

The following Paper having been received subsequently to the last Meeting of the Society on June 18th, was ordered to be published by the Council.

XXVII.—*On the Isolation of the Organic Radicals.*

By E. FRANKLAND.

Considering the importance of having positive proof of the existence of the hitherto hypothetical radicals entering, on the one hand, into the composition of the basic compounds of which alcohol is a type, and, on the other, giving rise to the acids of the series commencing with formic acid, it is somewhat remarkable that so few attempts have been made either to isolate these radicals, or at least to discover the simpler groups into which they are decomposed at the moment of their separation.

Although the method by which Bunsen* succeeded in isolating cacodyl, pointed out the conditions under which a similar separation of other radicals might be affected, yet, with the exception of an unsuccessful attempt made by Löwig to obtain ethyl, by the action of potassium upon chloride of ethyl, the subject does not seem to have received further attention until Kolbe† succeeded in isolating valyl ($C_8 H_9$) by an entirely different method, viz. by the electrolysis of valerianic acid.

The action of potassium upon cyanide of ethyl‡ induced me to hope, that by employing a body of less complex constitution, and a metal of a less electro-positive character, the radical might be separated without being at the same time broken up into the groups ($C_2 H_2$) and ($C_2 H_3$).

The weak affinity possessed by iodine for the organic groups, its

* *Annalen der Chemie*, Bd. XLII. s. 45.

† *Memoirs and proceedings of the Chemical Society*, vol. III. p. 285.

‡ *Quarterly Journal of the Chemical Society*, No. 1. p. 60.

energetic action upon metals, and the comparatively low temperature at which its organic compounds are decomposed with the separation of free iodine, suggested the combinations of this element as being well adapted for such experiments; and although, with the exception of potassium and sodium, probably no metal has any action upon these compounds at their ordinary boiling points, yet it appeared in the highest degree probable that, if the metal and iodide were exposed under pressure to a progressively increasing temperature, a point would be attained where the affinity of the metal for iodine overbalancing that of the radical for the same element, would determine the decomposition of the iodide. The nature of the products would, of course, depend greatly upon the temperature, and, perhaps, in some degree, upon the nature of the metal employed.

From the superior interest possessed by ethyl, I selected the iodide of that radical for my first experiments: the compound was prepared by placing 7 parts by weight of phosphorus into 35 parts of absolute alcohol, and adding, in small quantities at a time, 23 parts of iodine, the vessel being kept cool by immersion in ice-cold water; the liquid was then decanted from the sediment and distilled in a water-bath, the distillate twice washed with water, and allowed to stand for 24 hours over chloride of calcium, iodine having been previously added until the fluid remained permanently coloured; it was then distilled three times from chloride of calcium, mercury, and anhydrous oxide of lead: when thus purified, its boiling point, as indicated by a thermometer placed immediately above the liquid, was $71\cdot6^{\circ}$ C. (161° F.) at $746\cdot5$ m.m. pressure ($29\cdot39$ English inches); with the bulb of the thermometer immersed in the fluid, the temperature remained constant at $72\cdot2^{\circ}$ C. (162° F.); its specific gravity, as indicated by a carefully conducted experiment, was $1\cdot9464$ at 16° C. (61° F.).

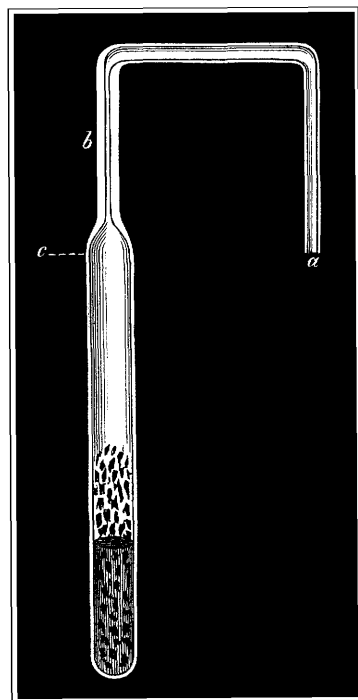
Burnt with oxide of copper,* $0\cdot5618$ grms. yielded $0\cdot3190$ grms. carbonic acid, and $0\cdot1607$ grms. water; numbers which indicate the following per-centage composition:

| | Calculated. | Expt. |
|---------------------|-------------|--------|
| 4 eqs. Carbon . . . | 300 | 15·42 |
| 5 „ Hydrogen . . . | 62·5 | 3·20 |
| 1 eq. Iodine . . . | 1585·5 | 81·38 |
| | <hr/> | <hr/> |
| | 1948·0 | 100·00 |

* In this analysis, about four inches of the front end of the combustion tube was filled with copper turnings and maintained at a heat just below visible redness during the whole operation. After the combustion, the liquid in the potash apparatus did not contain a trace of iodine

In order to subject this liquid, in contact with different metals, to temperatures considerably above its boiling point, and at the same time to preserve any gases that might be evolved, the following method was adopted: tubes of hard Bohemian glass, 1 cm. in diameter, the thickness of the glass being about 1.3 mm., were cut into lengths of 12 inches each, and carefully closed at one end before

FIG. 1.



the blow-pipe so as not to diminish the thickness of the glass. The metals, either finely granulated, or otherwise treated so as to expose a large surface, were then introduced, and the open extremity of the tube was drawn out to the thickness of a straw; about an inch of this narrow tube, at *b* Fig. 1., was then brought into the hottest portion of the flame, and the glass allowed to shrink up until a fine capillary bore was obtained; the narrow tube was then bent twice at right angles as shewn in the figure. The whole being now warmed, the open extremity (*a*) was immersed in the iodide of ethyl, which, by the subsequent contraction of the enclosed air, was forced into the apparatus in the required quantity; the tube (*a*) being then connected with an air-pump by means of a strong caoutchouc joint, the apparatus was exhausted, and the tube finally hermetically sealed at

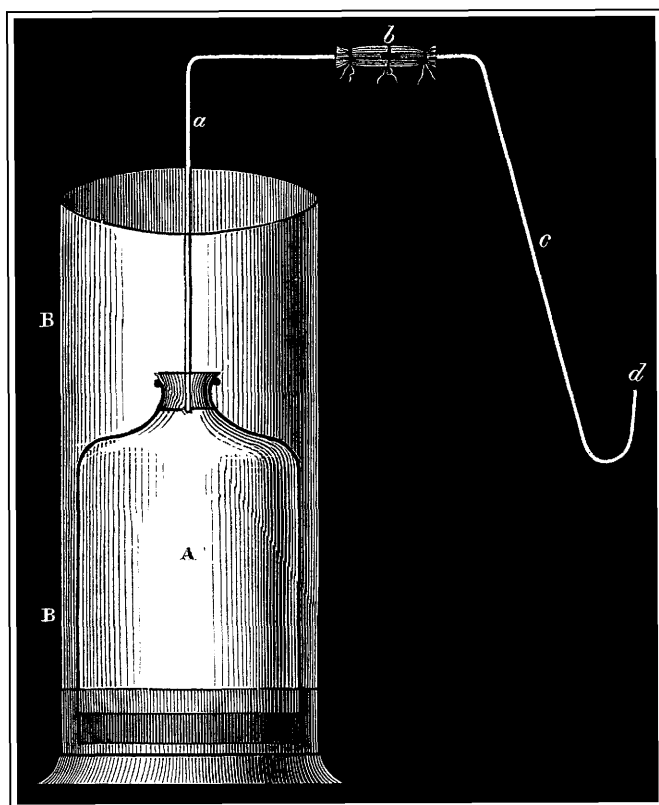
(*b*): as the liquid boiled violently during the exhaustion, it was easy to effect the expulsion of the last traces of air. The tubes thus prepared were afterwards exposed to the necessary heat by immersing them to half their length in an oil-bath.

ACTION OF ZINC UPON IODIDE OF ETHYL.

A preliminary experiment, conducted as above described, shewed that the decomposition of iodide of ethyl, by zinc, commences at a temperature of about 150° C. (302° F.), and proceeds with tolerable

rapidity when an extensive surface of the metal is exposed; white crystals gradually encrust the zinc and glass, whilst a colourless mobile liquid remains, equal in volume to only about half the iodide of ethyl employed, and very different from that liquid in appearance; it was further evident, from the cessation of ebullition soon after decomposition commenced, that a gas or highly elastic vapour had been generated. Having been maintained at the above temperature for about two hours, and the decomposition appearing to be complete, the tube was removed from the bath and allowed to cool. On, afterwards, breaking off its capillary extremity under water, about forty times its volume of gas was evolved, whilst the whole of the mobile fluid, above mentioned, disappeared; the gas had a strong ethereal odour, burnt with a bright flame, and was rapidly and completely absorbed by recently boiled absolute alcohol. On cutting off the upper portion

FIG. 2



of the tube, and introducing distilled water, the white mass of crystals dissolved with brisk effervescence, occasioned by the evolution of a considerable quantity of a gas possessing properties quite similar to those just mentioned. The solution of the crystals thus obtained possesses all the properties of a solution of iodide of zinc and, with the exception of a trace of undecomposed iodide of ethyl, appeared to contain no organic substance.

