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THE
ELECTROLYSIS
OF
ORGANIC COMPOUNDS

PAPERS
BY
HERMANN KOLBE
(1845-1868)

Amesic Club Reprints,
No. 15.

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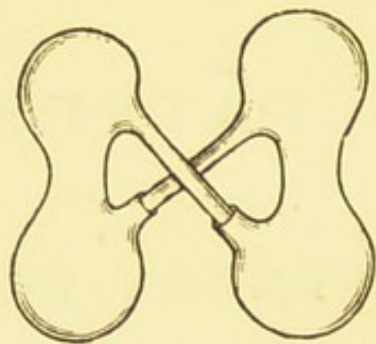
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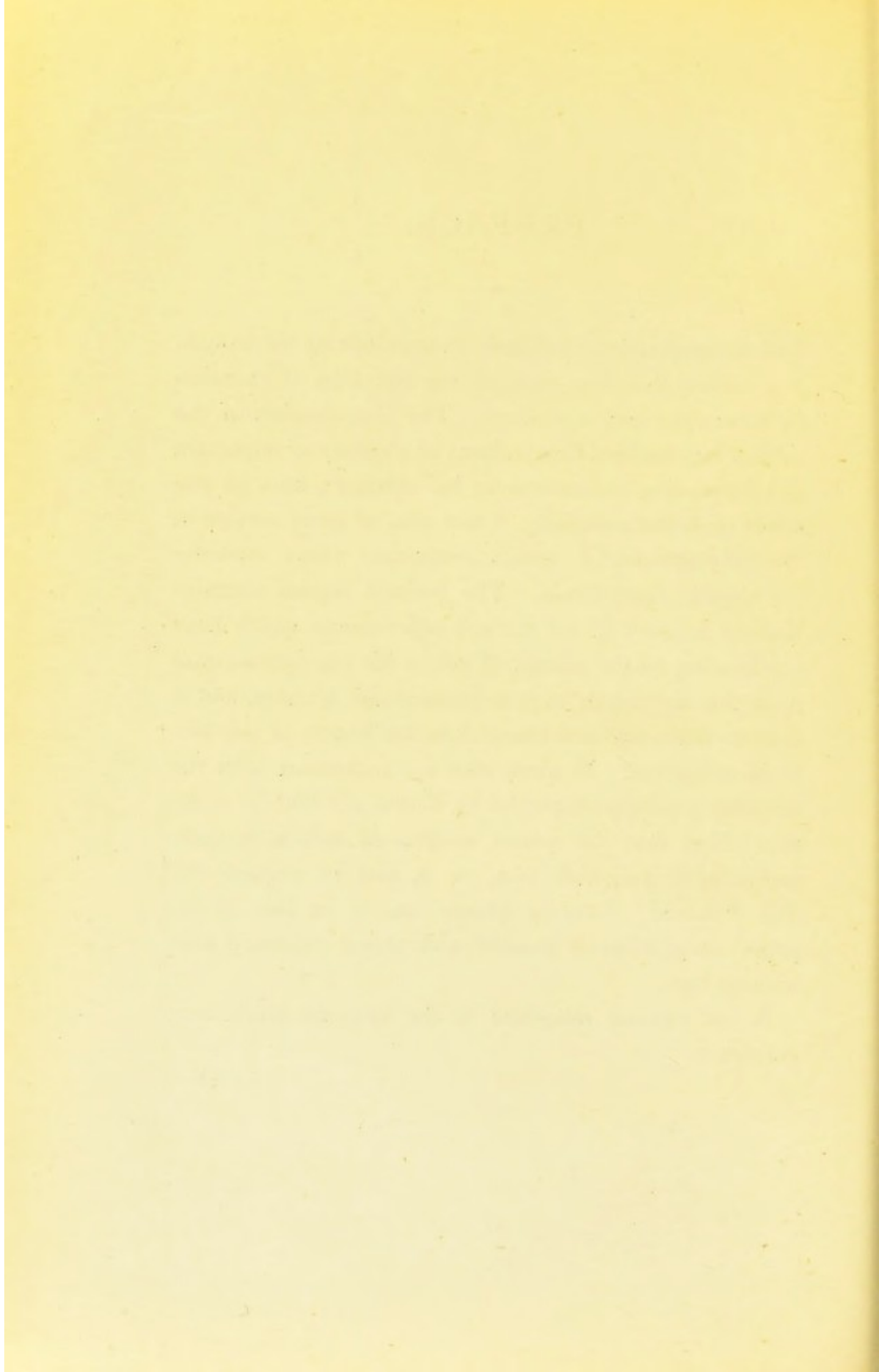


PREFACE.

THE decomposition of organic compounds by electrolysis is a subject that has engaged the attention of chemists for more than half a century. The investigation of the subject has enabled the synthesis of a variety of important and interesting substances to be effected ; and, in the hands of Kolbe especially, it was also of great service in the development of certain theoretical views concerning organic compounds. The present reprint contains Kolbe's account of his earliest experiments which have any bearing on the matter, as well as his classical memoir upon the electrolysis of valerianates and acetates, and it thus furnishes the first chapters in the history of this line of investigation. Readers who are unfamiliar with the formulæ generally employed by Kolbe will find it useful to recollect that the atomic weights of carbon, oxygen, and sulphur are, with him, 6, 8, and 16 respectively. The "barred" formulæ (made use of in one of the papers only) coincide exactly with those employed later without bars.

A few obvious misprints in the originals have been corrected.

L. D.



THE ELECTROLYSIS OF ORGANIC COMPOUNDS.

EARLY EXPERIMENTS.

WHAT would appear to be the earliest references by Kolbe to the effects of electrolysis upon solutions of organic substances, are found in his paper, "Contributions to the Knowledge of Conjugated Compounds," printed in the *Annalen der Chemie und Pharmacie*, Vol. 54 (1845), pp. 145-188. At the time at which this paper appeared, it seems as if Kolbe only regarded the application of electrolysis to such solutions as a means of submitting the dissolved substances to the reducing influence of hydrogen at the moment of its liberation. The following references are made in the paper to the reducing effects of the galvanic current:—

At pp. 155-156, where he states the effects of various reducing agents upon sulphite of perchloride of carbon, $C \ominus_2SO_2$ (Trichlormethyl-sulphonyl chloride), in converting it into a substance which he calls sulphite of chloride of carbon, and to which he assigns the formula $C \ominus SO_2$, he says:—

"Hydrogen brings about the same reduction when it comes into contact, in the nascent state, with dissolved sulphite of perchloride of carbon; for example, when iron or zinc is digested with an acidulated solution of that compound in highly diluted alcohol; or when the same liquid is decomposed by the galvanic current.*

* In order to guard against the compound being oxidized by the oxygen separated at the anode, the anode must be an easily oxidized metal. I employed amalgamated zinc plates.

