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THOMAS GRAHAM, Esq., V.P., in the Chair.

The following Donations to the Library have been made since the last Meeting :

“The Pharmaceutical Journal,” Vol. X. Nos. 1, 2, 3, 4, and 5 : by the Editor.

“Journal of the Franklin Institute,” Vol. XIX. Nos. 5 and 6 ; Vol. XX. Nos. 1 and 2 : by the Institute.

“Transactions of the Royal Society of Edinburgh,” Vol. IV—XIX ; Part 1, Vol. XX. ; and the “Proceedings of the Royal Society of Edinburgh,” Parts 35—39 : by the Society.

“On the Constitution of Codeine and its Products of Decomposition,” by Thomas Andrews, M.D. : by the Author.

“Report to General Sir Thomas Macdougall Brisbane, Bart., on the completion of the publication in the Transactions of the Royal Society of Edinburgh, of the observations made in his Observatory at Markertown,” by John Allen Brown : presented by the Author.

“On the Isomorphism and Atomic Volume of some Minerals,” by James D. Dana : by the Author.

“Berichte über die Mittheilungen von Freunden der Naturwissenschaften in Wien,” von Wilhelm Haidinger. Band V. and VI. 1848—9.

“Bulletin of the Royal Belgian Academy of Medicine,” Vol. IX. Nos. 3—7 : by the Academy.

“Quarterly Journal of the Geological Society,” Vol. VI. No. 23 by the Society.

“Setzungsberichte der Kaiserlichen Akademie der Wissenschaften, Mathematisch - Naturwissenschaftliche Classe.” Erste Abtheilung, (Jan. Feb. March, April).

“Haidinger’s Report,” Vol. V. and VI. 1849—50 : by the Society of the Friends of Natural Science in Vienna.

“Abhandlungen der Mathematisch-physikalischen Classe der Königlich Bayerischen Akademie der Wissenschaften.” Band V. 1, 2, 3 Abtheilungen.

"Chemical Investigation of the most important Mineral Waters of the Duchy of Nassau," by Dr. R. Fresenius: by the Author.

"Ueber den Antheil der Pharmacie an der Entwicklung der Chemie:" von Dr. Ludwig Buchner, Jun.

"Laurent and Gerhardt's Comptes Rendus," (from Quesneville's "Revue Scientifique"), Nos. 1—9: by M. Quesneville.

"Taylor's Calendar of the Meetings of the Scientific Bodies of London for 1850—1": by the Publisher.

"Silliman's American Journal for September, 1850": by the Editor.

"Quesneville's Revue Scientifique from December 1849 to May, 1850: by M. Quesneville.

"On the Power of Soils to absorb Manure," by Professor Way: by the Author.

"De Cerevisiæ vera Mixtione et indole Chemica, et de Methodo analytica alcoholis quantitatem recte explorandi," scripsit Dr. H. Wackenroder: by the Author.

The following Papers were read:

"On the Magnetic Attraction of Metals," by Mr. Richard Adie, Liverpool.

XXVII.—*Researches on the Organic Radicals.*

BY E. FRANKLAND, PH.D., F.C.S.

III. ON THE ACTION OF SOLAR LIGHT UPON IODIDE OF ETHYL.

The action of light in modifying and controlling chemical affinity has frequently been the subject of investigation, and the exceedingly curious and interesting results which have already been observed, seem to promise that this agent will become a most valuable assistant in chemical research. Gay-Lussac and Thénard were the first to point out, that chlorine and hydrogen may be preserved in contact for any length of time, without entering into combination, if the mixture be carefully preserved from light; but that with the presence of light, combination immediately commences, and proceeds with a rapidity proportional to the luminous influence. According to Faraday, iodine and olefiant gas combine most readily in sunshine; and the name phosgene gas was given to chlorocarbonic acid, because light was found to be essentially necessary to its formation. These are a few of the instances in which light has been observed to produce direct combination; but the cases in which it effects decomposition and changes the order of elective affinity, are much more numerous.

Under the influence of light, chlorine is enabled to decompose water, uniting with its hydrogen, and liberating pure oxygen gas: and, according to Grotthuss, the blue solution of iodide of starch

in water is completely decolorized with the production of hydriodic acid. Scheele, Seebeck, and others, found that nitric acid, exposed to sunlight, is converted into nitrous acid and oxygen, whilst many metallic oxides lose the whole or a part of their oxygen: thus, peroxide of lead is resolved into minium and oxygen; grey oxide of mercury into metallic mercury and red oxide; whilst red oxide of mercury, under water, is decomposed into grey oxide and oxygen gas. Oxide of silver is resolved into silver and oxygen; carbonate of silver into silver, oxygen, and carbonic acid; and oxide of gold into gold and free oxygen. Boullay finds that aqueous solution of perchloride of mercury is decomposed into protochloride of mercury, hydrochloric acid, and oxygen gas. In addition to these curious reactions, the highly interesting and important discoveries of Hunt, Daguerre, Herschell, and Talbot, need only be mentioned to establish the great scientific, as well as practical, importance of this remarkable function of light, which is also so completely under the control of the operator, admitting of being increased, diminished, or modified at pleasure, that there seems every probability of this agent becoming one of our most valuable means of composing, decomposing, and ascertaining the rational constitution of organic bodies, especially as it allows of being applied in such a convenient manner, and under circumstances in which other means are inapplicable.

It has been long known that certain inorganic bodies, containing iodine, such, for instance, as the iodides of silver and gold, undergo decomposition when exposed to light, the iodine compounds of the noble metals appearing to be most susceptible of this change. From the close relation of hydrogen to these metals, its iodide might be expected to possess the same susceptibility, and this is, in fact, found to be the case; for it is well known that aqueous hydriodic acid, even when preserved in closely stopped bottles, gradually turns brown on exposure to light, from the separation of free iodine, but the decomposition only becomes continuous when the iodine is removed as fast as it is liberated; it has also been observed, that when hydriodic acid gas is allowed to stand over mercury, its volume becomes reduced to one half, and the residual gas consists of pure hydrogen; but whether this reaction only occurs under the influence of light, has not yet been clearly established.

In a former memoir,* I pointed out the very close analogy existing between the functions of the compound alcohol-radicals, and those of the simple radical hydrogen, as exhibited, firstly, in the constitution

* Chem. Soc. Qu. J. III, 47.

of the vapours of their parallel compounds; secondly, in the decomposition of their respective iodides by zinc; and, thirdly, in the replacement of hydrogen by methyl, ethyl, amyl, &c., in cacodyl, in the new nitrogenous bases of Wurtz and Hofmann, and in those of M. Paul Thénard containing phosphorus. In order to add another link to the chain of evidence which already exists in support of this analogy, it appeared interesting to ascertain if the action of light upon the iodides of ethyl, methyl, &c., would yield results corresponding to those obtained from iodide of hydrogen under similar circumstances; and this link seemed to me also of greater importance, on account of the results thus produced by the simple action of an imponderable agent, being less likely to be influenced by the formation of secondary compounds, than in the action of zinc upon these bodies at an elevated temperature. My experiments have as yet been principally confined to the iodide of ethyl, and it is the results of the action of light upon this body, that I have now the honour to communicate to the Society.