For the collection and preservation of the gas, I used the apparatus shown in Fig. 2. *A* is a bell jar, open below and passing easily into the cylinder *BB*, its upper orifice is closed by a sound cork, through which passes the glass tube (*a*), which is bent above at right angles, and connected by the caoutchouc joint (*b*) with the gas-delivering tube (*c*); within the joint (*b*), and between the tubes (*a*) and (*c*), is placed a piece of glass rod, half an inch in length, and rather smaller in diameter than the flexible tube, so that by means of an external ligature, the communication can be opened or closed at pleasure, without injury to the caoutchouc connector.

It was absolutely necessary to collect the gas over water, and to allow it to stand at least twenty-four hours, in order that the vapour of undecomposed iodide of ethyl might be perfectly absorbed: during this time a diffusion between the gas and atmospheric air is constantly going on, and cannot be wholly prevented even by a layer of oil; since, therefore, in the present case, it was found that the absorption of oxygen by phosphorus could only be effected at a temperature considerably above the fusing point of the latter, which would render the correct estimation of the oxygen a matter of considerable difficulty, it appeared desirable to prevent the ingress of every trace of oxygen. This object was easily and perfectly attained by mixing some alkaline solution of sulphuret of potassium with the water used in the pneumatic operations, thus the passage of this gas into the receiver was rendered impossible.

An earthen vessel of convenient size, and admitting of the total immersion of the cylinder *BB* being filled with this sulphuretted water, the bell glass *A*, having the valve (*b*) open, was pressed beneath its surface until the included atmospheric air had been completely expelled through the tubes (*a*) and (*c*), which also become filled with the fluid on suction being applied at the orifice (*d*); the valve at (*b*) being then securely closed, the apparatus was ready for the reception of the gas.

One of the decomposition tubes before mentioned, in which about six grammes of iodide of ethyl had been exposed to the action of zinc was now brought beneath the vessel *A*, and the capillary portion

being cut through with a file, the compressed gas rushed into the receiver, at first with considerable violence, but afterwards in a slow stream, which did not entirely cease until after the lapse of nearly a quarter of an hour; the cylinder *BB*, filled with the prepared water, was now brought under the bell jar *A*, and the latter being lowered into it, both were removed from the large vessel: the gas, which I will call α , was then allowed to stand over the confining liquid for twenty-four hours before being used for further experiments.

After the lapse of twelve hours, the contracted portion of the tube from which the compressed gas had been evolved was cut off at *c* (Fig. 1), and a smaller bent tube and cork having been fitted to the orifice, distilled water was poured upon the residue, and the cork furnished with the gas-delivering tube immediately inserted; a rapid disengagement of gas ensued, which was allowed to escape until every trace of atmospheric air had been expelled; this gas, which I will call β , was then collected in a similar apparatus, and with like precautions to those used in the collection of α .

The gas α was first submitted to investigation; the determination of its specific gravity was made in a light glass flask capable of containing upwards of 200 cubic centimeters, and having a millimeter scale etched upon its neck; a few fragments of fused potash having been introduced into this flask, and fixed to the glass by being first moistened with water, and then gently heated, it was carefully filled with mercury, and inverted in a vessel containing the same metal. The apparatus *BB*, *A* being then conveniently arranged, the valve (*b*) was loosened, and the gas, acting under the external pressure, allowed to force out the water occupying the tubes (*a*) and (*c*) from the orifice (*d*), which had been previously immersed in quicksilver; as soon as the water had been completely expelled, and removed from the surface of the metal by blotting paper, the bent extremity of the tube (*c*) was introduced within the neck of the specific gravity flask, so that its orifice was somewhat above the level of the external mercury; by this last arrangement, the inconvenience of employing great pressure in *BB* to overcome that of the mercury was entirely avoided, an external column of water, a few inches in height, being sufficient to counteract the capillary action of the tubes. The gas was allowed to enter the flask until the external and internal mercury stood at the same level, and the tube (*c*) being removed, the rest of the gas in *A* was immediately transferred for eudiometrical analysis to a receiver standing over the mercury: a thermometer being now brought into the vicinity of the apparatus, the whole was allowed to remain for several hours in a room of constant temperature, until the

moist gas became perfectly dried by the pieces of fused potash. The thermometer, barometer, and height of the internal column of mercury above that in the outer vessel, were then read off by means of a telescope placed at the distance of a few feet, and the flask, after being securely stopped without bringing the hand in contact with it, was weighed, afterwards filled with dry air, and lastly with quick-silver, the weight being taken in each case.

The following numbers were obtained :

| | |
|---|---------------|
| Temperature of room | 6·2°C. |
| Height of barometer | 760·9mm. |
| Difference of mercury level | 19·4mm. |
| Weight of flask and gas. | 54·6213 grms. |
| Temperature in balance case | 7·8° C. |
| Weight of flask and air | 54·4838 grms. |
| Temperature in balance case | 8·0° C. |
| Capacity of flask | 211·23 Cbc. |
| From which the sp. gr. was calculated to be | 1·5250. |

The composition of this and of the following gases, was determined by the eudiometrical processes of Professor Bunsen, by which the estimations can be made with a degree of accuracy previously unattainable in this branch of chemical research: I gladly avail myself of this opportunity to express my warmest thanks to that gentleman for the very kind manner in which he placed his laboratory, and especially the whole of his admirably arranged eudiometrical apparatus, at my disposal during the progress of this investigation.

The gas to be examined was transferred into a short eudiometer, and rendered perfectly dry by means of a ball of potash, the volume being then noted with the necessary precautions, a recently ignited coke bullet, saturated with very strongly fuming sulphuric acid, was introduced and allowed to remain in the gas until the volume of the latter ceased to diminish. After the removal of the coke bullet, the sulphurous, and vapours of anhydrous sulphuric acid, were removed by a ball of moist peroxide of manganese, and the gas being lastly dried by a ball of fused potash, its volume was again noted. After a specimen of the gas had been removed for combustion with oxygen, and the remaining volume once more read off, absolute alcohol, well-boiled and still warm was introduced by means of a bent pipette, agitated with the gas and allowed to stand for several hours; the remaining volume, after correction for the tension of alcohol vapour, was regarded as pure nitrogen.

The specimen of gas removed after absorption by sulphuric acid was transferred into a long eudiometer, furnished with platinum wires for the transmission of the electric spark, and, its volume being taken, was exploded with measured quantities of oxygen and atmospheric air;* the volume being again read off, a ball of fused potash was introduced and allowed to remain in the gas until every trace of carbonic acid was absorbed; on the subsequent removal of the potash ball and another determination of the volume, the remaining gas was exploded with a known quantity of hydrogen in excess, and the resulting contraction ascertained.

It is almost unnecessary to state that the observations were always made, either when the gases were perfectly dry or fully saturated with vapour. The corrections for temperature were calculated according to Marchand's Tables in which the expansion-coefficient for each degree of the centigrade scale is taken as = 0.003665. Regnault's table of the expansive force of aqueous vapour was used in correcting for moisture; and for alcohol vapour, the numbers given by Schmidt were employed.

The volume of combustible gas, brought into the large eudiometer was found by deducting from the first reading, the due proportion

* The analysis of this gas presented some difficulties, its combustion in the usual manner with oxygen, produced such an intense explosion, that no ordinary eudiometer could resist its violence, the analysis was, therefore, conducted in a eudiometer 0.8 meter in length, and the gas, previous to combustion, was mixed with about 26 times its volume of atmospheric air, and 3 times its volume of oxygen, by this means, the violence of the explosion was moderated and, as shewn by Kolbe (Memoirs of the Chemical Society for 1846, p. 245), the oxydation of the nitrogen to nitric acid prevented; pure oxygen cannot be used for this purpose, since the excess required is too great to be afterwards determined by explosion with hydrogen, unless a eudiometer of inconvenient length be employed; this dilution, however, cannot be carried beyond a certain limit without interfering with the accuracy of the results, for when the explosion becomes exceedingly weak, a portion of the carbon is oxidized to carbonic oxide, instead of carbonic acid, as is shewn by the following experiments in which the gas was exploded with different quantities of atmospheric air and oxygen.

| | Vol. of gas. | Vol. of air and O. | O consumed. | CO ₂ generated. |
|--------|--------------|--------------------|-------------|----------------------------|
| (I.) | 1 | 36.3 | 4.40 | 2.82 |
| (II.) | 1 | 32.4 | 5.28 | 3.17 |
| (III.) | 1 | 28.8 | 5.36 | 3.28 |
| (IV.) | 1 | 18.7 | 5.54 | 3.26 |

In experiments (I.) and (II.) the explosion was very slight, and the subsequent combustion with hydrogen indicated a larger quantity of nitrogen than was contained in the gas and atmospheric air, a result which could only have been produced by an imperfect combustion. In experiment (No. IV.), the heat developed by the explosion was so great, that a portion of the mercury was volatilized, covering the internal walls of the eudiometer with a black film, the greater part of which soon became converted into white crystals of nitrate of mercury.

of nitrogen as ascertained in the small eudiometer. The third and fifth readings, viz.: the determination of the volume after the admission of oxygen and after absorption of carbonic acid, together with the first reading, gave data for calculating the amount of oxygen consumed, independently of the composition of atmospheric air, the variations in which would have introduced not unimportant inaccuracies into the analyses, had its average composition been made an element in the calculation. If, therefore, we denote the volume of combustible gas by (*c*), the quantity of nitrogen and oxygen contained in the mixture at the third reading, by (*N + O*) and the total volume of gas at the third reading by *A*, we obtain the following equation :

$$c + (N + O) = A.$$

Further, if we represent the volume at the fifth reading, viz.: the volume after absorption of carbonic acid, by *B* and the unknown volume of oxygen consumed, by *x*; then, as *B* contains all the nitrogen and oxygen originally contained in (*N + O*) minus the volume of oxygen which has been consumed by the combustible gas, it is evident that

$$(N + O) = B + x.$$

If then we substitute the quantity *B + x* for (*N + O*) in the first equation, we obtain the expression

$$c + B + x = A.$$

And hence for *x*, the value

$$x = A - B - c.$$

The quantity of carbonic acid generated was obtained by subtracting the fifth from the fourth reading, and finally the explosion of the remaining gas with hydrogen in excess, shewed whether or not perfect combustion had taken place; for if the gas remaining after the absorption of carbonic acid consisted only of oxygen and nitrogen then the quantity of the latter ought nearly to correspond with the amount introduced in the combustible gas and atmospheric air.