The hydrogen set free in the process always has a peculiar unpleasant smell."

At pp. 168-169, in the section on chlor-elayl hyposulphuric acid, $\text{HO} + \text{C}_2\text{H}_2\text{ClS}_2\text{O}_5$ (Chlormethyl-sulphonic acid), he says :—

"Metallic zinc dissolves in chlor-formyl hyposulphuric acid * with the evolution of hydrogen and the formation of chloride of zinc; the product is a mixture of the zinc salts of chlor-formyl hyposulphuric and chlor-elayl hyposulphuric acids. The separation of the second equivalent of chlorine from the chlor-formyl hyposulphuric acid clearly takes place, therefore, with greater difficulty than the elimination of the first equivalent. In that decomposition there is always a small part only of the chlor-formyl hyposulphuric acid converted into the compound richer in hydrogen. More of it is obtained when the evolution of hydrogen is maintained for a longer time by the addition of another acid—sulphuric acid, for example; but even in this way the last portions of the chlor-formyl hyposulphuric acid cannot be entirely removed. This succeeds only by the decomposition of the acidulated solution of a salt of chlor-formyl hyposulphuric acid or of sesquichloro-carbohyposulphuric acid † by means of the galvanic current. I proceeded according to the following method :

About 50 grms. of sesquichloro-carbohyposulphate of potash were dissolved in water, mixed with sulphuric acid, and digested with zinc until the liquid was quite saturated with zinc salts. The solution of the metal takes place with brisk evolution of hydrogen gas, which diffuses abroad, during the process, a peculiar disagreeable smell possessing some similarity to that of sulphuret

* [$\text{HO} + \text{C}_2\text{HCl}_2\text{S}_2\text{O}_5$ (Dichlormethyl-sulphonic acid).]

† [$\text{HO} + \text{C}_2\text{Cl}_3\text{S}_2\text{O}_5$ (Trichlormethyl-sulphonic acid).]

of carbon. The greater part of the zinc crystallises out as sulphate of zinc and potash when the hot concentrated solution cools. The liquid poured off from this is precipitated, boiling, with carbonate of potash, filtered, and evaporated to dryness, and the powdered residue is extracted with boiling alcohol of 80° . The dry saline mass which remains behind after the evaporation of the alcohol consists of a mixture of chlor-formyl and chlor-elayl hyposulphates of potash. The quantity of the latter is further increased by another similar treatment with zinc and sulphuric acid. I then dissolved the residue, which only contained a little chlor-formyl hyposulphuric acid, in water again, made it slightly acid with sulphuric acid, and submitted it, in a suitable vessel, to the decomposing action of the galvanic current generated by two cells of the Bunsen zinc-carbon battery. The electrodes were two amalgamated zinc plates.

The operation is interrupted when the evolution of hydrogen gas, which is brisk at first, ceases, and metallic zinc is deposited upon the anode. The dissolved zinc salts are precipitated by means of carbonate of potash, and the filtered and acidulated solution is again decomposed by the current; and this is repeated about three or four times, or until all has been converted into chlor-elayl hyposulphuric acid."

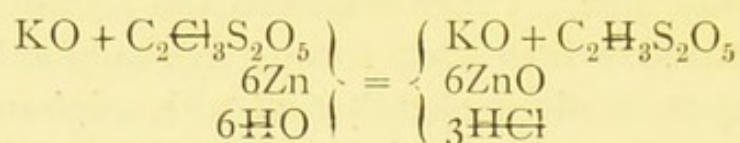
At pp. 174-176, in describing the preparation of methyl hyposulphuric acid, $\text{HO} + \text{C}_2\text{H}_3\text{S}_2\text{O}_5$ (Methyl sulphonic acid), he says:—

"I employed sesquichloro-carbohyposulphate of potash for its preparation.

70 grms. are dissolved in three times this quantity of water, and the *neutral* liquid is decomposed, in the same manner that I stated under chlor-elayl hyposulphuric acid, by the galvanic current from two cells of a Bunsen zinc-carbon battery. Two amalgamated zinc plates served

as electrodes. The decomposition proceeds quietly and without evolution of gas at first, with a somewhat considerable elevation of temperature. Only after a large part of the sesquichloro-carbohyposulphuric acid is converted into methyl hyposulphuric acid does hydrogen become free at the cathode. This circumstance can be made use of in order to determine at any time, approximately at least, how much chlorine has been exchanged for hydrogen.

According to the formula :



it is calculated that 57 grms. of zinc are necessary for the conversion of 70 grms. of sesquichloro-carbohyposulphate of potash. The deflection of the magnetic needle of a Weber's tangent galvanometer introduced into the circuit, amounted in these experiments, on the average, to between 50° and 60° , which corresponds, in the case of the instrument employed, to an average strength of current of about 82. Since with this strength of current, about 10 grms. of zinc are dissolved in an hour, the above decomposition would be finished in 6 hours.

After the action of the current for one hour, the liquid was so saturated with chloride of zinc that metallic zinc was deposited upon the cathode in large quantity. It was therefore precipitated, boiling, with carbonate of potash; the filtered alkaline solution was evaporated to the original volume and exposed anew to the action of the current for an hour, until the quantity of the separated carbonate of zinc had increased so greatly that reduction upon the cathode ensued.

It was only after 45 grms. of zinc, from the anode, were dissolved, in the course of repeated operations, that a

disengagement of hydrogen commenced at the other pole. The dissolved salts were now chlor-elayl hyposulphate and methyl hyposulphate of potash, mixed with a large excess of the chloride of potassium produced. In order to separate the latter as much as possible, I evaporated the solution to dryness and treated the residue with boiling alcohol of 80°. After the alcohol was distilled off, the soluble salts were again mixed with water and, after the addition of a little carbonate of potash, again decomposed by the current until 40 grms. of zinc were dissolved afresh. The evolution of hydrogen was very brisk at the end.

After the decomposition had continued altogether for 10 hours, I felt sure that the chlor-elayl hyposulphuric acid was completely converted into methyl hyposulphuric acid.

It is a remarkable phenomenon that in the decomposition of an *acid* solution of sesquichloro-carbohyposulphate of potash by means of the galvanic current, the exchange of the chlorine for hydrogen is at an end with the formation of chlor-elayl hyposulphuric acid, whereas, in presence of free alkali it extends to the third equivalent of chlorine also; for I have never obtained a trace of methyl hyposulphuric acid in the first case. It is difficult to explain to one's self why the hydrogen exerts towards chlorine, as soon as the acid to be decomposed is united to a base, a greater attraction than it does when the acid is presented to it in the free state."