It has been remarked by almost all chemists who have had occasion to employ iodide of ethyl, that this liquid slowly becomes brown, from the separation of iodine, when exposed even to diffused daylight; this observation, which I have myself of late also frequently had an opportunity of making, induced me to hope that a decomposition here occurs analogous to that suffered by iodide of hydrogen under the same influence. I find that the ethyl-compound, when exposed to direct solar light, rapidly becomes of a dark-brown colour; but, as is the case with hydriodic acid, this separation of iodine soon ceases, and when a certain intensity of colour has been attained, no further action takes place; if, however, the free iodine be removed by agitating the liquid with mercury, the action immediately recommences, and proceeds to the same point as before. This behaviour of the iodide under the influence of light, and in contact with mercury, indicated the method by which the action could be carried on continuously, and the products collected and preserved.

For this purpose, several glass flasks, of about 10 ounces capacity, were filled with mercury, and inverted in a vessel containing the same metal; a few drops of iodide of ethyl being then introduced into each, by means of a pipette, they were exposed to the direct rays of the sun. The surface of the mercury, where it was in contact with the liquid, soon became covered with a film of protoiodide, which, by the further action of the light, was converted into biniodide, whilst bubbles of gas were continually evolved, and gradually displaced the mercury from the flask: finally, the whole of the iodide

of ethyl disappeared, the gas and biniodide of mercury being the sole products of the decomposition. Although simple exposure to the sun's rays caused this action to take place with tolerable rapidity, yet it was very greatly accelerated by placing each flask near the focus of an 18-inch parabolic reflector, which was not, however, so highly polished as to cause a very considerable elevation of temperature, the heat never rising to the boiling-point of iodide of ethyl (71.6°C.): in this manner, a few hours' exposure sufficed to fill the flasks with gas, which was then transferred to the bell-glass figured in a former Memoir,* and allowed to stand over sulphuretted water for twelve hours. At the end of this time, all traces of iodide of ethyl vapour had been absorbed, and the gas was fit for the endiometrical operations.

As iodide of ethyl is not in the least acted upon by mercury at a temperature of 150°C. ,† it could scarcely be supposed that the comparatively low degree of heat to which these materials were exposed in the focus of the reflector, could play any important part in the decomposition; yet, in order to set this question entirely at rest, an inverted bell-jar containing iodide of ethyl confined over mercury, was surrounded by a glass cylinder, and this latter filled first with water, then with a solution of chloride of copper, and lastly, with a solution of bichromate of potash. When the outer cylinder was filled with water, the decomposition proceeded with as much rapidity as without the intervention of that fluid, whilst the temperature of the water was scarcely perceptibly raised during the operation; the same was the case when solution of chloride of copper was employed; but on substituting the solution of bichromate of potash, scarcely the slightest action was perceptible, even after several days' exposure to bright sunshine. Now since, according to Mr. Hunt, at whose suggestion I employed these liquids, the solution of chloride of copper absorbs nearly all the heating rays, and allows about 90 per cent of the actinic rays to pass, whilst the solution of bichromate of potash intercepts the actinic and gives free passage to the heating rays, it is evident that the decomposition before us is due to the chemical influence of light, and is totally independent of the heating rays of the solar spectrum.

The gas collected and preserved as just stated, was then submitted to the eudiometrical processes, minutely described in my former Memoir on the "Isolation of Ethyl,"‡ the observations were also made with similar precautions respecting temperature, pressure, and formation of nitric acid, during the explosion with excess of oxygen.

* Chem. Soc. Qu. J. II, 266.

‡ Chem. Soc. Qu. J. II, 269.

† Chem. Soc. Qu. J. II, 295.

The entrance of atmospheric nitrogen into the gas, during the time occupied in its purification from iodide of ethyl vapour, by standing over sulphuretted water, was sought to be avoided by using a deep bell-jar of comparatively small diameter, and an outer glass cylinder,* having its internal diameter only $\frac{1}{4}$ inch greater than the external diameter of the interior jar; thus a very small surface of liquid was exposed to the atmosphere, and, therefore, only a proportionably small amount of nitrogen could be absorbed, and transferred to the internal gas. The experiments detailed below, show that the plan was effectual, as none of the gases examined contained an appreciable amount of that element.

A determination of the specific gravity of the gas gave the following numbers :

Temperature of room	. . .	24.3° C.
Height of barometer	. . .	767.6 mm.
Height of inner column of mercury	. . .	13.6 „
Weight of flask and gas	. . .	31.6758 grms.
Temperature in balance-case	. . .	25.3° C.
Weight of flask filled with dry air	. . .	31.5559 grms.
Temperature in balance-case	. . .	25.7° C.
Capacity of flask	. . .	140.79 cbc.

From these data the specific gravity was calculated to be 1.7159.

To ascertain the composition of the gas, it was first subjected to the action of fuming sulphuric acid; two specimens were then exploded with atmospheric air and excess of oxygen, and the residue was treated with recently boiled absolute alcohol. The following numbers were obtained :

In absorption eudiometer.

I.

	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used (dry).	175.4	24.4°C.	6.3 ^{mm}	761.0 ^{mm}	121.51
Vols. after action of SO ₃ (dry).	150.6	19.5°,	19.0 „	759.5 „	104.08
Vol. after removal of specimen for combustion.	86.9	19.8°,	62.1 „	766.3 „	57.05
Vol. after absorp- tion by alcohol.	0.0	—	—	—	0.00

* See Fig. 2. *BB*, Chem. Soc. Qu. J. II, 266.

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In combustion eudiometer.

II.

	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used (moist). }	94.8	17.4°C.	601.0 ^{mm}	764.3 ^{mm}	13.24
Vol. after admission of air (moist). }	472.2	17.7° „	200.3 „	764.4 „	243.45
Vol. after admission of O (moist). }	567.0	17.9° „	112.8 „	763.9 „	338.30
Vol. after explosion (moist). }	525.7	18.1° „	150.5 „	763.6 „	294.66
Vol. after absorption of CO ₂ (dry). }	467.8	16.4° „	204.7 „	765.2 „	247.34
Vol. after admission of H (dry). }	683.3	17.3° „	11.9 „	765.7 „	484.36
Vol. after explosion (moist). }	517.9	17.7° „	157.5 „	765.1 „	288.16

III.