In none of the following analyses was the heat eliminated by combustion with excess of oxygen so great as to cause the volatilization of the quicksilver, the occurrence of which, when nitrogen is present, is always accompanied by the formation of nitric acid.

I.

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom. | Corrected vol. at 0° C. and 1 _m pressure | |
|---|------------------|---------------------|------------------------------------|---------|---|---|
| Gas used (dry). | 116.2 | 7.9 ⁰ C. | 14.9mm | 738.8mm | 81.75 | ✓ |
| After absorption by SO ₃ (dry). | 93.6 | 8.2 ⁰ | 30.5 " | 735.1 " | 64.03 | ✓ |
| After removal of specimen for com- bustion (dry.) | 82.3 | 9.0 ⁰ | 42.3 " | 735.3 " | 55.21 | |
| After absorption by alcohol. | 2.7 | 9.2 ⁰ | 42.8* | 732.9 " | 1.76 | |

II.

| | | | | | | |
|---|-------|------------------|--------|---------|-------|---|
| Gas used (dry). | 123.1 | 8.3 ⁰ | 6.1 " | 741.3 " | 87.83 | ✓ |
| After absorption by SO ₃ (dry.) | 98.8 | 7.7 ⁰ | 24.0 " | 739.4 " | 68.74 | ✓ |
| After removal of specimen for com- bustion (dry.) | 87.8 | 8.2 ⁰ | 37.3 " | 733.1 " | 59.31 | |
| After absorption by alcohol | 2.9 | 8.1 ⁰ | 56.5 " | 734.8 " | 1.86 | |

III.

| | | | | | | |
|---|-------|------------------|---------|---------|--------|---|
| Gas used (moist). | 102.2 | 8.4 ⁰ | 618.8 " | 735.7 " | 10.79 | ✓ |
| After admission of atmospheric air (moist). | 543.7 | 8.6 ⁰ | 160.8 " | 735.6 " | 298.60 | ✓ |
| After admission of O. (moist). | 569.1 | 8.7 ⁰ | 137.8 " | 735.6 " | 325.07 | ✓ |
| After combustion (moist). | 537.5 | 8.7 ⁰ | 166.7 " | 735.6 " | 291.96 | ✓ |
| After absorption of CO ₂ (dry). | 498.0 | 8.6 ⁰ | 202.7 " | 735.8 " | 257.37 | ✓ |
| After admission of H ₂ (dry.) | 626.9 | 9.0 ⁰ | 87.2 " | 735.6 " | 393.51 | ✓ |
| After combustion (moist). | 549.6 | 9.0 ⁰ | 155.4 " | 735.3 " | 303.96 | ✓ |

* The pressure of the stratum of alcohol, resting upon the mercury within the eudiometer in this and the following analyses, is calculated into millimeters of quick-silver and added to the difference of mercury level.

IV.

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
|---|------------------|------------------|------------------------------------|----------------------|--|
| Gas used (moist). | 104·0 | 8·3 ⁰ | 617·5 ^{mm} | 737·0 ^{mm} | 11·23 |
| After admission of atmospheric air (moist). | 538·3 | 8·3 ⁰ | 166·0 | 736·8 | 293·91 |
| After admission of O. (moist). | 577·0 | 8·0 ⁰ | 131·6 | 736·1 | 334·38 |
| After combustion (moist). | 544·3 | 7·9 ⁰ | 160·8 | 736·1 | 300·09 |
| After absorption of CO ₂ (dry). | 505·2 | 7·6 ⁰ | 196·4 | 733·5 | 263·99 |
| After admission of H (dry). | 636·5 | 8·3 ⁰ | 79·1 | 733·1 | 403·98 |
| After combustion (moist). | 532·0 | 8·3 ⁰ | 171·8 | 732·2 | 285·10 |

According to analyses I. and II., the original gas contained in 100 parts :

| | I. | II. | MEAN. |
|-------------------------------------|---------------|---------------|---------------|
| Gas absorbable by SO ₃ . | 21·68 | 21·73 | 21·70 |
| Gas unabsorbable by SO ₃ | 75·82 | 75·82 | 75·82 |
| Nitrogen | 2·50 | 2·45 | 2·48 |
| | <u>100·00</u> | <u>100·00</u> | <u>100·00</u> |

According to analyses III. and IV., the combustible gas, remaining after absorption by sulphuric acid, gave the following results :

| | III. | IV. |
|-----------------------------------|------|------|
| Oxygen consumed by 1 vol. | 5·48 | 5·47 |
| Carbonic acid generated by 1 vol. | 3·31 | 3·32 |

From the simple laws regulating the atomic volume of gaseous bodies, it is evident that no single gas could yield the results just given, it was also highly improbable that a gas having the general formula C_n H_n could, after the action of fuming sulphuric acid, be present, since these gases so far as is at present known, are all rapidly absorbed by that acid; and as the absence of hydrogen and light carburetted hydrogen had been proved by the solubility of the gas in alcohol, the conclusion was almost unavoidable that the mixture consisted of methyl and the hitherto unisolated radical ethyl. It will be seen, from the following calculations, how far this supposition

was borne out by the combined results of the eudiometrical and specific gravity experiments.

The estimation of the relative quantities of ethyl and methyl depends upon the circumstance, that ethyl consumes $6\frac{1}{2}$ times its volume of oxygen, and generates 4 times its volume of carbonic acid, whilst methyl consumes $3\frac{1}{2}$ volumes of oxygen, and generates 2 volumes of carbonic acid; but, as the volume of the mixed gases is known, we require only one other known quantity for the formation of two equations from which to determine the two unknown quantities; the contraction produced by the explosion of the gas with oxygen, and which is found by subtracting the fourth from the third reading, is a value in which both the oxygen consumed and carbonic acid generated are involved, and I have, therefore, made choice of this number for the second equation. As the quantity representing this contraction is compounded of the volume of combustible gas, *plus* oxygen consumed *minus* carbonic acid generated, it is clear that ethyl will produce a contraction equal to $3\frac{1}{2}$ times its own volume, and methyl a contraction equal to $2\frac{1}{2}$ times its volume. If, then, we represent the volume of combustible gas (obtained by subtracting the known amount of nitrogen from the observed volume) by A , the contraction produced during combustion by B , and the quantities of ethyl and methyl present, respectively by (x) and (y) , we obtain the following equations:

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

Hence the values of x and y are:

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

According to analysis (No. III.), 10·79 vols. containing 0·34 vols. nitrogen, and 10·45 vols. of combustible gas, consumed 57·25 vols. oxygen, and generated 34·59 vols. carbonic acid, causing a contraction equal to 33·11 vols. By substituting the numbers here representing the volume of combustible gas, and the contraction, for A and B in the above equations, we obtain the following numerical values for x and y :

$$\begin{aligned} x &= 6\cdot98 \\ y &= 3\cdot47 \end{aligned}$$

In analysis (IV.) 11·23 vols. containing 0·35 vols. nitrogen and 10·88 vols. of combustible gas, consumed 59·51 vols. oxygen and

generated 36.10 vols. carbonic acid producing a contraction of 34.29 vols.; from which we obtain as the values of x and y :

$$x = 7.09$$

$$y = 3.79$$

Hence, the 75.82 per cent. of combustible gas, left unabsorbed by fuming sulphuric acid, contained on the above supposition:

| | III. | IV. | MEAN. |
|--------------|-------|-------|-------|
| Ethyl . . . | 50.64 | 49.41 | 50.03 |
| Methyl . . . | 25.18 | 26.41 | 25.79 |
| | <hr/> | <hr/> | <hr/> |
| | 75.82 | 75.82 | 75.82 |

In order to ascertain the composition and state of condensation of the gaseous body absorbed by fuming sulphuric acid, the original gas was exploded with atmospheric air and oxygen, precautions, exactly similar to those already described, being observed. The following numbers were obtained:

V.

