 times its volume.

The gas collected at a still later period from the same liquid was free from carbonic acid, oxygen, and nitrogen gases, and agreed in composition with a mixture of the hydrides of propyl and butyl.

	Observed Volume.	Pressure.	Temp. Cent.	Corrected vol. at 0° +1 m. pressure.
Gas, ...	43·034	0·2821	19·5	11·335
After addition of oxygen, ...	151·465	0·3857	19·9	54·454
After addition of air, ...	417·	0·6439	20·6	249·70
After explosion, ...	372·644	0·6038	16·7	212·05
After absorption, ...	321·	0·566	15·2	172·11
After addition of hydrogen, . . .	405·	0·649	17·	247·45
After explosion, ...	353·032	0·5846	15·2	195·52

The relation here of hydrocarbon to condensation and carbonic acid is as—

11·335 : 37·65 : 39·94
100 : 332 : 352

The oxygen consumed is 5·88 times the volume of gas burned, while hydride of butyl alone requires 6·5 times its volume of oxygen for combustion.

The gas evolved on warming the light spirit of petroleum, as it is prepared for sale, after having been kept, however, for some months in a vessel not hermetically sealed, was found to be a mixture of nitrogen and oxygen, with nearly pure hydride of butyl.

After separating by potash the carbonic acid which had been allowed to occupy the space above the liquid, the gas was analysed; the oxygen which it contained was estimated by pyrogallate of potash in a separate experiment, and amounted to 15·37 per cent.

	Observed Volume.	Pressure.	Temp. Cent.	Corrected vol. at 0° + 1m. pressure.
Gas, ...	73·2	0·2399	7·	17·25
After addition of air, ...	273·3	0·4366	5·2	117·11
After addition of oxygen, ...	334·	0·4976	5·7	162·82
After explosion, ...	288·5	0·4523	6·4	127·5
After absorption, ...	228·5	0·3995	10·2	87·998
After admission of hydrogen, . . .	330·	0·5022	13·	158·2
After explosion, ...	317·5	0·4799	12·2	145·86

Deducting the nitrogen and oxygen contained in the gas, we have here a relation of hydrocarbon to condensation and carbonic acid as,—

9·64 : 35·32 : 39·502, or as
100 : 366 : 409

Closely corresponding to the relations in hydride of butyl, which are,—1 : 3·5 : 4.

This gas was therefore composed of—

28·74 nitrogen,
15·37 oxygen,
55·89 hydride of butyl,

and it would appear from this experiment that the light volatile liquids absorb and retain oxygen in greater proportion than that element is contained in atmospheric air.

The liquid condensed by the freezing mixture during the collection of these gases, and that obtained by subsequently heating the large body of liquid from which they were expelled to a higher temperature, not exceeding however 30° Cent., or the boiling point of hydride of amyl, was redistilled. It commenced to boil at 0° Cent.; a considerable portion passing over between 0° and 4° was collected separately; another fraction between 6° and 8° was also collected apart; the remainder nearly all distilled below 15° Cent.

The liquid distilling between 0° and 4° Cent. is nearly pure hydride of butyl, which has not yet been described. It is a perfectly clear, colourless, very mobile liquid, having an agreeable sweet smell, but eluding, by its great volatility, the sense of taste. It is insoluble in water, but dissolves in alcohol and ether, and alcohol of 98 per cent. absorbs between 11 and 12 times its volume of the vapour at a temperature of 21°·5 Cent. It burns with a yellow, not very luminous flame. Mixed in the gaseous state with twice its volume of chlorine, liquid chloride of butyl is formed, and the original 3 volumes become condensed into 2 volumes of hydrochloric acid.

The specific gravity of the liquid at 0° Cent. is 0·600. It is therefore the lightest liquid at present known.

The vapour-density determined by Dumas' method, the vapour being absorbed by alcohol, gave the following results :—

Temperature of air, . .	13·8 C.	Temperature of sealing, .	40° C.
Barometer, ...	·7615 m.	Capacity of globe, . . .	185·6 cc.
Empty globe, ...	30·577 grms.	Air bubble, ...	7·8 cc.
Globe and substance, . .	30·788 grms.	Temperature of alcohol, .	14° C.

Hence vapour density=2·11.

Hydride of butyl, C_4H_{10}, requires by calculation 2·006.

The liquid, analysed eudiometrically in the gaseous state, gave the following numbers :—

Analysis of Butyl Hydride.

	Observed Volume.	Pressure.	Temperature Cent.	Corrected vol. at 0°+1 m. pressure.
Gas, ...	35·04	0·1944 M.	5° C.	6·691
After addition of oxygen, ...	326·	0·4810	4·8° C.	154·11
After explosion, ...	294·8	0·4507	4° C.	130·95
After absorption of CO_2, ...	256·9	0·4215	9° C.	104·83

Hence we have,—

	Gas.	Condensation.	Carbonic Acid.
	6·691	23·16	26·12
or,	·100	346	390

Hydride of butyl requires—

100 : 350 : 400

The liquid collected between 6°+8° Cent. is not very different from this last. It is, however, a mixture of hydride of amyl with hydride of butyl. Its sp. gr. at 0° Cent. was found to be ·6004. The vapour density was 2·178, and the composition in the gaseous state is shown by the following numbers:—

	Observed Volume.	Pressure.	Temperature Cent.	Corrected vol. at 0°+1 m. pressure.
Gas, ...	15·3	0·4392	19·3	9·39
After oxygen, ...	264·5	0·6912	19·3	185·22
After explosion, ...	223	0·6509	17·9	149·12
After absorption, ...	166·8	0·6154	19·5	106·78

Hence we have,—

	Gas.		Condensation.		Carbonic Acid.
	9·39	:	36·10	:	42·34
or,	100	:	384	:	450

Hydride of butyl requires,—

100 : 350 400

It was not to be expected, from the manner in which the gases were collected that any single portion would correspond exactly in composition with any member of the series, and some attempts which were made to separate the gases from each other by washing with alcohol, did not yield more conclusive results than those already obtained with the mixtures.

From the foregoing experiments we may, I think, safely conclude, that all the homologues of marsh gas, excepting marsh gas itself, are present in the liquid as it comes to this country, and there appears to be little doubt that marsh gas, and perhaps even free hydrogen, will be found among the gases which are evolved with the oil at the springs.