OBSERVATIONS ON THE OXIDIZING
POWER OF OXYGEN WHEN DIS-
ENGAGED BY MEANS OF VOLTAIC
ELECTRICITY.*

I N describing in a former paper † the properties of sesquichloro-carbohyposulphuric acid, I stated that this body resists the action of the most powerful oxidizing agents, such as chromic acid, nitric acid, and even nitrohydrochloric acid. I likewise stated the change it undergoes by the action of a voltaic current, when an easily oxidizable metal is used for the positive pole. By this means another copulated acid is produced, in which one or more equivalents of chlorine are replaced by corresponding proportions of hydrogen.

I have since observed that this acid is completely decomposed on employing two platina plates as electrodes; by which arrangement oxygen is disengaged at the positive pole. The following details, which contain a more perfect account of this observation, I hope will be acceptable to the Society.

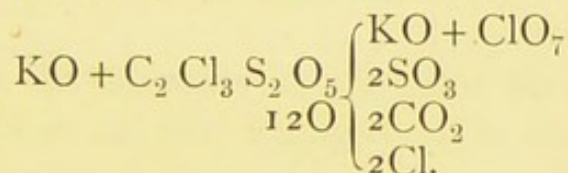
On decomposing a concentrated solution of sesquichloro-carbohyposulphate of potash by a strong voltaic current (obtained by four elements of Bunsen's battery), at the commencement no hydrogen can be observed at the negative pole in consequence of the formation of the above-mentioned copulated acids, whilst chlorine, carbonic acid, and afterwards oxygen, are evolved at the positive pole. At the moment decomposition commences a

* [From Memoirs and Proceedings of the Chemical Society of London. Vol. 3 (1848), pp. 285-287. Read December 7, 1846.]

† Liebig's *Annalen der Chemie*, liv. pp. 156, 160.

distinct acid reaction of the solution is perceptible, owing to the formation of free hydrochloric and sulphuric acids; in a later stage of the process, these acids increasing in quantity, hydrogen appears at the negative pole, until finally, after all the hydrochloric acid has been decomposed, and the disengagement of chlorine has ceased, small octahedral crystals of perchlorate of potash are deposited from the solution, which now contains a large amount of free sulphuric acid and bisulphate of potash. The formation however of perchloric acid in this process is always preceded by that of chloric acid; for on evaporating the solution in an earlier stage of the decomposition, beside the before-mentioned octahedral crystals, the well-known rhombic plates of chlorate of potash are obtained.

The following formula represents the most probable decomposition sesquichloro-carbohyposulphuric acid undergoes by the action of a voltaic current:—



The production of perchloric acid in an acid solution is certainly a fact worthy of attention, for according to all the observations hitherto made, combination between chlorine and oxygen could only be effected in presence of a free alkaline basis ready to unite with the newly formed acid; but ascertained as it is by a great number of careful experiments, it is another proof of the unparalleled negative power of oxygen when evolved by means of voltaic action.

These observations induced me to make the following experiments.

A neutral solution of chloride of potassium was decomposed in the same manner by a strong voltaic current;

it immediately became alkaline, whilst hydrogen and chlorine were disengaged. The formation of chlorate of potash, which took place under these circumstances, can evidently be considered only as the result of the ordinary chemical action of chlorine upon caustic potash. On mixing however a solution of chloride of potassium with sufficient sulphuric acid to set free all the muriatic acid, and passing the voltaic current through it as before, chlorate of potash was nevertheless formed, which was subsequently converted into perchlorate of potash.

The transformation of oxy-acids of chlorine, such as liquid hypochloric acid (ClO_2), or of a solution of chlorate of potash, into perchloric acid by means of voltaic action, has been mentioned by Berzelius. I have ascertained, moreover, that when a voltaic current is passed through hydrochloric acid, especially when previously mixed with some sulphuric acid, free chloric and perchloric acids are formed, after the disengagement of a considerable quantity of chlorine.

A concentrated solution of chloride of ammonium evolves hydrogen at the negative pole but neither oxygen nor chlorine at the positive pole. But the surface of the platina plate representing the latter pole is covered with small yellowish oily drops of chloride of nitrogen, which as soon as the two poles are brought into contact decomposes with a more or less violent explosion, chlorine and nitrogen being evolved. This experiment illustrates at once the formation of this compound and its highly explosive character.

Cyanide of potassium if dissolved in water is easily oxidized by a voltaic current, and converted into cyanate of potash, but I did not succeed in obtaining a per-cyanate of potash. I was not more successful in endeavouring to form a fluorate of potash from the fluoride of potassium by the same means.

I have not prosecuted my experiments further upon inorganic substances, having from some observations on the behaviour of organic compounds under the action of the voltaic current obtained results of so much greater interest, as to induce me to give them my exclusive attention; and at a future time, when I have completed the investigation, I shall beg leave to communicate it to the Chemical Society.

ON THE DECOMPOSITION OF VALE-
RIANIC ACID BY THE VOLTAIC
CURRENT.*

THE very remarkable changes which a series of organic compounds undergoes by means of the voltaic current, have induced me to make that mode of decomposition the subject of a thorough investigation. As however the numerous difficulties which present themselves in researches of this nature, and the immense extent of the field which opens before us, do not admit of the results being communicated in a complete and connected form, I beg to lay before the Chemical Society a short preliminary notice of the changes which valerianic acid undergoes when exposed to the oxidizing action of the voltaic current, reserving a more complete description of the products obtained till the investigation shall have been brought to a close.

When the voltaic current, excited by six pairs of Bunsen's carbo-zinc battery, is permitted to act on a concentrated neutral solution of valerianate of potash in

* [From Memoirs and Proceedings of the Chemical Society of London, Vol. 3 (1848), pp. 378-380. Read April 19, 1847.]

the cold, two plates of platinum forming the electrodes, a brisk evolution of gas takes place simultaneously from both; the gases evolved consist of hydrogen, carbonic acid and a new carbo-hydrogen, but contain no traces of oxygen gas as long as the solution of valerianate of potash does not become too much exhausted. At the same time a light oily liquid separates at the surface, having an agreeable æthereal odour, and the alkaline solution ultimately consists chiefly of carbonate and bicarbonate of potash, the latter of which generally separates during the operation in a crystalline form.

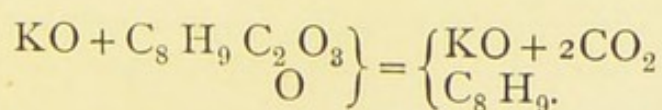
The neutral æthereal oil is a mixture of two compounds; the one containing oxygen, the other perfectly free from it. By the action of an alcoholic solution of potash the former is decomposed, and the latter can then, by means of water, be separated unchanged. In the pure state it exists in the form of a light colourless æthereal oil, possessing an agreeable aromatic smell. It is insoluble in water, but soluble in alcohol and æther; it boils at 108° C. without decomposition, and has the composition $C_8 H_9$. Oxygen and iodine are without action upon it, but chlorine, bromine, and fuming nitric acid form with it products of substitution.