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1m pressure. |
|---|---------------|------------------|------------------------------|----------------------|--|
| Gas used (moist). | 99.6 | 7.4 ⁰ | 621.5 ^{mm} | 735.9 ^{mm} | 10.35 |
| After admission of atmospheric air (moist.) | 508.9 | 7.2 ⁰ | 192.4 „ | 735.8 „ | 265.66 |
| After admission of oxygen (moist.) | 559.5 | 7.2 ⁰ | 146.0 „ | 735.8 „ | 317.37 |
| After combustion (moist.) | 530.8 | 7.1 ⁰ | 172.0 „ | 736.1 „ | 287.95 |
| After absorption of CO ₂ (dry). | 494.3 | 7.3 ⁰ | 206.8 „ | 741.3 „ | 253.72 |
| After admission of H (dry). | 701.3 | 7.3 ⁰ | 24.1 „ | 741.2 „ | 489.80 |
| After combustion (moist.) | 563.3 | 7.3 ⁰ | 142.8 „ | 741.5 „ | 324.29 |

VI.

| | | | | | |
|---|-------|------------------|---------|---------|--------|
| Gas used (moist). | 108.1 | 9.2 ⁰ | 610.3 „ | 734.9 „ | 12.12 |
| After admission of atmospheric air (moist.) | 533.7 | 9.2 ⁰ | 167.5 „ | 734.9 „ | 288.45 |
| After admission of oxygen (moist.) | 589.9 | 9.0 ⁰ | 117.1 „ | 734.2 „ | 347.49 |

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
|---|---------------|------------------|------------------------------|----------------------|--|
| After combustion } (moist). | 557·6 | 8·9 ^o | 146·6mm | 734·3mm | 312·76 |
| After absorption } of CO ₂ (dry). | 518·7 | 9·0 ^o | 181·2 ,, | 733·1 ,, | 277·13 |
| After admission of } H (dry). | 706·3 | 9·0 ^o | 18·2 ,, | 732·6 ,, | 488·47 |
| After combustion } (moist). | 558·0 | 8·8 ^o | 146·4 ,, | 732·4 ,, | 312·18 |

According to analysis (No. V.) 10·35 vols., containing 10·10 vols. of combustible gas, consumed 49·95 vols. oxygen, and generated 30·63 vols. carbonic acid; but 10·35 vols. of the original gas would contain, according to the mean of the analyses I. and II., 7·85 vols. of combustible gas unabsorbable by fuming sulphuric acid, which would consume (vide analyses III. and IV.) 43·02 vols. of oxygen, and generate 26·06 vols. carbonic acid; leaving 6·93 vols. oxygen and 4·57 vols. carbonic acid, as the oxygen consumed and carbonic acid generated by 2·25 vols. of the gas removed by fuming sulphuric acid.

Analysis (No. VI.) leads to a similar result, 12·12 vols., containing 11·82 vols. of combustible gas, consumed 58·54 vols. oxygen, and generated 35·63 vols. carbonic acid; and as this quantity of the original gas would contain 9·19 vols. of the mixture of ethyl and methyl, which would consume 50·36 vols. oxygen and generate 30·51 vols. carbonic acid, therefore, the remaining 2·63 vols. of gas absorbed by sulphuric acid consumed 8·29 vols. oxygen, and generated 5·00 vols. carbonic acid.

Hence the results yielded by the gas absorbable by sulphuric acid may be thus expressed :

| | V. | VI. | MEAN. |
|-----------------------------------|------|------|-------|
| Oxygen consumed by 1 vol. . . | 3·08 | 3·11 | 3·09 |
| Carbonic acid generated by 1 vol. | 2·03 | 1·95 | 1·99 |

The gas removed by sulphuric acid appears, therefore, to have exactly the composition and state of condensation possessed by clayl, 1 vol. of which requires, for its combustion, 3 vols. of oxygen, and generates 2 vols. of carbonic acid, numbers which sufficiently coincide with those just given, when we consider that any errors of observation are concentrated upon a small portion of the combustible gas.

To control this result, a quantity of the original gas, perfectly dried by passing over chloride of calcium, was allowed to stream through a

Liebig's potash apparatus containing perchloride of antimony, which rapidly combines with the gas absorbable by sulphuric acid, but has no action upon ethyl, as shewn below, or upon methyl. An indefinite quantity of the brown crystallizable liquid thus obtained was carefully burnt with oxide of copper, the front end of the combustion-tube being furnished with a layer of copper turnings. After the combustion, the weight of the potash apparatus was found to have increased by 0.1164 grms., and that of the chloride of calcium tube by 0.0473 grms. These numbers correspond with the following atomic proportion :

$$\begin{aligned} \text{C} : \text{H} &= 0.0053 : 0.0053 \\ \text{C} : \text{H} &= 2 : 2 \end{aligned}$$

A result which completely confirms the eudiometrical analyses. Whether this body be really identical with elayl, or only isomeric with it, must be decided by further researches.

The per-centage composition of the gas *a* may, therefore, according to the mean of the foregoing analyses, be expressed as follows :

| | |
|----------------|--------|
| Elayl . . . | 21.70 |
| Ethyl . . . | 50.03 |
| Methyl . . . | 25.79 |
| Nitrogen . . . | 2.48 |
| | 100.00 |

The theoretical specific gravity of a mixture possessing this composition, agrees closely with that found by experiment as is seen from the following simple calculation :

$$\begin{array}{r r r r r} \text{C}_2 \text{H}_2 & = & 21.70 & \times & 0.96742 & = & 20.9930 \\ \text{C}_2 \text{H}_3 & = & 25.79 & \times & 1.03652 & = & 26.7319 \\ \text{C}_4 \text{H}_5 & = & 50.03 & \times & 2.00390 & = & 100.3551 \\ \text{N} & = & 2.48 & \times & 0.96740 & = & 2.3992 \\ \hline & & 100.00 & & & & \frac{150.4792}{100} = 1.504793 \end{array}$$

Specific gravity as found by experiment . . . 1.5250

EXAMINATION OF THE GAS β .

This gas which occupies only about $\frac{1}{10}$ of the volume of the last, was treated in a similar manner : the eudiometrical experiments gave the following numbers :

| I. | | | | | |
|---|------------------|-------------------|------------------------------------|----------------------|--|
| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
| Gas used (dry). | 160.6 | 13.2 ⁰ | 4.3 ^{mm} | 737.8 ^{mm} | 112.37 |
| After absorption by SO ₃ (dry). | 156.2 | 12.6 ⁰ | 8.7 „ | 741.7 „ | 109.44 |
| After removal of specimen for combustion (dry). | 128.8 | 13.9 ⁰ | 37.8 „ | 742.1 „ | 86.32 |
| After absorption by alcohol. | 8.2 | 14.0 ⁰ | 42.3 „ | 742.0 „ | 5.26 |

These numbers, reduced for 100 parts, give :

| | |
|---|-------|
| Gas absorbable by SO ₃ | 2.61 |
| Combustible gas unabsorbable by SO ₃ | 91.46 |
| Nitrogen | 5.93 |

100.00

The combustion, with oxygen, of the gas remaining after treatment with fuming sulphuric acid, gave the following results :

| II. | | | | | |
|---|------------------|-------------------|------------------------------------|----------------------|--|
| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
| Gas used (moist). | 116.9 | 13.5 ⁰ | 598.9 ^{mm} | 741.8 ^{mm} | 14.64 |
| After admission of atmospheric air (moist). | 454.3 | 13.4 ⁰ | 240.8 „ | 741.8 „ | 211.97 |
| After admission of O (moist). | 540.2 | 13.5 ⁰ | 160.5 „ | 741.7 „ | 293.25 |
| After combustion (moist). | 502.0 | 13.4 ⁰ | 195.9 „ | 741.8 „ | 255.71 |
| After absorption of CO ₂ (dry). | 463.8 | 13.3 ⁰ | 236.6 „ | 738.5 „ | 221.96 |
| After admission of H (dry). | 716.8 | 13.3 ⁰ | 13.7 „ | 738.4 „ | 495.32 |
| After combustion (moist). | 551.8 | 13.5 ⁰ | 154.9 „ | 738.8 „ | 300.96 |

| III. | | | | | |
|---|------------------|-------------------|------------------------------------|----------------------|--|
| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
| Gas used (moist). | 121.2 | 13.6 ⁰ | 594.3 „ | 738.7 „ | 15.33 |
| After admission of atmospheric air (moist). | 448.0 | 13.7 ⁰ | 247.7 „ | 738.6 „ | 204.42 |

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
|--|---------------|-------------------|------------------------------|----------------------|--|
| After admission of O (moist). | 529.4 | 14.0 ⁰ | 171.27 ^{mm} | 39.3 ^{mm} | 280.08 |
| After explosion (moist). | 488.0 | 14.3 ⁰ | 209.4 ,, | 739.8 ,, | 240.34 |
| After absorption of CO ₂ (dry). | 440.9 | 13.5 ⁰ | 254.7 ,, | 742.0 ,, | 204.72 |
| After admission of H (dry). | 662.7 | 13.9 ⁰ | 52.2 ,, | 742.1 ,, | 435.04 |
| After explosion (moist). | 520.6 | 14.0 ⁰ | 178.0 ,, | 742.2 ,, | 273.49 |

According to analysis (No. II.) 14.64 vols., containing 13.75 vols. combustible gas, consumed 57.54 vols. oxygen, and generated 33.75 vols. carbonic acid, producing a contraction of 37.54 vols. In analysis (No. III.) 15.33 vols., containing 14.40 vols. combustible gas, consumed 60.96 vols. oxygen, and generated 35.62 vols. carbonic acid, suffering a diminution of volume during combustion equal to 39.74 vols.; numbers which correspond with the following proportions:

| | Vol. of comb. gas. | O. consumed. | CO ₂ generated. |
|------|--------------------|--------------|----------------------------|
| II. | 1 | 4.18 | 2.46 |
| III. | 1 | 4.23 | 2.47 |

From the behaviour of the gas with fuming sulphuric acid, and from the results of its combustion with oxygen, there can be no doubt that it is a mixture of the same ingredients as the gas α , the only difference being in the relative proportions of the two; and if we apply the formulæ before given, we obtain the annexed values for (x) and (y):

ANALYSIS NO. II.

$$\begin{aligned}x &= 3.17 \\y &= 10.58\end{aligned}$$

ANALYSIS NO. III.

$$\begin{aligned}x &= 3.74 \\y &= 10.66\end{aligned}$$

From which, omitting the nitrogen, we obtain the following percentage composition:

| | I. | II. | |
|--------|--------|-------|--|
| Elayl | 2·78 | | |
| Ethyl | 22·41 | 25·25 | |
| Methyl | 74·81 | 71·97 | |
| | 100·00 | | |

The determination of the atomic constitution of the crystalline body from which this gas is evolved, would be attended with great difficulty, as it is rapidly decomposed on coming in contact with the atmosphere, the crystals becoming almost instantaneously brown with the simultaneous production of an oxyiodide of zinc.