	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used (moist). }	98.2	17.3°C.	595.4 ^{mm}	764.9 ^{mm}	14.29
Vol. after admission of air (moist). }	511.9	17.6° „	161.5 „	764.7 „	282.85
Vol. after admission of O (moist). }	602.9	18.1° „	85.1 „	764.8 „	375.53
Vol. after explosion (moist). }	559.8	18.2° „	123.6 „	765.3 „	328.57
Vol. after absorp- tion of CO ₂ (dry). }	501.9	17.0° „	176.2 „	764.4 „	277.90

Analysis No. I. proves that the gas is a mixture, and contains in 100 parts :

Gas absorbable by SO ₃	14.34
Gas unabsorbable by SO ₃	85.66
	<hr/>
	100.00

And the perfect disappearance of the gas left unabsorbed by sulphuric acid, on subsequent treatment with about an equal volume of absolute alcohol, proves the absence of hydrogen and hydride of methyl (light

carburetted hydrogen), as also any appreciable amount of nitrogen, which might have permeated the sulphuretted water used to confine it during purification.

Analysis No. II. shows that 13·24 vols. of the gas remaining after the action of fuming sulphuric acid, consumed 77·72 vols. oxygen, and generated 47·32 vols. carbonic acid, causing a contraction, on explosion, equal to 43·64 vols.

According to analysis, No. III. 14·29 vols. combustible gas consumed 83·34 vols. oxygen, and generated 50·67 vols. carbonic acid, causing a contraction of 46·96 vols.

If we take into consideration the composition of the gases evolved by the action of zinc upon iodide of ethyl,* together with the proof given below, that the gas absorbed by sulphuric acid has exactly the composition and state of condensation of olefiant gas, there can scarcely be a doubt that the gaseous mixture remaining after the action of sulphuric acid, consists of ethyl and hydride of ethyl; and by forming two equations, in which the volume of the mixture and the amount of contraction produced by explosion with oxygen are taken into account, it is easy to ascertain their respective volumes, even independently of the quantity of oxygen consumed and carbonic acid generated, although these latter values may be used to control the result arrived at, by employing the amount of contraction only in the calculation. I prefer employing the observed contraction as the known quantity in the second equation, to either the volume of oxygen consumed or that of carbonic acid generated, because the number representing it is obtained from two readings which are least liable to slight sources of error, and contains within itself the results of the entire analysis, viz: the volume of combustible gas, the oxygen consumed, and the carbonic acid generated.

It will be obvious, on inspecting its formula, that 1 vol. of ethyl requires for its combustion 6·5 vols. oxygen, and generates 4 vols. carbonic acid; and as the contraction, which occurs on explosion, is equal to the volume of the combustible gas + the volume of oxygen consumed — the amount of carbonic acid generated, it is evident that the gas in question will cause a contraction equal to 3·5 times its own volume; and for similar reasons—since hydride of ethyl consumes 3·5 times its own volume of oxygen, and generates twice its volume of carbonic acid—this gas must produce a contraction, on explosion, equal to 2·5 times its own volume.

* Chem. Soc. Qu. J. II, 277.

If then, we represent the volume of this combustible mixture by A , the contraction produced by explosion with excess of oxygen by B , and the volumes of ethyl and hydride of ethyl respectively by x and y , we have the following equations:

$$\begin{aligned}x + y &= A \\ \frac{7}{2}x + \frac{5}{2}y &= B\end{aligned}$$

from which the values of x and y are found to be

$$\begin{aligned}x &= \frac{2B - 5A}{2} \\ y &= \frac{7A - 2B}{2}\end{aligned}$$

and by substituting the numbers found in analyses Nos. II. and III., for A and B we have

	II.	III.
x	10.54	11.23
y	2.70	3.06
	<hr/> 13.24	<hr/> 14.29

Hence, the gas unabsorbed by fuming sulphuric acid contains in 100 parts:

	II.	III.	MEAN.
Ethyl	79.61	78.59	79.10
Hydride of Ethyl	20.39	21.41	20.90
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

In order to ascertain the composition and state of condensation of the gaseous body absorbed by fuming sulphuric acid, the original gas, before being exposed to the action of that acid, was exploded with atmospheric air and excess of oxygen. The following results were obtained:

IV.					
	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used } (moist).	96.3	9.4°C.	575.9 ^{mm}	747.5 ^{mm}	15.16
Vol. after admission of air and O (moist) }	590.7	9.5° „	68.9 „	746.7 „	381.83
Vol. after explosion } (moist).	549.2	9.7° „	105.4 „	746.7 „	335.34
Vol. after absorption of CO ₂ (dry). }	492.1	7.4° „	158.1 „	752.1 „	284.59

According to this analysis, 15·16 vols. of the gas consumed 82·08 vols. oxygen, and generated 50·75 vols. carbonic acid; but analysis No. I. shows that this quantity of gas contains 12·99 vols. of the mixture of ethyl and hydride of ethyl, which, according to the mean of analyses Nos. II. and III., would consume 75·99 vols. oxygen, and generate 46·24 vols. carbonic acid; thus leaving 6·09 vols. oxygen, and 4·51 vols. carbonic acid as the oxygen consumed and carbonic acid generated by the 2·17 vols. of the gas absorbable by sulphuric acid, 1 vol. of which must, therefore, have consumed 2·81 vols. O and generated 2·08 vols. carbonic acid.

Vol. of comb. gas.	O consumed.	CO ₂ generated.
2·17	6·09	4·51
1 :	2·81 :	2·08

When we reflect that in this experiment all the errors of observation are concentrated upon a very small proportion of the gas submitted to analysis, the numbers obtained agree sufficiently with those yielded by the combustion of olefiant gas, to allow safely of the conclusion that the body absorbed by sulphuric acid is the gas in question; for 1 vol. of olefiant gas consumes 3 vols. oxygen and generates 2 vols. carbonic acid.

The composition of the gases evolved by the action of light upon iodide of ethyl, in presence of mercury, may therefore, according to the mean of the above analyses, be thus centessimally expressed:

Ethyl	.	.	.	.	.	67·76
Hydride of ethyl	.	.	.	.	.	17·90
Olefiant gas	.	.	.	.	.	14·34
						<hr/>
						100·00

The theoretical specific gravity of a gaseous mixture of this composition agrees closely with that found by experiment, as shown by the following calculation:

$$\begin{array}{rcl}
 \text{C}_4 \text{H}_5 & = & 67\cdot76 \times 2\cdot00390 = 135\cdot7843 \\
 \text{C}_4 \text{H}_5, \text{H} & = & 17\cdot90 \times 1\cdot03652 = 18\cdot5537 \\
 \text{C}_4 \text{H}_4 & = & 14\cdot34 \times 0\cdot96742 = 13\cdot8728 \\
 \hline
 & & 100\cdot00 \qquad \qquad \qquad 168\cdot2108 \\
 & & \hline
 & & 100 \qquad \qquad \qquad = 1\cdot682108
 \end{array}$$

Specific gravity, as found by experiment . . . 1·7159

Hence the decomposition suffered by iodide of ethyl, under the

influence of light, and in presence of mercury, is expressed by the following equation :

a small portion of the liberated ethyl being at the same time transformed into equal volumes of olefiant gas and hydride of ethyl :

The slight deficiency of olefiant gas, as exhibited by the analyses, may very probably be owing to the different solubility of the two gases in the sulphuretted water which was used as the confining medium, during their purification from the vapour of iodide of ethyl.