The oil containing oxygen, which in the first instance was found mixed with this substance, I have not yet been able to obtain in a pure state; but several circumstances render it more than probable that it is formed by the union of valerianic acid with the oxide of the above carbo-hydrogen. An alcoholic solution of potash treated with it is found to contain as a product of decomposition a considerable amount of valerianate of potash. But on account of the small quantity of material which has been at my disposal, I have not succeeded in separating the alcohol $C_8 H_{10} O_2$, which must have been formed at the same time.

The gaseous carbo-hydrogen, which is evolved with the hydrogen, is a substance analogous to olefiant gas; it is characterized by a peculiar æthereal smell, and has a specific gravity double that of olefiant gas. It unites with chlorine even in the dark, forming a heavy oily liquid, having a marked similarity to chlorelayl, and is generally composed of a mixture of several products of substitution. Its rational composition is expressed by the formula $C_8 H_8$. The changes which valerianic acid undergoes, in accordance with the foregoing experiments, are capable of a very simple explanation, if we consider that acid as a conjugated combination of the carburetted hydrogen, or the radical $C_8 H_9$ with oxalic acid, in a similar manner to the new view taken of the constitution of acetic acid. For whilst by the addition of one atom of oxygen oxalic acid becomes converted into carbonic acid, this radical is set free; but a portion of it unites with the excess of oxygen to form an oxide, and this enters into combination with a portion of undecomposed valerianic acid, giving rise to a new æther, $C_8 H_9 O + C_8 H_9 C_2 O_3$.

Another portion of the radical is probably decomposed at the moment of its formation, in consequence of the concomitant evolution of heat into hydrogen and the gaseous carbohydrogen $C_8 H_8$. This latter view is supported by the fact, that if the temperature of the solution of valerianate of potash exceeds a certain point during the decomposition, not a single drop more of the ætherial oil is produced.

The following formula will throw light on this decomposition:—



Both butyric and acetic acids are acted on in a similar

manner to valerianic acid ; the products of decomposition of acetic acid are all gaseous, and appear to contain oxide of methyl. Butyric acid gives in addition to the gaseous compounds a volatile oil composed of $C_6 H_7$.

The minute description of this product will form the subject of a future memoir.

The foregoing investigation has been carried out during the late session in the laboratory of Dr Lyon Playfair, as whose assistant I have been engaged during that time ; and I cannot allow this opportunity to pass by without thanking him for the kindness and liberality which he has shown in placing his laboratory at my disposal, in leaving so much of my time on my own hands, and in rendering me every assistance in his power.

RESEARCHES ON THE ELECTROLYSIS
OF ORGANIC COMPOUNDS.*

THE following investigation has chiefly arisen from some former observations† respecting the transformations of chloro-carbo-hyposulphuric acid, hydrochloric acid, and several other substances under the influence of oxygen, when liberated in the circuit of the galvanic current.‡ The facility with which, particularly the former acid, resisting in the moist way the most powerful oxidizing processes, is decomposed under these circumstances, appears to point to electrolysed oxygen as one of the most valuable oxidizing agents which are at the disposal of the chemist. Its application in chemical decompositions acquires additional importance, since its intensity may be varied, either by concentrating and

* [From The Quarterly Journal of the Chemical Society of London, Vol. 2 (1850), pp. 157-184.]

† Observations on the oxydizing action of oxygen when disengaged by means of voltaic electricity in the "Memoirs and Proceedings of the Chemical Society," vol. III. p. 285.

‡ In the above cited investigation it was intended to state, that in the oxidation of hydrochloric acid by means of the electrical current, chloric acid appears at the positive pole even without the presence of an alkali. The sense of the sentence has been seriously altered by a misprint on page 287, line 8 from the top, *hypochloric* having been substituted for "hydrochloric acid." The sentence should have been as follows: "I have ascertained that when a voltaic current is passed through hydrochloric acid, especially when previously mixed with some sulphuric acid, free chloric and perchloric acids are formed after the disengagement of a considerable quantity of chlorine."

heating the liquid, or by increasing or diminishing the number of elements producing the electrical current.

Starting from the hypothesis that acetic acid is a conjugated compound of oxalic acid and the conjunct methyl, I considered it, under these circumstances, not at all improbable that electrolysis might effect a separation of its conjugated constituents, and that, in consequence of a simultaneous decomposition of water, carbonic acid, as a product of the oxidation of oxalic acid, might appear at the positive, while methyl, in combination with hydrogen, viz., as marsh-gas, would be observed at the negative pole.

The decomposition, which actually takes place, is not in perfect accord with this supposition, as will be seen by the experiments hereafter described. The results obtained, however, are by no means less interesting, and deserve particular attention, opening as they do a prospect that the electrolytical decomposition of organic compounds will afford most important disclosures with reference to their chemical constitution.

After having made some preliminary experiments with several acids belonging to the acetic acid series, the products of the oxidation of valerianic acid appeared particularly suited for minutely following out the course of this decomposition. I therefore consider it convenient, first to describe the phenomena attending the decomposition of this acid, inasmuch as they form the basis for further experiments.

ELECTROLYSIS OF VALERIANIC ACID.

Valerianic acid being, like acetic acid, a bad conductor of electricity, I employed in the electrolytical decomposition a concentrated solution of its potash salt, prepared by neutralizing carbonate of potash, free from