If, instead of allowing the tube to stand for twelve hours, as in the above instance, water be poured upon the residue immediately after the gas *a* has ceased to be evolved, the resulting gaseous mixture differs widely from that just described, in the relative proportions of ethyl and methyl composing it, as is shown by the following analysis of gas thus prepared and collected over mercury; the elayl, which was present only in small quantity, and the vapour of iodide of ethyl were removed by the introduction of a coke bullet saturated with fuming sulphuric acid, and the sulphurous acid, &c., by the subsequent insertion of a potash ball. The gas was perfectly absorbed by alcohol, and therefore contained no trace of nitrogen.

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C and 1 ^m pressure. |
|---|------------------|------------------|------------------------------------|----------------------|---|
| Gas used (moist) | 139·0 | 8·3 ⁰ | 577·5 ^{mm} | 732·2 ^{mm} | 19·76 |
| After admission of atmospheric air (moist). | 487·9 | 8·3 ⁰ | 213·2 ,, | 731·5 ,, | 241·53 |
| After admission of O (moist). | 558·6 | 8·4 ⁰ | 142·8 ,, | 731·2 ,, | 314·42 |
| After combustion (moist). | 502·9 | 8·3 ⁰ | 199·2 ,, | 731·0 ,, | 255·55 |
| After absorption of CO ₂ (dry). | 435·8 | 8·2 ⁰ | 260·5 ,, | 733·1 ,, | 199·95 |

These numbers lead to the proportion :

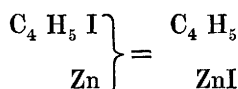
$$x : y = 9·47 : 10·29$$

Or in 100 parts :

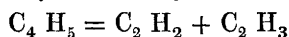
| | | | | |
|--------|---|---|---|--------|
| Methyl | . | . | . | 52·07 |
| Ethyl | . | . | . | 47·93 |
| | | | | 100·00 |

It appears, therefore, evident that the easily condensible ethyl is merely mechanically retained in the interstices of the crystals, and gradually evaporates under ordinary atmospheric pressure, but, as the absolute volume of methyl does not perceptibly diminish under the same circumstances, it is highly probable that the latter body enters into the chemical constitution of the crystals.

From the foregoing facts, the decomposition of iodide of ethyl by zinc may be thus expressed :



A portion of the ethyl thus set free is at the same time decomposed into equal volumes of elayl and methyl :



whilst the iodide of zinc combines with a small proportion of methyl, forming a white crystalline compound, probably of definite constitution. The analyses of the gas α indicate a slight excess of methyl over elayl, which would, to a small extent, have been increased had the gases α and β been collected in the same receiver; this excess of methyl over elayl is without doubt caused by the presence of a trace of moisture either in the iodide of ethyl, or adhering to the zinc, since, as will be shown below, iodide of ethyl and water in contact with zinc are decomposed into oxyiodide of zinc and two volumes of pure methyl.

As ethyl must have a considerably higher boiling point than either elayl or methyl, it might be expected that, on breaking off the extremity of the decomposition tube, the two last named bodies would escape first, and that the gas produced by the ebullition of the last portion of the condensed fluid would be pure ethyl; to ascertain if this were the case, a couple of tubes were charged and subjected to heat, as before described, their capillary extremities were afterwards broken off under quicksilver, and the gas allowed to escape until it issued in a slow regular stream, the beaks of the tubes were then brought beneath a receiver filled with mercury, in which the remainder of the gas was collected. 180 c.c. were obtained from the two tubes. Any elayl or vapour of iodide of ethyl that might be present was absorbed by fuming sulphuric acid, the vapours of which together with sulphurous acid being afterwards removed by a bullet of fused potash.

Two analyses of the gas, made with all the before mentioned precautions, gave the following numbers :

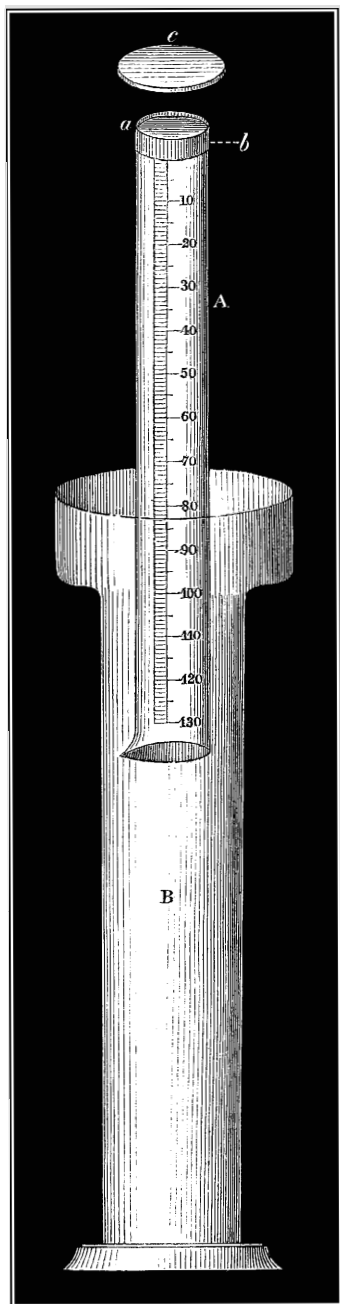
| I. | | | | | |
|---|------------------|-------------|------------------------------------|----------------------|--|
| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
| Gas used (moist). | 90·0 | 12·6° | 626·0 ^{mm} | 751·1 ^{mm} | 9·82 |
| After admission of atmospheric air (moist). | 475·9 | 12·6° | 216·4 ,, | 751·2 ,, | 238·32 |
| After admission of O (moist). | | | | | |
| After combustion (moist). | 484·8 | 12·5° | 208·0 ,, | 752·0 ,, | 247·17 |
| After absorption of CO ₂ (dry). | 436·1 | 11·7° | 255·0 ,, | 753·3 ,, | 208·37 |
| After admission of H (dry). | 617·7 | 12·4° | 88·2 ,, | 753·2 ,, | 392·92 |
| After combustion (moist). | 548·2 | 12·6° | 148·4 ,, | 752·8 ,, | 311·00 |

| II. | | | | | |
|---|------------------|-------------|------------------------------------|----------------------|--|
| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
| Gas used (moist). | 91·8 | 12·8° | 623·1 ^{mm} | 752·7 ^{mm} | 10·40 |
| After admission of atmospheric air (moist). | 471·2 | 13·0° | 219·9 ,, | 752·6 ,, | 234·56 |
| After admission of O (moist). | | | | | |
| After combustion (moist). | 498·8 | 12·8° | 194·0 ,, | 751·1 ,, | 260·19 |
| After absorption of CO ₂ (dry). | 454·3 | 13·0° | 237·2 ,, | 741·5 ,, | 218·69 |
| After admission of H (dry). | 644·7 | 13·1° | 63·9 ,, | 740·8 ,, | 416·41 |
| After explosion (moist). | 532·7 | 13·0° | 151·8 ,, | 740·0 ,, | 293·39 |

These analyses exhibit the following relations between the volumes of combustible gas, oxygen consumed, and carbonic acid generated :

| | Vol. of comb. gas. | O. consumed. | CO ² generated. |
|-----|--------------------|--------------|----------------------------|
| I. | 9·82 | 63·47 | 38·80 |
| | = 1 | : 6·46 | : 3·95 |
| II. | 10·40 | 67·26 | 41·50 |
| | = 1 | : 6·47 | : 3·99 |

FIG. 3.



The gas consists, therefore, of pure ethyl, which theoretically consumes $6\frac{1}{2}$ times its volume of oxygen, and generates 4 times its volume of carbonic acid, numbers which agree almost exactly with those found in the above analyses.