The action of light upon iodide of hydrogen and iodide of ethyl is therefore perfectly analogous ; in the one case we have the simple radical hydrogen eliminated, and in the other the compound radical ethyl. This reaction is also perfectly parallel with that produced by the action of heat upon iodide of ethyl in presence of zinc,* except that, in this last decomposition, a considerably larger portion of the ethyl is transformed into hydride of ethyl and olefiant gas. The proportion of ethyl which undergoes this transformation in the two reactions just mentioned, and in one which I describe below, is worthy of remark : it is best seen from the composition of the gases left after the action of fuming sulphuric acid.

I. Gases evolved by action of zinc upon iodide of ethyl :

II. Gases evolved by action of light upon iodide of ethyl in presence of mercury :

III. Gases evolved by action of light upon iodide of ethyl in presence of mercury and water :

As the hydride of ethyl occupies exactly the same volume as the ethyl from which it is derived, it is evident that, in the first reaction,

* Chem. Soc. Qu. J. II, 281.

exactly $\frac{1}{3}$ rd, and in the second and third very nearly $\frac{1}{3}$ th of the ethyl evolved undergoes this transformation.

It was not without interest to ascertain if the action of light upon iodide of ethyl is modified in any way by the presence of water, as was the case in the corresponding reaction with zinc, where the whole of the ethyl was converted into hydride of ethyl by the assumption of an atom of hydrogen from the water, whilst the oxygen of the latter united with zinc to form an oxyiodide.

ACTION OF LIGHT UPON IODIDE OF ETHYL IN PRESENCE OF MERCURY AND WATER.

Iodide of ethyl, mixed with about twice its volume of distilled water, was exposed, as before, to the direct solar rays : precisely the same phenomena were observed as when the iodide alone was used, although the production of gas seemed to take place more rapidly when water was present. The gases were collected, purified from iodide of ethyl vapour, and examined by the methods described above.

A determination of the specific gravity of the gas gave the following numbers :

Temperature of room	20·3°C.
Height of barometer	765·9 ^{mm}
Height of internal column of mercury	12·9 „
Weight of flask and gas	33·5639 grms.
Temperature in balance-case	21·3°C.
Weight of flask filled with dry air	33·4492 grms.
Temperature in balance-case	21·2°C.
Capacity of flask	140·65 cbe.

From which the specific gravity was estimated at 1·6944.

The eudiometrical analysis gave the following readings :

In absorption eudiometer.

I.					
	Observed vol.	Temp.	Difference of mercury level.	Barom ² .	Corrected vol. at 0° C. and 1 ^m pressure.
Volume of gas used } (dry).	181·1	20·3°C.	55· ^{mm}	765·9 ^{mm}	128·17
Vol. after action of } SO ₃ (dry).	153·3	18·7° „	3·4 „	764·9 „	109·25
Vol. after admission } of alcohol.	0·0	—	—	—	0·00

In combustion eudiometer.

II.

	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used } (moist)	96.0	19.2°C.	585.7 ^{mm}	764.9 ^{mm}	14.59
Vol. after admission of air (moist). }	516.5	19.4° „	144.8 „	764.7 „	290.87
Vol. after admission of O (moist). }	605.2	19.7° „	64.9 „	764.5 „	385.24
Vol. after explosion } (moist).	562.3	20.0° „	103.1 „	764.2 „	337.23
Vol. after absorption } of CO ₂ (dry).	503.8	18.8° „	156.4 „	765.5 „	287.08
Vol. after admission } of H (dry).	689.7	21.1° „	2.6 „	762.9 „	486.75
Vol. after explosion } (moist).	518.1	21.6° „	153.3 „	762.5 „	283.27

From analysis No. I. it follows that the gas contains in 100 parts :

Gas absorbable by SO ₃	.	.	.	14.76
Gas unabsorbable by SO ₃	.	.	.	85.24
				<hr/> 100.00

And its perfect absorption by alcohol proves the absence of hydrogen, hydride of methyl, and nitrogen.

Analysis No. II. shows that 14.59 vols. of the gas left intact by fuming sulphuric acid consumed 83.57 vols. oxygen, and generated 50.15 vols. carbonic acid, causing a contraction, on explosion, equal to 48.01 vols.

From a simple inspection of these figures, it is evident that we have the same gaseous mixture to deal with as in the previous decomposition of iodide of ethyl without the presence of water, and, on applying the formulæ given above, we obtain the following values for x and y :

$$\begin{array}{rcl}
 x & = & 11.535 \\
 y & = & 3.055 \\
 \hline
 & & 14.590
 \end{array}$$

Hence the gas, before being acted upon by fuming sulphuric acid, consisted of :

Ethyl	67·39
Hydride of ethyl	17·85
Olefiant gas	14·76
	<hr/>
	100·00

The determination of its specific gravity, given above, also confirms this result, as is seen from the annexed calculation :

$$\begin{array}{rcl}
 \text{C}_4 \text{H}_5 & = 67\cdot39 \times 2\cdot00390 & = 135\cdot0430 \\
 \text{C}_4 \text{H}_5 \text{H} & = 17\cdot85 \times 1\cdot03652 & = 18\cdot5019 \\
 \text{C}_4 \text{H}_4 & = 14\cdot76 \times 0\cdot96742 & = 14\cdot2791 \\
 & & \hline
 & 167\cdot8240 & \\
 & \hline
 & 100 & \\
 & \hline
 & = 1\cdot67824 &
 \end{array}$$

Specific gravity as found by experiment . . 1·6944

The presence of water consequently exerts no modifying influence over the decomposition of iodide of ethyl by light, the products formed with and without the presence of water being identical both in composition and relative proportion. The transformation of ethyl into hydride of ethyl, when its iodide is decomposed by zinc in contact with water, is therefore probably owing to the high affinity of zinc for oxygen, rather than that of ethyl for hydrogen, although both affinities no doubt take part in causing the resolution of water into its elements.

The above decomposition of iodide of ethyl by light, depending, as it does, directly upon the chemical rays, furnishes us with the materials for the construction of an actinometer of considerable delicacy, since the volumes of gas (corrected for tension of iodide of ethyl vapour, &c.) evolved in equal times, would give us the relative quantities of the actinic influence falling upon a given surface during these times ; thus daily, or even hourly readings of the instrument could be made during the time the sun is above the horizon, and a register of the actinic influence, in different localities, be kept with as much ease as registers of the atmospheric pressure and temperature. I have not ascertained how small a quantity of light can determine the decomposition of the iodide ; but very weak diffused daylight, as for instance, on a very cloudy or foggy day, is sufficient to produce a very considerable disengagement of gas, the volume of which could of course be read off at stated times with the greatest facility, and without even interrupting the action of the instrument.

I have also studied the action of solar light upon the iodide of

methyl, as well as upon the iodides of ethyl and methyl in contact with the various metals, which has led to the discovery of an entirely new series of organo-metallic radicals, possessed of very remarkable and interesting properties; the results of these researches I hope shortly to have the honour of laying before the Royal Society.