chloride, with pure valerianic acid, distilling at 175° (347° F.)*

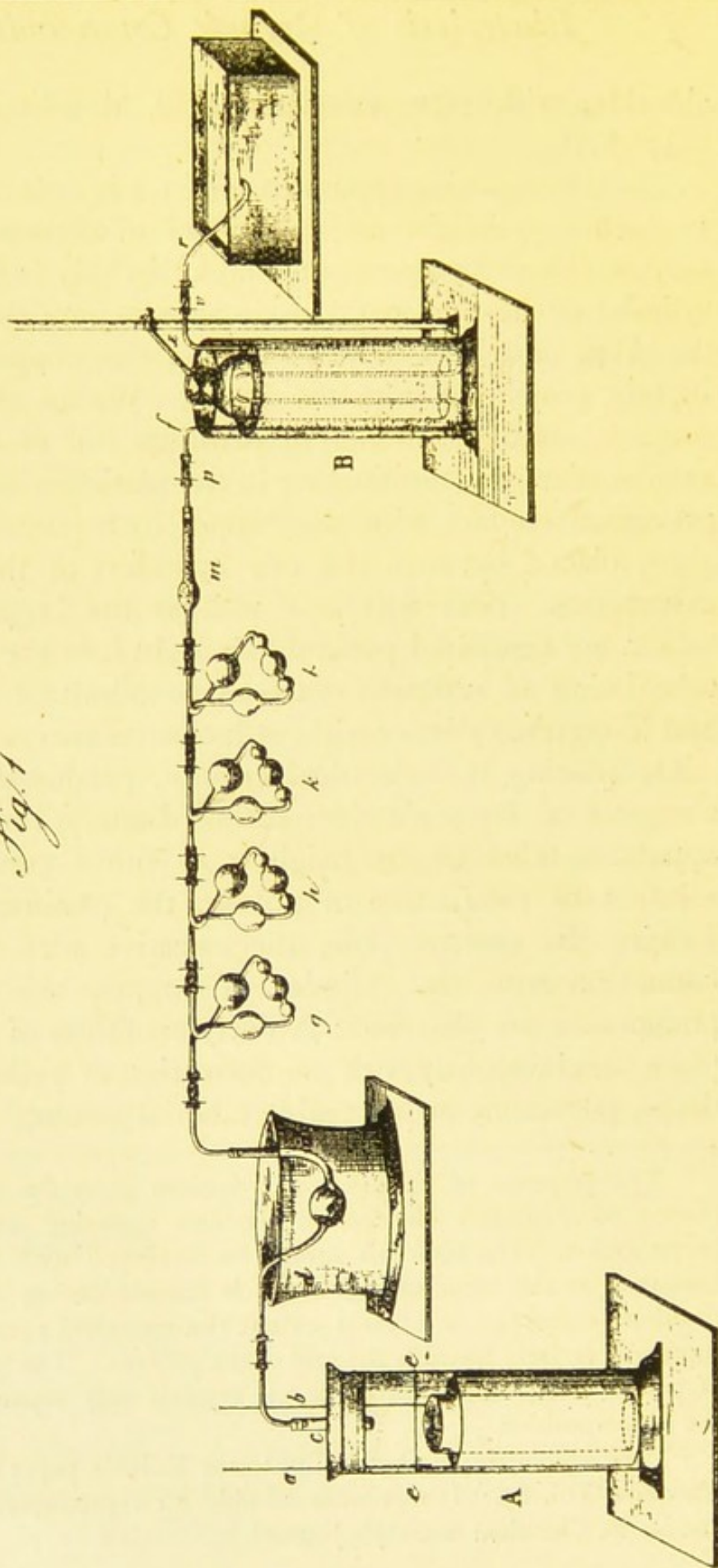
The decomposing apparatus, *Fig. 1*,† is a glass cylinder, 11 inches in height and $2\frac{1}{2}$ inches in diameter, which may be closed by means of a cork; in this is fastened a cylinder of sheet copper, closely approaching the sides of the glass, and to which is soldered the copper wire *a*, slightly projecting from the vessel. Within the copper sheet is another cylinder of platinum foil of somewhat smaller diameter, terminating in the platinum wire *b*, and prevented contact with the copper by a narrow ring of glass, placed between the two cylinders at their lower extremities. Both wires, as well as the large delivery tube *c*, are cemented perfectly air tight into the cork, the tube being of sufficient diameter to admit of emptying and filling the cylinder without inconvenience.

On passing the electrical current, produced by four elements of Bunsen's zinco-carbon battery, through the apparatus filled to the height *c c*, with a concentrated solution of valerianate of potash, the platinum wire *b* forming the positive pole, the negative wire being in connexion with the cylinder of copper, the following phenomena are observed: A lively evolution of gas takes place simultaneously with the formation of yellowish oily drops, possessing an agreeable ethereal odour; on agita-

* The presence of chloride of potassium gives rise to the formation of secondary chlorinated products requiring more minute investigation. The soda salt cannot be employed with advantage, inasmuch as the bicarbonate, which is formed during the decomposition, enfeebles to a great extent the electrical current, interrupting it entirely towards the end of the process. The bicarbonate of potash being more soluble, a few crystals only separate during the decomposition.

† [The accompanying figure illustrates Kolbe's paper in *Liebig's Annalen*, Vol. 69. It was more suitable for reproduction than the one in the *Chemical Society's Journal*.]

Fig. 1



tion with the liquid, the oil remains undissolved, even on the addition of potash.

The remarkably odorous gases which are evolved during the process, contain, after complete expulsion of air from the apparatus, no longer a trace of oxygen, and may be ignited without fear of explosion. Carbonic acid and hydrogen, however, are present in considerable quantities, in conjunction with a third gas burning with a highly luminous flame, and imparting to the mixture its peculiar odour.

After the action of the current had been continued for several hours, the stratum of oily liquid on the surface had increased to the height of several lines, while the valerianate of potash was almost completely converted into a mixture of carbonate and bicarbonate of potash, the latter generally crystallizing towards the end of the operation.

With a view of ascertaining at which pole each of these products was liberated, I endeavoured to separate the electrodes by means of a porous diaphragm, which allowed me to collect separately the substances disengaged at either pole. I employed for this purpose a porous cell of clay, into which a small glass tube of nearly equal diameter, and open at both ends, was fastened air tight by means of a caoutchouc joint. This arrangement containing the platinum foil, forming the positive pole, and admitting of being closed by a cork furnished with a delivery tube, was introduced into the copper cylinder of the decomposing apparatus.

Both cylinders were now filled with a solution of the neutral valerianate to the height of about one inch above the caoutchouc joint. It was found that on closing the circuit, only hydrogen and free potash were disengaged at the copper pole, while all the other products, the ethereal oil, carbonic acid, the odorous gas, and the free acid,

(which, in this arrangement, prevented the formation of a carbonate,) appeared at the positive pole.

VALYL.

In the experiments instituted for the preparation* of the etherial oil, I preferred removing the product from time to time with a pipette, which I introduced through the open glass tube *c*, the process being continued until the solution was entirely exhausted of valerianic acid.

The alkaline residue was now again introduced into a porcelain dish, and neutralized with pure valerianic acid; the neutral solution being again repeatedly subjected to the process of electrolysis, until a sufficient quantity of oil had been collected.

The impure product, after repeated agitation with water, exhibits the following properties: It is miscible with alcohol and ether in all proportions, insoluble in water, and of lower specific gravity than that liquid. It possesses an agreeable etherial odour. Chloride of calcium is dissolved by it, particularly in the cold, and hence the slight turbidity which is observed when the clear anhydrous liquid is subjected to ebullition. It commenced boiling a few degrees above 100° (212° F.), the temperature rapidly rising to 160° (320° F.) and even higher; the last products possess a penetrating disagreeable odour, and differ in a remarkable manner from the liquid which passed over at a lower temperature. The quantity of carbon found in the distillate, collected at different temperatures, diminishes with the rise of the boiling point, decreasing from 80 to 76 per cent., while

* The decomposing apparatus employed in this and the following experiments, was placed in a vessel of water at the temperature of 0° C. The solution of valerianate of potash being moderately heated, hardly a trace of the oil is produced, the decomposition taking place in an entirely different manner.

the amount of oxygen, varying between 6 and 10 per cent., is found in the inverse proportion. The disagreeably smelling oil distilling towards the end of the operation, appears to be formed only by the action of chloride of calcium on the original compound ; but even when distilled in vacuo at very low temperatures, the distillates collected at different stages of the process exhibit a composition not less variable.