Although the results just given scarcely admit a doubt as to the identity of the gas with the radical ethyl, yet, in order further to assure myself that the gas was single, and not a mixture, I submitted it to diffusion, which at the same time served to control the previous specific gravity determination. For this purpose a glass tube (*A* Fig. 3) 10 inches long, $\frac{3}{8}$ inch in diameter, and furnished with an etched millimeter scale, was used; it was stopped at one extremity (*a*) by a plug of gypsum (*b*) 5^{mm} in thickness, the end of the tube being so ground, that whilst it could be closed perfectly gas-tight by the smeared glass plate (*c*), the latter rested very nearly in contact with the surface of the plaister plug. Before use, the instrument was calibrated in the usual manner, the stratum of gypsum perfectly dried, and the upper end of the tube closed by the glass plate: one leg of a small syphon being now inserted into the open extremity of the tube *A*, the latter was immersed with its mouth downwards in the vessel *B*, filled with quicksilver, until the metal came in contact with the inner surface of the plaister plug; the syphon being removed, the tube remained filled with quicksilver, whilst the pores

of the gypsum continued open. The gas, perfectly freed from moisture, was now introduced, its volume noted with the proper precautions, and after the tube had been so adjusted, by means of a vertically sliding holder, that the inner and outer quicksilver surfaces stood at the same level, the glass plate was removed, and the diffusion commenced. During the operation, the volume of the gas gradually increased, and therefore to preserve it at the exact pressure of the atmosphere, it was necessary to keep the inner and outer mercury at the same level, by slowly raising the sliding holder. When the diffusion had continued for 10 minutes, it was interrupted by replacing the glass plate in its former position, and the gas, being first dried by a bullet of potash, its volume was again read off.

The mixture of gas, and atmospheric air thus obtained, was divided into two portions, one of which was introduced into a short eudiometer, for the determination of the relative quantities of air and gas present, and the other transferred to a combustion eudiometer, in which it was exploded with atmospheric air and oxygen, the necessary proportions of the two latter being calculated from the composition of the gaseous mixture as indicated by absorption with alcohol in the short eudiometer :

I.

Determination of the augmentation in volume during diffusion.

| | Observed vol. | Temp. C. | Difference of mercury level | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
|------------------------|---------------|-------------------|-----------------------------|----------------------|--|
| Gas used (dry). | 138·2 | 14·2 ⁰ | 13·4 ^{mm} | 741·9 ^{mm} | 95·70 |
| After diffusion (dry). | 158·3 | 14·1 ⁰ | 3·0 ,, | 741·9 ,, | 111·22 |

The estimation of the relative quantities of combustible gas and atmospheric air present in the mixture after diffusion, gave the following numbers :

II.

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
|-----------------------------------|---------------|-------------------|------------------------------|----------------------|--|
| Gas used (moist). | 115·1 | 14·0 ⁰ | 57·2 ^{mm} | 745·8 ^{mm} | 74·09 |
| After absorption by } alcohol. | 56·4 | 14·0 ⁰ | 81·1 ,, | 745·8 ,, | 34·32 |

The mixture contained, therefore, in 100 parts :

| | | | | | |
|-----------------|---|---|---|---|-------|
| Combustible gas | . | . | . | . | 53·68 |
| Atmospheric air | . | . | . | . | 46·32 |

100·0

From these numbers, taken in connection with those given in No. 1, the volume of air which had entered, and the volume of gas that had escaped, during the diffusion, are found to be as follows :

| | |
|-------------------------------|-------|
| Volume of air entered | 51.52 |
| Volume of gas escaped | 36.00 |

The combustion of the second portion of the same mixture, in the large eudiometer, gave the following results :

III.

| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corrected vol. at 0° C. and 1 ^m pressure. |
|---|------------------|-------------------|------------------------------------|----------------------|--|
| Gas used (moist). | 134.6 | 14.2 ⁰ | 583.2 ^{mm} | 741.3 ^{mm} | 18.68 |
| After admission of air (moist). } | 483.7 | 14.1 ⁰ | 217.9 ,, | 741.6 ,, | 235.35 |
| After admission of O. (moist). } | 578.5 | 14.1 ⁰ | 131.2 ,, | 741.6 ,, | 329.17 |
| After combustion (moist). } | 543.8 | 13.7 ⁰ | 162.2 ,, | 742.0 ,, | 294.16 |
| After absorption of CO ₂ (dry). } | 495.5 | 13.6 ⁰ | 207.4 ,, | 744.8 ,, | 253.64 |

Analyses No. II. and No. III. show that 18.68 vols. of the gaseous mixture contained 10.03 vols. of combustible gas, which consumed 65.50 vols. oxygen, and generated 40.52 vols. carbonic acid, numbers which express the following proportion :

| | | | | |
|--------------------|---|--------------|---|----------------------------|
| Vol. of comb. gas. | : | O. consumed. | : | CO ² generated. |
| 1 | : | 6.53 | : | 4.04 |

The gas has, therefore, suffered no change in its state of condensation, or in the relative proportion of carbon to hydrogen, by being submitted to diffusion, a result which can only be produced by a single gas, or by a mixture of two or more gaseous bodies, whose relative proportions are expressed by their diffusion coefficients ; the latter case must necessarily be of very rare occurrence, and in the present instance can scarcely be admitted as possible. This method might, in almost every case, be employed with advantage, to determine whether or not any specimen of gas be simple or mixed.

The determination of the specific gravity of ethyl, from the above

facts, depends upon Graham's well-known law, that the rapidity with which gases diffuse, is directly as their volumes, and inversely as the square roots of their densities; therefore, if we denote the volume of air which entered the diffusion apparatus by (*a*), the volume of gas escaped by (*b*), and the required specific gravity of the gas by (*x*), we have the following equation :

$$a : b = 1 : 1 \frac{1}{\sqrt{x}}$$

from which the following value for *x* is obtained :

$$x = \frac{a^2}{b^2}$$

If in this equation, we substitute for (*a*) and (*b*) the numbers deduced from analyses II. and III. we obtain :

$$x = \frac{51.52^2}{36^2} = 2.0481$$

The specific gravity of the mixture of ethyl, methyl, elayl, and nitrogen, was found by weighing, to be 1.525, from which the specific gravity of ethyl is calculated to be 2.0462, a number closely corresponding with that just given.

By employing a long diffusion eudiometer, provided with a mechanical arrangement for regulating the pressure, and by using a perfectly dry porous substance in the place of gypsum, the specific gravities of gases could, no doubt, be determined in this manner with very great accuracy.

The whole of the above facts taken together, prove beyond doubt, when iodide of ethyl is decomposed by zinc, at an elevated temperature, and that the radical ethyl is present amongst the gaseous products, and may easily be separated in a state of perfect purity.

Ethyl is a colourless gas, possessing a very slight ethereal odour,* burning with a brilliant white flame, and having a specific gravity of 2.00394. According to the combined results of the specific gravity and eudiometrical experiments, it contains 2 vols. of carbon vapour and 5 vols. of hydrogen condensed into one volume.

* This odour, which is at first very strong, probably depends upon the presence of a trace of some foreign body, for after purification by standing over water, and subsequent treatment with fuming sulphuric acid, it almost entirely disappears; perfectly pure ethyl is, therefore, probably, like methyl, inodorous.

| | | |
|-------------------------------|---|---------|
| 2 vols. carbon vapour | = | 1·65844 |
| 5 vols. hydrogen | | 0·34550 |

| | | |
|-----------------------------|--|---------|
| 1 vol. ethyl gas | | 2·00394 |
| Found { by weighing | | 2·0462 |
| { by diffusion | | 2·0481 |

It is incondensable at a temperature of -18° C. ($-0\cdot5^{\circ}$ F.).

Allowed to stream slowly through a serpentine glass tube, immersed in a freezing mixture at -18° C., it retained its gaseous condition unaltered, but at 3° C. ($37\cdot5^{\circ}$ F.), and exposed to a pressure of $2\frac{1}{4}$ atmospheres, in an Oerstedt's hydrostatic condenser, it is converted into a colourless transparent and mobile liquid, which instantly re-assumes the gaseous condition on the pressure being removed; its boiling point, at ordinary pressures, may, therefore, be estimated at about -23° C. ($9\cdot5^{\circ}$ F.) 1 vol. of absolute alcohol, at $14\cdot2^{\circ}$ C. (58° F.), and $744\cdot8^{\text{mm}}$ pressure, absorbs about 18·13 vols. of ethyl: agitated with a small quantity of alcohol, over mercury, the gas rapidly disappeared, with the exception of a small bubble, which did not amount to $\frac{1}{10}$ per cent, on afterwards throwing up a few drops of water, the alcohol assumed a milky appearance, followed by a rapid disengagement of gas, which, in a few seconds, amounted to very nearly the original volume. Ethyl is not acted upon by fuming sulphuric acid; it is scarcely affected by concentrated nitric acid and chromic acids, and does not combine with iodine or sulphur, even on the application of heat; in the case of the latter element, sulphuretted hydrogen is copiously evolved, and carbon separated, as the temperature approaches redness. Mixed with half its volume of oxygen, and conducted over spongy platinum, it remains unchanged at ordinary temperatures, but on a gentle heat being applied, the sponge becomes incandescent, water is formed with the simultaneous separation of a small quantity of charcoal, and a gas, probably light carburetted hydrogen, insoluble in alcohol, burning with a feebly illuminating flame, and generating much carbonic acid, is the remaining product of the decomposition. Like methyl, ethyl is not absorbed by perchloride of antimony, even under the influence of bright sunlight; chlorine has no action upon it in the dark, but when equal volumes of the two gases are exposed to diffused daylight, combination rapidly takes place, accompanied by a contraction of volume, and the production of a colourless liquid. Bromine also acts upon ethyl, when exposed to bright sunlight, with the application of a gentle heat. I have not yet completed the

examination of the products of this and the former reaction, and must, consequently, defer the communication of further details to a future opportunity.