The foregoing experiments form, I think, another link in the chain of evidence which establishes the homology of hydrogen with the radicals of the series to which ethyl and methyl belong, and the simplicity of the decomposition by which the ethyl is here separated from the iodine by the action of an imponderable agent, seems, to some extent, to disarm of their force several of the arguments lately employed with so much ingenuity by Dr. Hofmann* against the formulæ which I proposed for these bodies. In order to decide upon the truth or falsity of the views entertained by MM. Laurent and Gerhardt respecting these compounds, according to whom their formulæ ought to be doubled, and the bodies themselves classed amongst the members of the marsh-gas series, Dr. Hofmann undertook the examination of the products resulting from the action of heat upon valeric acid, in the hope of obtaining the hitherto unknown member of the marsh-gas family, represented by the formula $C_8 H_{10}$, which, if identical with the gas evolved by the action of zinc upon iodide of ethyl, would render necessary the doubling of the formula of the latter gas; whereas, if the body $C_8 H_{10}$ were not identical with the so-called ethyl, it would afford strong evidence in favour of my formula being the correct one. Unfortunately, Dr. Hofmann did not succeed in obtaining this body, and thus the question was left in the same condition as before.

In a former memoir† I have described two separate series of carbo-hydrogens isomeric with each other, the one consisting of the bodies which I consider as the alcohol radicals, and the other containing the members of the marsh-gas family, which I regard, from the mode in which they are formed, as the hydrides of these radicals; thus:

Radicals.			Marsh-gas family, or hydrides.					
Methyl	C_2	H_3	{ Hydride of methyl (light carburetted hydrogen) }					
Ethyl	C_4	H_5	„	ethyl	.	.	.	$C_4 H_5$. H
Propyl	C_6	H_7	„	propyl	.	.	.	$C_6 H_7$. H
Butyl	C_8	H_9	„	butyl	.	.	.	$C_8 H_9$. H
Amyl	C_{10}	H_{11}	„	amyl	.	.	.	$C_{10} H_{11}$. H
&c.			&c.					

* Chem. Soc. Qu. J. III, 121.

† Ib. III, 50.

It is obvious, on inspecting the above columns, that the members on the left hand are isomeric with those on the line next below them in the right hand column. Now, two of these bodies, which are represented as isomeric in the table just given, have been already obtained; viz., methyl ($C_2 H_3$) by the electrolysis of acetic acid* and the decomposition of iodide of methyl by zinc;† and hydride of ethyl by the decomposition of cyanide of ethyl (not perfectly anhydrous) by potassium,‡ and by the action of zinc upon iodide of ethyl in presence of water,§ and it is therefore only requisite to establish the *identity* or *isomerism* of these bodies, in order to test the correctness of the two views which have been proposed. As both the bodies in question are gaseous at ordinary temperatures, and do not change this condition under a pressure of 20 atmospheres, it is evident that their physical properties cannot assist us in deciding the question; besides, even assuming them to be isomeric, I should not expect any difference either in their boiling points or specific gravities. Under these circumstances, chlorine appeared to be the agent best suited to determine the point at issue; because, although we could only expect to obtain substitution products, yet the nature of these products must at once give us the key to the atomic weight of the bodies before us; for if we found $\frac{1}{6}$ th of the hydrogen substituted by chlorine, then, according to the usual interpretation of this phenomenon, we must assume the simplest atom to contain 6 atoms of hydrogen, and if, under similar circumstances, $\frac{1}{3}$ rd of the hydrogen were substituted, we should have an equal right for judging the simple atom to contain only 3 equivalents of hydrogen.

The action of chlorine upon the so-called hydride of ethyl in diffused daylight has already been studied by Kolbe and myself,|| and we find that 1 vol. of hydride of ethyl, and 1 vol. of chlorine give 1 vol. hydrochloric acid and 1 vol. of a gas having the formula $C_4 H_5 Cl$, but which is only isomeric, and not identical, with chloride of ethyl; we proposed for it the formula:

which represents 1 atom of methyl conjugated with another atom of the same group in which 1 atom of hydrogen has been replaced by chlorine. From considerations deduced from the production of hydride of ethyl, I now regard this chlorine compound as $C_4 \begin{smallmatrix} H_2 \\ Cl \end{smallmatrix} H$,

* Chem. Soc. Qu. J. II, 173.

† Ibid. II, 267.

‡ Chem. Soc. Qu. J. I, 60.

§ Ibid. II, 288.

|| Chem. Soc. Qu. J. I, 66.

hydride of ethyl in which 1 atom of hydrogen in the group $C_4 H_5$ has been replaced by chlorine; and this view explains why the body in question is isomeric and not identical, with chloride of ethyl. However, in whatever way this compound is viewed, it is evident that $\frac{1}{6}$ th of its hydrogen has been replaced by chlorine.

It was now necessary to study the action of chlorine upon the body to which I assign the formula $C_2 H_3$. As there are difficulties which I have not yet been able to overcome, in the way of procuring this body *pure* by the action of zinc upon iodide of methyl, I employed Kolbe's method by the electrolysis of acetic acid. The apparatus used was the same as that described by that chemist in his memoir, except that the gases evolved from the positive pole were allowed to stream through a long series of bulbs filled with a solution of caustic potash, by which every trace of carbonic acid was removed; behind this bulbéd tube were fixed three Liebig's potash apparatus, the first filled with fuming sulphuric acid, the second with solution of potash, and the third with concentrated sulphuric acid, the last being employed to dry the gas perfectly before it passed into the tubes* which were destined afterwards to be used for the experiments: the system of tubes terminated in a delivery-tube leading to the mercury-trough. As soon as the gas evolved in this last was perfectly absorbed by recently-boiled alcohol, a specimen was collected for analysis, and the tubes now filled with the pure gas were hermetically sealed at one end, and the caouchouc connector at the other being securely tied, cut, and covered with melted wax, they were taken asunder and reserved for the subsequent experiments.

The specimen of the gas collected as just described, was exploded with excess of oxygen, and gave the following numbers.

	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used (moist).	100.0	16.5°C.	576.4 ^{mm}	752.5 ^{mm}	15.28
Vol. after admission of O (moist).	323.3	17.0° „	330.7 „	751.8 „	123.77
Vol. after explosion (moist).	266.4	17.2° „	390.5 „	751.6 „	86.83
Vol. after absorption of CO ₂ (dry).	206.2	16.4° „	455.8 „	749.3 „	57.09
Vol. after admission of H (dry).	521.6	17.1° „	136.0 „	748.9 „	300.83
Vol. after explosion (moist).	332.5	16.8° „	320.6 „	749.0 „	129.73

* The form of these tubes is shown in a figure given in this *Journ.* Vol. I, p. 6 Fig. I, e—f.