It appears that the impure oil is a mixture of at least two substances, its deportment with an alcoholic solution of potash affording a powerful argument in favour of this opinion.

On boiling a mixture of this oil with an alcoholic solution of potash in a flask connected with the lower extremity of a Liebig's condenser, placed in such a position as continually to return the condensed products to the boiling fluid, the following phenomena are observed. Immediately on the application of heat, bubbles of a gaseous body are seen to rise, possessing the characteristic odour of the compound, which, in the electrolytical decomposition of valerianate of potash, accompanies the evolution of hydrogen and carbonic acid : hence, it appears that this gas, which is held in solution by the liquid, becomes liberated when heat is applied. In a short time the evolution ceases, and the odour of the gas is no longer perceptible ; when in a full state of ebullition the oil, previously colourless, assumes a yellowish tint, and becomes slightly turbid, while a heavy, apparently oily liquid collects at the bottom of the flask, which on examination is found to be an aqueous solution of valerianate of potash. To effect complete decomposition of the constituent affected by potash, at least half an hour's ebullition is necessary.

On mixing the liquid after boiling, with a large excess of water, a light ethereal oil separates, which, after stand-

ing for some time, collects on the surface into a clear transparent layer; repeatedly washed with fresh portions of water, and subsequently dried by chloride of calcium, it exhibits a pretty constant boiling point at 108° (226.4 F.). The fraction distilling at this temperature, when subjected to a second rectification boiled at the same point, the first three-fourths of the product being collected. The quantity of pure substance thus obtained exceeds half the original volume of the impure oil. The purified compound presents itself in the form of a clear pellucid fluid of agreeable odour, and first insipid, though afterwards of a burning taste; miscible with alcohol and ether in all proportions, it is perfectly insoluble in water, which readily precipitates it from its alcoholic and ethereal solutions. It boils exactly at 108° (226.4° F.), distilling without change to the last drop. It is inflammable, and burns with a strongly luminous smoky flame. It dissolves chloride of calcium, but to a less extent than the impure oil. Its specific gravity at 18° (64.4 F.) is 0.894 , that of the vapour being 4.053 .

By combustion with oxide of copper* the following results were obtained:

I.	0.1825	gram.	of substance	gave
	0.5630	,,	,,	carbonic acid, and
	0.2610	,,	,,	water.

* It is impossible to burn this substance, so rich in carbon, with either protoxide of copper or chromate of lead alone, a small quantity of metallic carbide being formed, which occasions a deficiency in the carbon amounting to between 0.5 and 0.8 per cent.; hence combustion with oxygen is absolutely necessary, the latter being conveniently evolved from small pieces of perchlorate of potash placed at the posterior end of the combustion tube, a plug of dry asbestos preventing contact with the protoxide of copper. In addition to this precaution, it is necessary to attach to the common bulbs a tube containing solid potash, in order to absorb the aqueous vapour volatilized in the gases passing through the potash apparatus.

II. 0.1578 gm. of substance gave
 0.4855 ,, ,, carbonic acid, and
 0.2260 ,, ,, water.

These numbers lead to the formula

	$C_8 H_9$		Experiment.	
	Theory.			
8 equiv. of Carbon .	600.0	84.2	84.1	84.0
9 ,, ,, Hydrogen .	112.5	15.8	15.9	15.8
	<hr/>	<hr/>	<hr/>	<hr/>
	712.5	100.0	100.0	99.8

This compound possesses the composition of the, hitherto hypothetical, radical of the still unknown alcohol belonging to butyric acid (C_8H_9O, HO), or the radical which, in valerianic acid, we assume to be in combination with oxalic acid. I propose to call it valyl.

Without entering here minutely into the question, whether valyl is indeed the radical of an alcohol corresponding to methyl, ethyl, and amyl; I will only mention one fact, which, in support of such a supposition, may seem of some importance; viz. that the specific gravity of its vapour exactly coincides with the number indicated by theory. According to the analogy of the methyl and ethyl series this compound would contain 4 vol. of carbon vapour, and 9 vol. of hydrogen condensed into 1 vol., hence the density of its vapour would be 3.9387, viz.:

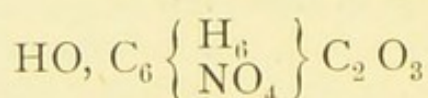
4 vol. of Carbon	3.3168
9 ,, ,, Hydrogen	0.6219
1 vol. of Valyl	3.9387

Experiment gave the following results:

Substance employed	0.2085 gm.
Volume of vapour observed	63.3cc
Temperature	133.3° C.
Barometer	752.9 ^{mm}
Mercury-column	64.0 ^{mm}
Pressing oil-column at 17° C	262.0 ^{mm}

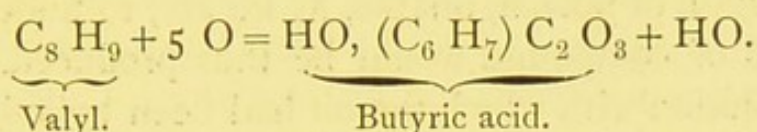
The specific gravity of valyl vapour as calculated from the foregoing numbers is 4.053, closely coinciding with the theoretical value.

Valyl is difficultly acted on by oxidizing agents; moderately strong nitric acid, or a mixture of chromate of potash and sulphuric acid have very little action upon it even after continuous ebullition; strong fuming nitric acid, however, especially after the addition of sulphuric acid, completely oxidizes this compound, nitrous fumes being evolved, while the oil gradually disappears. On neutralizing with carbonate of baryta, evaporating the filtrate to dryness, and extracting the residue with strong boiling alcohol the nitrate of baryta remains undissolved. The alcoholic liquid when evaporated leaves a saline residue, the distillation of which, with sulphuric acid, yields a yellow acidulous liquid, possessing in an eminent degree, the characteristic odour of butyric acid. On neutralizing the solution with freshly precipitated carbonate of silver, and filtering whilst boiling, a crystalline silver salt is deposited on cooling, which is readily darkened by exposure to light, or by continued ebullition with the mother liquor. The dry salt does not detonate when heated. The potassium, barium, and lead salts, do not appear to crystallize; want of material has prevented me from determining the composition of this acid, and of its salts by analysis; considering, however, the mode of its formation, the peculiar and unmistakable odour of butyric acid, and its yellow colour, it becomes very probable that this compound is a mixture of butyric acid, and of nitrobutyric acid.



corresponding to nitro-metacetic acid.