In the hope of avoiding the formation of methyl and ethyl, during the preparation of ethyl, I was led to try what influence the presence of water, alcohol, and ether, would have upon the decomposition of iodide of ethyl by zinc, and although the expectation of preventing the secondary decomposition of the ethyl was not realized, yet the results of the experiments are, in other respects, not wholly uninteresting.

ACTION OF ZINC UPON IODIDE OF ETHYL IN PRESENCE OF
WATER.

Equal volumes of water and iodide of ethyl were introduced together with zinc into a decomposition tube, which was then exhausted, hermetically sealed, and exposed to heat, as before described; decomposition commenced and proceeded at a lower temperature than that required for inducing the action of zinc upon iodide of ethyl alone; the fluid contents of the tube became thick and oleagenous, and during the subsequent cooling solidified to a white, soft, amorphous mass. On afterwards opening the tube, under sulphuretted water, a large quantity of gas rushed out with great violence, and was collected in the apparatus, with the precautions already described. No gas was evolved on subsequently treating the residue with water.

The eudiometrical examination of the gas gave the following results:

I.

| | Observed vol. | Temp. C. | Difference of mercury level. | Baromf. | Corrected vol. at 0° C. and 1 ^m pressure. |
|--|------------------|------------------|------------------------------------|---------------------|--|
| Gas used (dry). | 55·9 | 7·4 ⁰ | 74·9 ^{mm} | 741·3 ^{mm} | 36·27 |
| After action of fuming SO ₃ (dry). } | 55·9 | 7·7 ⁰ | 73·3 „ | 739·8 „ | 36·24 |

The gas remaining after the action of fuming sulphuric acid was so nearly absorbed by alcohol, that the extremely small residue could not be estimated.

| | Observed vol. | -Temp. C. | Difference of mercury vol. | Baromf. | Corr. vol. at 0° C. and 1 ^m pressure. |
|---|------------------|------------------|----------------------------------|---------------------|--|
| Gas used (moist). | 100.5 | 8.0 ⁰ | 621.3 ^{mm} | 739.6 ^{mm} | 10.77 |
| After admission of atmospheric air } (moist). | 514.1 | 8.0 ⁰ | 187.9 ,, | 739.0 ,, | 271.25 |
| After admission of O. (moist). | 540.6 | 8.0 ⁰ | 162.7 ,, | 738.5 ,, | 298.21 |
| After explosion } (moist). | 513.9 | 7.8 ⁰ | 188.3 ,, | 738.0 ,, | 270.69 |
| After absorption } of CO ₂ (dry). | 488.0 | 7.6 ⁰ | 212.0 ^{mm} | 738.1 ^{mm} | 249.78 |
| After admission of H (dry). | 717.9 | 7.7 ⁰ | 10.2 ,, | 737.9 ,, | 508.08 |
| After explosion } (moist). | 612.0 | 8.0 ⁰ | 100.1 ,, | 737.8 ,, | 374.40 |

III.

| | | | | | |
|---|-------|------------------|----------|----------|--------|
| Gas used (moist). | 155.0 | 8.2 ⁰ | 558.6 ,, | 737.8 ,, | 25.75 |
| After admission of atmospheric air } (moist). | 521.2 | 8.0 ⁰ | 182.1 ,, | 737.3 ,, | 277.08 |
| After admission of O. (moist). | 573.0 | 8.0 ⁰ | 135.1 ,, | 737.7 ,, | 331.00 |
| After explosion } (moist). | 509.1 | 7.8 ⁰ | 193.1 ,, | 738.0 ,, | 265.79 |
| After absorption of CO ₂ (dry). | 449.6 | 7.9 ⁰ | 246.2 ,, | 738.8 ,, | 215.24 |
| After admission of H (dry). | 665.1 | 8.1 ⁰ | 52.0 ,, | 737.9 ,, | 443.04 |
| After explosion } (moist). | 629.2 | 8.5 ⁰ | 82.7 ,, | 736.9 ,, | 394.12 |

These analyses show that the gas does not contain a trace of clayl, and further, that it requires for its combustion $3\frac{1}{2}$ vols. of oxygen generating 2 vols. of carbonic acid :

| | Vol. of comb. gas. | O. consumed. | CO ₂ generated. |
|---------------|--------------------|--------------|----------------------------|
| Analysis II. | 10.77 | 37.66 | 20.91 |
| = | .1 | 3.50 | 1.94 |
| Analysis III. | 25.75 | 90.01 | 50.55 |
| = | .1 | 3.50 | 1.97 |

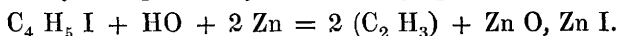
These are, however, precisely the results obtained in the analysis of methyl* with which this gas exactly coincides in all its properties. It is colourless, nearly insoluble in water, but soluble in alcohol, 1 vol. of which, at 8·8° C. (48° F.) and 665·5^{mm} pressure, absorbs 1·22 volumes; it possesses, at first, a slight ethereal odour, which, by heating the gas first with alcohol, and afterwards with concentrated sulphuric acid, entirely disappears, leaving the methyl perfectly inodorous. It is incondensable at a temperature of —18° C. (—0·5° F.); mixed with chlorine it remains unacted upon in the dark, but in diffused daylight the colour of the chlorine rapidly disappears, proving that combination has taken place; it does not combine with iodine or sulphur even when these substances are heated in the gas.

There can, therefore, be no doubt, that the gaseous product of the decomposition of iodide of ethyl and water by zinc is pure methyl, and that it is identical with the gas evolved by the action of potassium upon cyanide of ethyl,† and by the electrolysis of acetic acid.‡

An attempt to condense methyl, by the application of pressure, was unsuccessful; at 3° C. (37·5° F.) and under a pressure of 20 atmospheres (the highest which the apparatus at my disposal would bear) it exhibited no signs of liquefaction.

The white residue remaining in the decomposition tube, after the escape of the gas, exhaled a strong odour of ether, but contained no other organic substance, the white amorphous mass consisted of oxydide of zinc.

The formation of methyl by the action of zinc upon water, and iodide of ethyl is explained by the following equation :



The generation of methyl, during this decomposition, might also be explained by assuming, that the radical ethyl is split up into the groups (C₂ H₂) and (C₂ H₃), and that the former is retained in the residue whilst the latter escapes as gas : to convince myself that this was not the case, I submitted a weighed quantity (2·268 grms.) of iodide of ethyl to the action of water and zinc in the manner already described; after the decomposition was ended, and the tube perfectly cooled, the latter was opened, the gas allowed to escape, and the residue quickly mixed with cold oxide of copper and burnt in a

* Quarterly Journal of the Chemical Society for April 1848, p. 65.

† Journal of the Chemical Society for April 1848, p. 60.

‡ Annalen der Chemie. Bd., LXXIX. s. 279.

combustion tube, as in an ordinary organic analysis. The weight of the potash apparatus increased by 0.132 grms. equivalent to 0.036 grms. carbon: this is, however, only $\frac{1}{5}$ of the quantity of carbon required, if the products of the decomposition are elayl, methyl, and iodide of zinc, for, on this supposition, the residue from 2.268 grms. iodide of ethyl, containing the corresponding quantity of elayl, ought to yield 0.641 grms. carbonic acid (= 0.175 grms. C.) instead of 0.132 grms. as found in the above experiment. The occurrence of a large quantity of oxyiodide of zinc in the residue is also, in itself, a sufficient proof that the ethyl on its separation from iodine is converted, by the assumption of an atom of hydrogen, into 2 vols. of methyl gas.

This conclusion is also further confirmed by the fact, that iodide of ethyl and water heated in an hermetically sealed tube to the temperature employed in the above production of methyl, are transformed into ether, and a concentrated solution of hydriodic acid. This formation of ether also explains the occurrence of that body in the white residue, and the production of carbonic acid on its subsequent combustion with oxide of copper.

The transformation of iodide of ethyl, in contact with water and zinc, into oxyiodide of zinc and 2 volumes of methyl, furnishes a convenient method for preparing that radical in large quantities perfectly pure; upwards of 300 cubic centimetres being obtained from a single decomposition tube of the dimensions previously stated. It is necessary that the operator should take precautions to preserve himself from the danger attending the possible explosion of the tubes during the decomposition; the apparatus ought, therefore, always to be enclosed in a strong wooden case, open behind, and having a double plate-glass window in front through which the progress of the operation may be watched. The quantity of iodide of ethyl introduced into each tube of the above dimensions, ought not to exceed 3.5 grms., and the temperature of the oil-bath should not be allowed to rise above 180° C. (356° F.) During the whole of the foregoing experiments, no instance of explosion occurred, although the pressure within the tubes must, in many instances, have amounted to between 80 and 100 atmospheres.

ACTION OF ZINC UPON IODIDE OF ETHYL AND ALCOHOL.

This experiment was conducted in precisely the same manner as the last, absolute alcohol being substituted in the place of water.

The appearances presented during decomposition, and the quantity of gas evolved on subsequently opening the tube, were almost exactly identical with those observed in the decomposition of iodide of ethyl in the presence of water. The residue, in which the odour of ether was easily recognized, did not evolve a further quantity of gas on the addition of water.