The proportion between the volumes of combustible gas, oxygen consumed, and carbonic acid generated, may therefore be thus stated :

Vol. of comb. gas.	O consumed.	CO ₂ generated.
15.28	51.41	29.74
1 :	3.36 :	1.95

The numbers required theoretically for methyl are :

1 :	3.5 :	2
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A number of tubes, some of the same, and others of exactly double the capacity of those containing methyl, were then prepared and filled with dry chlorine by displacement; they were afterwards sealed at one extremity, the caoutchouc connector at the opposite end being securely tied and covered with melted wax.

ACTION OF CHLORINE UPON AN EQUAL VOLUME OF METHYL.

Two tubes of exactly the same capacity, the one containing chlorine, and the other methyl, were quickly connected together by inserting their narrow necks into a strong caoutchouc connector, and securing them by silk ligatures; they were placed in perfect darkness for 18 hours, to allow the gases to become thoroughly mixed. On being afterwards exposed to diffused daylight, the colour of the chlorine rapidly disappeared, showing that combination ensued. After being allowed to stand in the light for several hours, the tubes were hermetically sealed, and their contents submitted to eudiometrical examination. On breaking off their extremities under mercury, it was evident that no contraction of volume had taken place; but the dense fumes caused by allowing a few bubbles of the gas to escape into the atmosphere, proved that hydrochloric acid was one of the products of the reaction, and that the two gases had not simply united to form chloride of methyl. The contents of both tubes were transferred into a eudiometer, and the volume of hydrochloric acid was estimated by absorption, first with a ball of aqueous tribasic phosphate of soda, and afterwards with a bullet of fused potash, which last also dried the residual gas perfectly.

The following numbers were read off :

	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used (dry).	145.6	19.2°C.	10.0 ^{mm}	769.2 ^{mm}	103.27
Vol. after absorption of HCl (dry).	81.2	18.4°,	80.6°,	766.1°,	52.14

Thus, it appears that the products of the action of 1 vol. of chlorine on 1 vol. of methyl, are 1 vol. of hydrochloric acid and 1 vol. of another gas, which must necessarily have the empirical formula $C_2 H_3 Cl$, expressing 4 vols. This is exactly the result obtained by Kolbe and myself in acting with an equal volume of chlorine upon the hydride of ethyl obtained by the action of potassium upon cyanide of ethyl, and thus, up to the present point, the experiments seem to prove the *identity* of the two bodies—the so-called methyl, and the hydride of ethyl. But these experiments admit also of a different interpretation; for if we assume that the chlorine acted upon only half of the methyl employed, then the following equation would express the reaction :

2 vols. of chlorine acting upon 1 vol. of methyl produce 1 vol. hydrochloric acid, and 1 vol. of chlormethyl $C_2 \begin{pmatrix} H_2 \\ Cl \end{pmatrix}$ which last remains mixed with the excess of methyl employed. It would be very difficult to determine directly whether the gas in question is a mixture or a single gas; or, in other words, whether methyl and hydride of ethyl yield *identical* or *isomeric* results when acted upon by an equal volume of chlorine; but this question can be easily decided by employing an additional volume of chlorine, by which, if the view of the reaction just stated be correct, the excess of methyl will also undergo the process of substitution, and the result should be 1 vol. of methyl gas, in which 1 atom of hydrogen has been replaced by chlorine $\left\{ C_2 \begin{pmatrix} H_2 \\ Cl \end{pmatrix} \right\}$ and 2 vols. hydrochloric acid.

ACTION OF 2 VOLUMES OF CHLORINE UPON 1 VOL. OF METHYL.

Two tubes were connected together, the one having a capacity exactly twice as great as the other, the first being filled with dry chlorine, and the last with methyl; as in the former experiment, they were excluded from light for 18 hours, to secure the perfect mixture of the two gases, before allowing the chlorine to act. On afterwards bringing the tubes into diffused daylight, their interior became

bedewed with minute drops of an ethereal fluid, which, however, again disappeared after the lapse of a few minutes, and on opening the tubes under mercury, after the action was completed, no contraction of volume was perceived to have taken place. The contents being transferred to a eudiometer, the hydrochloric acid was determined as before.

The following numbers were obtained :

	Observed vol.	Temp.	Difference of mercury level.	Barom ^r .	Corrected vol. at 0° C. and 1 ^m pressure.
Vol. of gas used (dry). }	157·3	18·3° C.	9·7 ^{mm}	767·5 ^{mm}	111·71
Vol. after absorption of H Cl (dry). }	60·3	18·5° „	97·5 „	773·8 „	38·19
Vol. of residual gas.	38·19			Vol. of H Cl.	
	1	:		73·52	
				1·92	

Hence it follows that 1 vol. methyl and 2 vols. chlorine, yield 2 vols. hydrochloric acid, and 1 vol. of another gas, which must have the formula $C_2 H_2 Cl$, expressive of 2 vols. of vapour ; but this is the formula and state of condensation of the radical methyl in which 1 atom of hydrogen has been replaced by chlorine ; and the action of 2 vols. of chlorine upon 1 vol. of methyl is therefore correctly expressed in the equation given above.

As a final proof of the correctness of this mode of interpretation, and of the *isomerism* of methyl and hydride of ethyl, it remained only to try the action of 2 vols. of chlorine upon 1 vol. of the latter body. For this purpose, hydride of ethyl was procured by the action of zinc upon iodide of ethyl in presence of water, a process which, as I have shown,* yields that gas in a state of absolute purity. One volume of this gas, perfectly dried, being mixed, as before described, with 2 vols. of chlorine, and the intimate mixture then exposed to diffused daylight, combination rapidly ensued, and the walls of the tubes became wetted with a considerable quantity of an oleaginous fluid, which did not disappear or diminish even after the lapse of several weeks, during which time the tubes had been hermetically sealed. On breaking off their ends under mercury, a considerable contraction was observed to have taken place, the residual gas not occupying more than $\frac{3}{4}$ rds of the original volume. It was transferred into a eudiometer, and on being treated with a ball of phosphate of

* Chem. Soc. Q. J. II, 291.

soda, was so nearly absorbed, that the very small volume of gas remaining after its action could not be determined. This experiment allows us to conclude that 2 vols. of chlorine with 1 vol. of hydride of ethyl yield 2 vols. hydrochloric acid, and a liquid which, from the volumes of the gases taking part in its formation, has probably the formula $C_4 H_4 Cl_2$ and the same percentage composition as the oil of olefiant gas ($C_4 H_3 Cl + H Cl$); but whether the oily liquid produced in the above reaction be identical with this body, I have not been able to determine, as the quantity of the gaseous hydride of ethyl which would be required to form a sufficient amount of liquid to be subsequently purified for analysis would be very great.