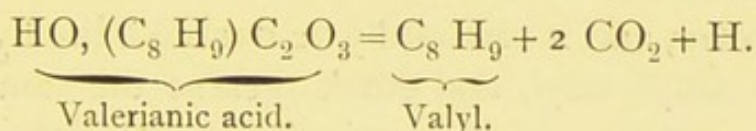
The following equation represents the transformation of valyl into butyric acid.



Dry chlorine has no action on valyl in the dark, the minutest ray of light, however, suffices for the immediate production of hydrochloric acid vapours, while chlorinated substitution compounds are simultaneously formed. By an excess of chlorine the liquid gradually becomes converted into a semi-fluid almost viscid mass: direct combination of chlorine and valyl, without elimination of hydrogen does not occur under these circumstances.

The action of bromine on valyl, although less powerful, is attended with similar phenomena; iodine is dissolved in considerable quantity by it without however entering into combination; sulphur likewise has no action upon it.

The decomposition of valerianic acid into valyl and carbonic acid, with the simultaneous evolution of hydrogen is represented by the following equation:



which is so extremely simple, that further elucidation would be superfluous were not other products formed at the same time. In order clearly to understand this peculiar reaction, we must direct our attention to the study of the two bodies occurring with it; viz.: the oxygenated constituent of the impure oil, and the odorous gas evolved with the carbonic acid. If we consider the fact of the elimination of valyl at the oxygen pole of the battery, the idea naturally suggests itself, that a partial oxidation of it into oxide of valyl may there be effected; the supposition, however, that the original oil consists

•f a mixture of valyl and its oxide is immediately dis-
countenanced by its peculiar deportment with an alco-
holic solution of potash, unable, as we are, to understand
what kind of compound would be thus produced. The
potash solution with which the oil had been boiled, when
diluted with water to separate the valyl, evaporated to
dryness, and distilled with sulphuric acid, was found to
contain a considerable quantity of valerianic acid. The
presence of this acid may be most easily explained, by
assuming the existence and decomposition in the liquid,
of a valerianic ether, an assumption which would lead us
to consider the oxygenated constituent of the original oil
as valerianate of oxide of valyl. The formation of this
ether will be easily understood, if we bear in mind, that
together with valyl and oxygen, valerianic acid is likewise
liberated at the positive pole simultaneously with oxide
of valyl in the nascent state.

It is true, that in the above decomposition by an
alcoholic solution of potash, according to the analogy of
the compound ethers generally, hydrated oxide of valyl
should have been liberated.

If, however, and it can hardly be doubted, the hydrated
oxides of amyl, valyl, and ethyl, present the same rela-
tion with reference to their miscibility with water, as do
valerianic, butyric, and acetic acids, the ratios of whose
solubility are inversely as their atomic weights, it is at
once intelligible why, with so small a quantity of sub-
stance at my disposal, I did not succeed in separating
the hydrated oxide of valyl from a liquid containing
alcohol in solution.

The presence of this compound, however, was proved
to a certain extent by the following observations. The
alcohol containing valerianate of potash was diluted with
water to separate the valyl, and distilled off from the
valerianate. On introducing the first portion of the

distillate into a boiling mixture of bichromate of potash and dilute sulphuric acid, a product passed over, possessing in an eminent degree the characteristic odour of both butyric and acetic acids. A further confirmation of this view of the composition of the crude oil is afforded by analysis.

The substance for investigation was repeatedly washed with water, (first with a dilute alkaline solution), dried over chloride of calcium, and distilled in vacuo at a low temperature.

0.1175 gm. of the distillate gave
 0.3320 „ „ carbonic acid, and
 0.1475 „ „ water.

corresponding to the following composition per cent. :

Carbon	.	.	.	77.0
Hydrogen	.	.	.	13.8
Oxygen	.	.	.	9.2
				100.0

If, starting with the formula $C_8 H_9 O$, $(C_8 H_9) C_2 O_3$ for the oxygenated oil, we calculate from the quantity of oxygen found, the per-centage of carbon and hydrogen belonging to this compound, we arrive at the following composition :

18 equivs.	Carbon	.	.	.	31.0
18	„	Hydrogen	.	.	5.1
4	„	Oxygen	.	.	9.2
					45.3

by subtracting these numbers from the above we obtain carbon and hydrogen exactly in the proportion required by the composition of valyl ($C_8 H_9$).

	Experiment.	Theory.
Carbon . . .	46.0	46.1
Hydrogen . . .	8.7	8.6

A similar mixture, prepared at a different period, when subjected to combustion gave the following numbers :

0.2647 grm. of substance gave
 0.7600 „ „ carbonic acid, and
 0.3420 „ „ water.

and a similar calculation leads us to the following results :

Experimental per-centage.		Composition of valerianate of valyl.	Composi- tion of valyl.	Theory.				
Carbon . . . 78.3	} minus	{ 25.0	=	53.3	53.4			
Hydrogen . . . 14.3						{ 4.2	10.1	10.0
Oxygen . . . 7.4						{ 7.4	63.4	63.4
100.0		36.6		63.4	63.4			

It now only remains to determine the nature of the gas evolved with carbonic acid, in the decomposition of valerianate of potash. In order to separate this gas from the vapour of valyl evaporated with it, as well as from carbonic acid, I passed it from the decomposing apparatus through a system of tubes, (*fig. 1*). *d d* is an empty tube blown out to a bulb in the lower part, and surrounded by a frigorific mixture. In this tube the larger quantity of valyl vapour is condensed, a small portion which may have escaped liquefaction being arrested in a Liebig's apparatus *g*, filled with alcohol, the vapours of which are condensed in a similar apparatus *h* containing water. The two following bulbs *k* and *l* are filled with a solution of potash, while the tube *m* contains potash in the solid form, serving, both for the separation of carbonic acid, and for the complete desiccation of the gas. Finally, to obtain a perfect mixture, the evolved gases were collected in the gas-holder *B*, which consists of a cylinder of glass, 3 inches in diameter, and 11 inches in height, containing an inverted bell-jar, open at the lower extremity,

and enclosing one vertical branch of each of the two U-shaped tubes *s* and *x*. The bell-glass is fixed by a holder in its lowest position, and the apparatus filled with mercury to such an extent, that the two tubes through which the air contained in the bell-jar is expelled, rise only a few lines above its surface. The tube *s*, moreover, at its horizontal extremity is connected by an airtight caoutchouc joint with the tube *m*, while the branch *x* communicates in the same manner with the delivery tube *r*, which may be opened or closed at pleasure by depressing or elevating it from the mercury of the trough; both the connectors being, moreover, furnished with caoutchouc valves.