The eudiometrical analysis led to the following results :

I.

| | Observed vol. | Temp. C. | Diff. of mercury level. | Barometer. | Corr. vol. at 0° C. and 1 pressure. |
|---|------------------|------------------|-------------------------------|------------|---|
| Gas used (dry). | 122·7 | 8·8 ⁰ | 6·1mm | 732·3mm | 86·32 |
| After action of fuming SO ₃ (dry). | 120·9 | 8·2 ⁰ | 8·2 „ | 740·0 „ | 85·89 |
| After removal of specimen for com- bustion (dry). | | 84·3 | 9·0 ⁰ | 43·8 „ | 732·6 „ |
| After absorption by alcohol. | 3·1 | 8·6 ⁰ | 31·9 „ | 732·1 „ | 2·06 |

II.

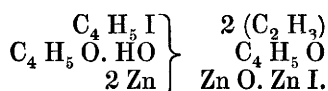
| | Observed vol. | Temp. C. | Diff. of mercury level. | Barometer. | Corr. vol. at 0° C. and 1 ^m pressure. |
|---|------------------|------------------|-------------------------------|------------|--|
| Gas used (moist). | 136·7 | 8·0 ⁰ | 576·9 „ | 741·0 „ | 20·73 |
| After admission of atmospheric air (moist). | 504·0 | 8·3 ⁰ | 192·6 „ | 741·3 „ | 264·37 |
| After admission of O (moist). | | 574·6 | 8·4 ⁰ | 128·7 „ | 741·1 „ |
| After explosion (moist). | 526·3 | 8·2 ⁰ | 172·3 „ | 740·9 „ | 286·39 |
| After absorption of CO ₂ (dry). | 482·3 | 7·9 ⁰ | 213·2 „ | 738·2 „ | 246·08 |
| After admission of H (dry). | 702·0 | 8·0 ⁰ | 23·7 „ | 737·7 „ | 486·95 |
| After explosion (moist). | 566·1 | 8·1 ⁰ | 140·9 „ | 737·3 „ | 323·44 |

Analysis No. I, proves the absence of clay and the presence of 3·66 per cent nitrogen. Analysis No. II, gives the following

proportion of combustible gas to oxygen consumed and carbonic acid generated :

| | | |
|--------------------|-------------|----------------------------|
| Vol. of comb. gas. | O consumed. | CO ₂ generated. |
| 19·97 | 70·76 | 40·31 |
| = 1 | : 3·54 | : 2·02 |

The gas has, therefore, the same composition and state of condensation as that evolved by the action of zinc upon iodide of ethyl and water, with which it also exactly coincides in physical properties. The presence of oxyiodide of zinc and ether in the residue leave no room for doubt that 1 eq. iodide of ethyl, with 1 eq. alcohol and 2 eqs. zinc, give rise to 2 eqs. methyl, 1 eq. ether, and 1 eq. oxyiodide of zinc :



ACTION OF ZINC UPON IODIDE OF ETHYL AND ETHER.

Equal volumes of iodide of ethyl and ether were heated with zinc in a sealed tube, to a temperature of about 150° C. (302° F.), until the action appeared complete : on being allowed to cool, the residual thick, oily fluid did not solidify. When the beak of the tube was afterwards broken off, only a few cubic inches of gas were evolved, but, on pouring water upon the residue, a strong effervescence, produced by the disengagement of a much larger volume of gas, occurred. The two specimens of gas were collected in the same receiver, and, on being submitted to analysis, yielded the following results :

I.

| | Observed vol. | Temp. C. | Diff. of mercury level. | Barometer. | Corr. vol at 0° C. and 1 ^m pressure. |
|---|------------------|-------------------|-------------------------------|---------------------|---|
| Gas used (dry). | 185·2 | 12·9 ⁰ | 19·7 ^{mm} | 744·2 ^{mm} | 128·12 |
| After absorption by SO ₃ (dry). | 175·1 | 13·0 ⁰ | 4·3 „ | 741·4 „ | 123·20 |
| After removal of specimen for com- bustion (dry). | 105·7 | 14·3 ⁰ | 65·8 „ | 745·9 „ | 68·31 |
| After absorption by alcohol. | 7·4 | 14·1 ⁰ | 71·2 „ | 746·4 „ | 4·58 |

| II. | | | | | |
|---|------------------|-------------------|------------------------------------|----------------------|--|
| | Observed vol. | Temp. C. | Difference of mercury level. | Barom ^r . | Corr. vol. at 0° C. and 1 ^m pressure. |
| Gas used (moist). | 48·3 | 13·0 ⁰ | 361·7 ^{mm} | 740·0 ^{mm} | 16·92 |
| After admission of atmospheric air (moist). | 312·6 | 13·1 ⁰ | 92·2 „ | 739·8 „ | 189·83 |
| After admission of O (moist). | | | | | |
| After combustion (moist). | 309·9 | 12·7 ⁰ | 98·1 „ | 739·4 „ | 186·67 |
| After absorption of CO ₂ (dry) | 260·5 | 12·9 ⁰ | 144·6 „ | 738·3 „ | 147·68 |
| After admission of H. (dry) | 388·1 | 13·0 ⁰ | 14·8 „ | 737·9 „ | 267·87 |
| After admission of O (dry). | 427·2 | 13·3 ⁰ | 12·8 „ | 737·3 „ | 295·12 |
| After combustion (moist). | 302·0 | 13·4 ⁰ | 102·4 „ | 737·1 „ | 179·40 |

According to analysis No. I, the per-centage composition of the gas may be thus expressed :

| | |
|---|--------|
| Gas absorbable by SO ₃ | 3·84 |
| Gas unabsorbable by SO ₃ | 89·71 |
| Nitrogen | 6·45 |
| | 100·00 |

Analysis No. II, exhibits the following relation between the volumes of combustible gas, oxygen consumed and carbonic acid generated :

| | | |
|--------------------|-------------|----------------------------|
| Vol. of comb. gas. | O consumed. | CO ₂ generated. |
| 15·83 | 67·31 | 38·99 |
| = 1 | : 4·25 | : 2·46 |

These numbers indicate that the combustible gas, not absorbed by fuming sulphuric acid, is a mixture, one of the constituents of which must have a higher atomic weight than methyl. From the small residue left after the action of alcohol, which precludes the presence of hydrogen and light carburetted hydrogen, from the occurrence of ethyl, and the behaviour of iodide of ethyl in contact with zinc, alone, and in presence of water and alcohol, we may

safely conclude that the gas in question is a mixture of ethyl and methyl, and, on applying the formula previously given, we find that the 15·83 vols. of combustible gas, insoluble in fuming sulphuric acid, consist of 4·57 vols. ethyl and 11·26 vols. methyl: therefore, omitting nitrogen, the per-centage composition of the original gas may be thus stated :

| | |
|------------------|--------|
| Elyl | 4·10 |
| Ethyl | 27·68 |
| Methyl | 68·22 |
| | 100·00 |

Although these experiments cannot by any means be considered as a complete investigation of the action of zinc upon iodide of ethyl in presence of ether, yet they afford sufficient evidence that the separation of the elements of water from the ether has been effected, producing a transformation of ethyl into 2 vols. of methyl; the elements of water have not, however, been so readily eliminated as altogether to prevent the formation of ethyl. The olefiant gas owes its origin, no doubt, to the secondary decomposition of a portion of the ethyl into $(C_2 H_2)$ and $(C_2 H_3)$, whilst the group $(C_4 H_4)$, remaining after the separation of the elements of water from ether, would probably be found in a dark-coloured oily liquid, which collected in small quantity on the surface of the water poured upon the residue in the decomposition tube; the composition of this dark-coloured liquid, and the state in which the gases are retained by the oleagenous residue, have not yet been determined.

In conclusion, I will describe, very briefly, the behaviour of iodide of ethyl in contact with several other metals, at elevated temperatures: after exposure for 12 hours to a heat varying from 150° to 200° C. (302° — 392° F.), iron, lead, copper and mercury scarcely affected the decomposition of a trace of iodide of ethyl; but heated with arsenic to about 160° C. (320° F.), the iodide was rapidly decomposed, a heavy blood-red liquid, probably $As I_3$, being formed, which solidifies into brilliant crystals on cooling. The opening of the tube proved that the internal vacuum was unimpaired, and the crystalline mass evolved no gas on being treated with water, in which it was very slightly soluble; the remaining fragments of arsenic possessed a remarkably brilliant metallic lustre, which gave them the appearance of antimony. Tin also effected the decomposition of iodide of ethyl, at about the same temperature; the iodide became gradually replaced

by a yellowish oily fluid, which solidified to a crystalline mass on cooling: no gas was evolved either on opening the tube or subsequently treating the residue with water. It would be interesting to ascertain into what combination the radical ethyl enters in the two last decompositions. Finally, iodide of ethyl is rapidly decomposed by potassium, at about 130° C. (266° F.); methyl gas, and a yellowish ethereal fluid which has not been investigated, are the products of the decomposition.

Although the foregoing investigation furnishes the materials, yet I refrain from giving any general views on the probable constitution of the radicals of the series to which ethyl and methyl belong, until I have extended the inquiry to some other members of the same series, as well as to the compounds of the electro-negative class of radicals of which formyl, acetyl, &c. are members.