The results of these experiments on the action of chlorine upon methyl and hydride of methyl do not agree quite so nearly with theoretical calculations as I could wish, owing to a slight amount of impurity contained in the methyl, as indicated by the analysis of that gas, the quantity of oxygen consumed being rather too far below the theoretical volume to be accounted for by possible errors of observation. I have been at great pains to remove this foreign body, but without success: Dr. Kolbe found the same difficulty when he first investigated this gas, and attributed the smaller quantity of oxygen consumed to the presence of a trace of oxide of methyl. As the impurity can only be present, however, in very minute quantity, it could scarcely have any material influence upon the results of the experiments, and I therefore think they allow us safely to conclude,

1st. That there exist two series of hydrocarbons of the form $C_n H_{n+1}$, the members of the one series being isomeric with those of the other, and

2nd. That the formula of the gaseous hydrocarbon obtained by the electrolysis of acetic acid is $C_2 H_3$, its atom being represented by 2 volumes of vapour; whilst the gas procured by the action of potassium upon cyanide of ethyl (not anhydrous), and by the action of zinc upon iodide of ethyl in presence of water, has the formula $C_4 H_6$, its atom being represented by 4 volumes of vapour.

As soon as I have succeeded in procuring pure methyl by the action of zinc upon its iodide, I intend to repeat these experiments and make them more complete.

Although Dr. Hofmann regards the decision of the above question as sufficient to establish the correctness of one or the other of the views which have been advanced respecting these radicals, on the one hand by MM. Laurent and Gerhardt, and on the other by Dr. Kolbe and myself, yet I do not deem it superfluous to offer a few remarks upon the arguments which Dr. Hofmann has used with so much

skill against the formulæ we have proposed for the bodies in question, especially as several of these arguments appear, at first sight, very conclusive.

The objections which this chemist has made to these bodies being considered as radicals may be thus expressed :

1st. The new radicals do not combine directly with the metalloids ; none of them have been found capable of reproducing a methyl-, ethyl-, or amyl-compound.

2nd. The volume of their vapours are different from that of all other known hydrocarbons.

3rd. The boiling-points of the compounds in question are in favour of their formulæ being doubled.

4th. The decomposition of the iodides of the alcohol-radicals by zinc is not *perfectly* analogous to that of hydriodic acid.

5th. The formulæ of these bodies require to be doubled to remove the discrepancy exhibited by the boiling-points of amylene, hydride of amyl, and amyl.

The first objection follows naturally, from the circumstance that, up to the time of the isolation of these bodies, we were only acquainted with one basic or electro-positive radical, in a separate form ; viz., cacodyl, which has unfortunately been looked upon by some chemists as a type of all other organic radicals, which they therefore expected to find endowed with similar powerful affinities. Such a partial view of the essential characters of a compound radical could not have been formed from a careful comparison of the varied properties of the simple radicals, which are undoubtedly the true types of their representatives in the organic world. A slight glance at the habits and affinities of these elementary bodies, exhibits to us the most widely-different powers of combination. Commencing with potassium and terminating with hydrogen, gold, platinum, iridium and nitrogen, we have a series of bodies which, although they all readily pass from one form of combination to another, when already combined, yet, when once isolated, exhibit as we ascend the scale an increasing reluctance to enter into union. Taking these reactions of the simple radicals then into consideration, it would be neither difficult nor visionary to predict that their organic representatives would be found possessed of as great a variety of disposition, and that we should have a corresponding series of bodies, commencing with cacodyl, zinc-methyl, zincethyl, stibethyl, &c., and terminating with the radicals of the alcohol family (the perfect representatives of hydrogen) exhibiting a similar decrease of combining power ; and, since the organic groups are so instable in their nature, and so liable to metamorphosis from

the slightest causes, that we are unable to expose them without utter destruction to the powerful influences which we can bring to bear upon an elementary body, it surely ought to be a matter of no great surprise, if the members of the least electro-positive extremity of the series should elude all our attempts to bring them again uninjured into combination. If nitrogen were decomposed at a red heat, by what means could we recombine that radical when once isolated? I am at present engaged in filling up the gap in the series between cacodyl and ethyl, and have been lately occupied in studying the properties of an organo-metallic radical, which seems to occupy a position about midway in the series, entering into direct combination with several of the metalloids, but with a degree of affinity immensely less than that exhibited by cacodyl or zinc-methyl.

Dr. Hofmann objects to the present formulæ of the radicals, in the second place, because their vapour-volumes are different from those of all other known carbo-hydrogens. In carefully considering this objection in all its bearings upon the subject, I have been quite unable to see its force, or to find in this difference of vapour-volume other than a very strong proof in favour of the bodies in question being the true radicals; for had their vapour-volumes corresponded with those of other carbo-hydrogens, it would, in my opinion, have afforded striking evidence of their being no radicals at all. Here, in order to seek for analogy, we must again return to the simple radical hydrogen, which presents such close relations to these organic groups, and in perfect harmony with them, has its atom represented by 2 volumes. The action of chlorine upon all the other hydrocarbons indicates that they contain an atom of hydrogen in combination with another group, and therefore their single atoms, like those of the hydrides of methyl, ethyl and amyl, are represented by 4 volumes of vapour, and they cannot possibly be brought forward as analogies for controlling the formulæ of the radicals themselves, with which the members of the series $C_n H_n$ and $C_n H_{n-6}$ are, by their properties and reactions, placed out of all connection.

But the objection which has the greatest apparent weight, and the one to which Dr. Hofmann evidently attaches the highest importance, is the 3rd; viz., "That the boiling-points of the compounds in question are in favour of their formulæ being doubled." The application of the beautiful and highly-interesting law of Professor Kopp to the controlling of the formulæ of an entirely new class of bodies, should be made with great caution; for although we can by its means unerringly predict the boiling-points of the members of the classes of compounds upon which that law was first founded, yet the extension

of the list of organic bodies has proved, beyond doubt, that the difference of 18° or 19°C. for each addition or subtraction of the elements $\text{C}_2 \text{H}_2$, by no means obtains when we apply it to other classes of compounds; in fact, these discrepancies might naturally be expected from a consideration of the effect which a difference in the specific and latent heat of different atoms must have upon the thermal properties of the compound; for it could not be expected that the boiling-point of water, for instance, should be raised through the same number of degrees by the addition of $\text{C}_2 \text{H}_2$, as that of other bodies having a much less specific and latent heat: hence we find that the difference in the boiling-point, produced by the addition of the elements $\text{C}_2 \text{H}_2$ depends entirely upon the nature of the groups to which these elements are added. In the alcohols and the series of acids $\text{C}_n \text{H}_n \text{O}_4$, the elevation in the boiling-point produced by each addition of the elements $\text{C}_2 \text{H}_2$ varies from 16° to 21°C. giving the mean number 18.5°C. and it was principally upon these series of bodies containing, in addition to water, two radicals—viz., ethyl, methyl, &c., and oxygen, that Kopp's law was founded; but if we examine bodies of more simple constitution, containing two radicals without water, we find the increase of the boiling-point produced by each addition of the elements $\text{C}_2 \text{H}_2$ widely different from the above number. Thus, at the first step, we find between oxide of methyl and oxide of ethyl a difference of at least 51°C. ; for, according to Gay-Lussac and Dumas, oxide of ethyl boils at 35.5°C. whilst oxide of methyl is incondensable at -16°C. The iodides of ethyl and methyl differ by about 30°C. , and the chlorides of ethyl and amyl by 91°C. , equivalent to 30°C. for each term of $\text{C}_2 \text{H}_2$, whilst the difference between chloride of ethyl and chloride of methyl is at least equally great, since the boiling-point of the former is 11°C. and the latter is still gaseous at -18°C. : the sulphides also exhibit a difference varying from 34° to 47°C. for each equivalent of $\text{C}_2 \text{H}_2$. From these facts, it is easily perceived that the difference in the boiling-points produced by the addition or subtraction of the term $\text{C}_2 \text{H}_2$ rapidly *increases* as the complexity of the compounds *decreases*; therefore we might reasonably expect that the radicals themselves, containing as they do only one group consisting of two elements, would exhibit a still greater difference, which is precisely what is found to be the case; amyl and valyl differ by 47°C. and ethyl and methyl will probably be found to differ to a still greater extent.

Although I am averse to drawing analogies from the habits of the hydrocarbon family $\text{C}_n \text{H}_n$, conceiving its members to have no connection with the groups in dispute, yet, since the *vapour-volume* of

these bodies has been brought forward as an argument in favour of doubling the formulæ of the radicals, I cannot refrain from referring to the *boiling-points* of these hydrocarbons $C_n H_n$, which, from the fact of their formulæ having already been once doubled, are not likely to undergo that process again by any discrepancies in this respect. The boiling-points of two of these—viz., butyrene and valerene, have been determined with tolerable exactness; the first was found by Faraday to boil at $-17.8^\circ C.$; and the last by Balard at $39^\circ C.$, and by myself at $35^\circ C.$; but as Balard's amylene was still mixed with small quantities of a body having a *higher* boiling-point, and the valerene obtained from iodide of amyl contained hydride of amyl, a compound boiling at a *lower* temperature, perhaps the mean $37^\circ C.$ would be the most correct number. Here then we have two homologous bodies, differing from each other by the elements $C_2 H_2$, and approaching as near to valyl and amyl, in composition, as bodies belonging to a different family well could do—for valerene and butyrene differ only from amyl and valyl by containing one equivalent of hydrogen less—yet their boiling-points differ to the extent of $54.8^\circ C.$, which would require us to multiply their already doubled formulæ by 3 to reduce them to the standard of Kopp's law.

	Boiling-point.	Difference.
Amyl ($C_{10} H_{11}$) . .	155° C. }	47° C.
Valyl ($C_8 H_9$) . .	108° „ }	
Valerene ($C_{10} H_{10}$) .	37° „ }	54.8° „
Butyrene ($C_8 H_8$) .	17.8° „ }	

It does not therefore seem, that any argument in favour of doubling the formulæ of the radicals can be drawn from their boiling-points, but on the contrary, these boiling-points, taken in connection with those of their compounds, give additional evidence that the formulæ assigned to them are the correct ones.

A few words will suffice to remove the fourth objection, which is founded upon an experiment, in which Dr. Hofmann failed to produce the body zinc-hydrogen ($Zn H$), by passing hydrochloric acid gas over metallic zinc, at an elevated temperature. The formation of zinc-hydrogen, under these circumstances, would have completed the analogy between the decomposition of chloride of hydrogen, and iodide of methyl; but as zinc is only very slowly acted upon by dry hydrochloric acid gas, even at a high temperature,* the acid gas

* Chem. Soc. Qu. J. III, 47.

is always in excess, and consequently no other result than the one obtained could be looked for, any more than we could expect to preserve potassium in a stream of hot hydrochloric acid; for the series of bodies to which zinc-amyl, zinc-ethyl, and zinc-methyl belong, increase in the energy of their affinities as their atomic weights decrease; therefore we might predict, that zinc-hydrogen, if such a body exist, will be endowed with still more violent reactions than zinc-methyl. Now this last is instantaneously decomposed, with explosion, in hydrochloric acid gas; and therefore zinc-hydrogen, with perhaps still more powerful affinities, could not exist for a moment in a stream of that gas, or in other words, could never be formed in such an atmosphere. The action of iodide of methyl upon zinc-methyl is, however, but very slow even at an elevated temperature, to which circumstance we owe the presence of this body amongst the products of the decomposition of iodide of methyl by zinc; and if we ever obtain the body zinc-hydrogen, it must be by bringing nascent hydrogen, evolved from some nearly neutral body, in contact with zinc.

As the fifth objection, "that the formulæ of these bodies should be doubled to remove the discrepancies in the boiling-points of valerene, hydride of amyl and amyl," is not considered by Dr. Hofmann himself to have much weight, on account of the different vapour-volumes of the compounds precluding a proper comparison, I will only remark on this head, that the assimilation of an atom of hydrogen *with doubling* of the vapour-volume, and the same assimilation *without* increase of volume are widely different circumstances, from which we might naturally expect very different results as regards the boiling-points of the compounds thus produced; and, accordingly, when 2 vols. amyl vapour unite with 2 vols. hydrogen, to form 4 vols. hydride of amyl vapour, a depression of the boiling-point, from 155° to 30° C. = 125° C., takes place; but this cannot be regarded as extraordinary, unless it can be proved that the boiling-point of hydrogen is not 125° C. *below* that of hydride of amyl, for we are entitled to assume, *à priori*, that the boiling-point of such a body would be the mean of those of its constituents. When, however, 4 vols. of valerene vapour unite with 2 vols. of hydrogen, to form 2 vols. of amyl vapour, the 4 vols. of valerene are absorbed, as it were, into the two volumes of hydrogen, in other words, the 6 volumes are condensed to 2, and the consequence is that the boiling-point rises 118° C.

I have thus endeavoured to remove, *seriatim*, the objections which have been so ably and ingeniously made by Dr. Hofmann, to the

formulae proposed by Dr. Kolbe and myself, for the groups which we conceive to represent, when isolated, hydrogen—and in ethyl, methyl, and amyl compounds, the hydrogen contained in the parallel combinations of this element. That these groups do not belong to the marsh-gas family, as suggested by MM. Laurent and Gerhardt is, I think, proved by the action of chlorine upon methyl, as detailed above; whilst the production of, and action of chlorine upon the hydrides of these groups, clearly indicates that these hydrides form the so-called marsh-gas family: hence we should gain no single advantage by doubling the present formulae of the bodies in dispute, but on the contrary, we should then either have to assume the existence of a *third* class of isomeric compounds, of undefined constitution, or to double our present formula for hydrogen, and represent the simplest isolable molecule of that element by $H + H$, we should then have :

Or adopting the notation of Messrs. Laurent and Gerhardt, these formulae would be thus written :

which also shows that the views advocated by these chemists on the one hand, and Dr. Kolbe and myself on the other, exhibit no greater difference with respect to ethyl, methyl, &c., than they do with regard to hydrogen.

* This view of the rational constitution of these bodies was first suggested by Mr. Brodie, at a recent meeting of the Society.