When the evolution of gases, occasioned by closing the galvanic circuit in the decomposing apparatus, had lasted nearly half an hour without interruption, and all the air contained in its different parts had evidently been expelled, the caoutchouc valve *v* was closely tied, while the holder with which the bell-jar had been depressed in the mercury, was gradually elevated as the vessel became filled with the gas generated by the decomposition. When a sufficient quantity of gas had been collected in this manner, the evolution was interrupted by breaking contact. By now tying the valve *p*, the gases contained in the gas-holder were no longer in connexion with the generating apparatus. By opening the valve *v*, and depressing the bell-jar, the quantity of gas required could easily be collected over mercury, and then transferred into the eudiometer, or into the glass balloon, for the determination of its specific gravity.

In determining the specific gravity, the following numbers were obtained:

Vol. of gas in bal-			
loon.	.	15° C.	755.9 ^{mm} 86.4 c.c.

Weight of balloon filled with gas .	15° C	771.0 ^{mm}	61.628 gm.
Weight of balloon filled with air .	15° ,,	771.0 ,,	61.672 ,,

From the above numbers, the specific gravity is calculated as 0.604.

In performing the eudiometrical analysis, I availed myself of the circumstance of the odorous constituent being absorbed by sulphuric acid. I therefore introduced into a measured volume of the gas a coke ball, saturated with strong fuming acid; the sulphurous acid, together with the sulphuric vapours, being subsequently removed by a moistened ball of potash.

In this manner, the following numbers were obtained :

I.

	Vol. observed.	Temp.	Bar.	Height of mercury above level in the trough.	Corrected vol. 0° C. 1 ^m . Press.
Original vol. (dry)	117.7	9.9	765.9 ^{mm}	65.0 ^{mm}	79.6
After absorp- tion with sul- phuric acid and potash (dry)	88.8	9.0	761.1 ,,	93.3 ,,	57.4

The quantity of odorous substance in the mixed gases absorbable by sulphuric acid, consequently amounts to 27.8 per cent.

The residual gas, no longer possessing any odour, and burning with a pale blue, non-luminous flame, was transferred into a eudiometer furnished with platinum wires, and exploded with oxygen, when it was found to consist of pure hydrogen.

Another portion of the above mixture, when exploded with oxygen, gave the following results :

II.

	Vol. observed.	Temp.	Bar.	Height of mercury above level in the trough.	Corrected Vol. o° C. 1 ^m Press.
Original vol. (moist). }	1111.8	11.0	759.4 ^{mm}	353.7 ^{mm}	42.4
After admis- sion of oxygen (moist). }	324.6	11.1	759.3 ,,	141.9 ,,	189.5
After com- bustion (moist). }	222.7	11.1	759.0 ,,	242.3 ,,	108.4
After absorp- tion of CO ₂ (dry). }	146.0	13.0	759.1 ,,	318.2 ,,	61.4

The gas remaining after the absorption of carbonic acid consisted only of pure oxygen, as had been ascertained in a previous experiment.

The above analysis leads to the following results :

Volume of com- bustible gas.	Oxygen cons ^d .	Carbonic acid prod ^d .
42.4 . . .	85.7 . . .	47.0
or 100.0 . . .	202.1 . . .	110.8

The mixture of gases under investigation containing, according to experiment II, 72.2 per cent. of hydrogen, requires 36.1 vol. of oxygen for its combustion; it is therefore evident that the remaining 27.8 vol. require 166 (= 202.1—36.1) vol. of oxygen, in order to produce 110.8 vol. of carbonic acid. These numbers stand very nearly as, 1 : 6 : 4, or, in other words, 1 volume of the odorous gas requires 6 vol. of oxygen to produce 4 vol. of carbonic acid. Four vol. of carbonic acid consisting, however, of 2 vol. of carbon and 4 vol. of oxygen, and altogether 6 vol. of oxygen having disappeared, 2 vol. having evidently served for the combustion of 4 vol. of

hydrogen, it is obvious that the odorous gas contains 2 vol. of carbon and 4 vol. of hydrogen condensed into one volume; hence its specific gravity is, 1.934.

2 vol. of Carbon vapour	. . .	1.658
4 „ „ Hydrogen	. . .	0.276
		1.934
1 „ „ C ₄ H ₄	. . .	1.934

According to the above experiment, the specific gravity of a mixture of 72.2 vol. of hydrogen, and 27.8 vol. of the carbo-hydrogen, is equal to 0.604; hence it follows that the specific gravity of the latter alone is, 1.993, closely coinciding with the result of experiment.

The odorous carbo-hydrogen evolved at the positive pole in the electrolytical decomposition of valerianate of potash, according to these experiments, exhibits the composition of olefiant gas, but possesses a specific gravity double that of this compound. In this respect, it agrees with the carbo-hydrogen discovered by Faraday, and named by Berzelius *ditetryl*, with which it, in fact, appears identical by its comportment with chlorine.

If the mixed gases, washed with potash and alcohol, and collected in the gas-holder, be passed through a chloride of calcium tube into a flask (provided with three tubulures, one of which terminates in a narrow aperture), and mixed with perfectly dry chlorine, an excess being carefully excluded and light as much as possible avoided, the sides of the flask become quickly covered with oily drops, which soon collect into larger globules, and flow out from the lower aperture, while hydrochloric acid, formed by the direct combination of chlorine with the free hydrogen, is disengaged. During the whole process a slight evolution of heat is perceptible.

About half an ounce of the oily liquid, which had been collected in the vessel placed under the lower aperture of the flask, was first treated with slightly alka-

line, and afterwards with pure water, in order to separate dissolved hydrochloric acid; and it was then dried over fused chloride of calcium, and subjected to a fractional distillation. The portion which boiled between 125°C . (257°F .) and 130°C . (266°F .) forming by far the larger quantity, was separately collected and purified by repeated rectifications, when a nearly constant boiling-point at 123°C . (253.4 F .) was obtained.

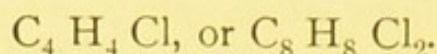
This compound possesses the following properties. It is a clear colourless ethereal liquid, insoluble in and heavier than water. It has an agreeable sweetish odour and taste, deceptively similar to that of Dutch liquid. It dissolves with facility in alcohol and ether, and boils at the constant temperature of 123°C . (253.4 F .); mixed with alcohol it burns with a luminous smoky flame, with evolution of hydrochloric acid. Its specific gravity at 18°C . (64.4 F .) is 1.112, the density of its vapour 4.426, the latter being calculated from the following data:

Substance employed	. . .	0.244 gm.
Vol. of vapour observed	. . .	67.7 c. c.
Temperature	. . .	139.0°C .
Bar. pressure	. . .	751.0 mm.
Col. of mercury to be deducted	51.0	„
Pressure of oil col. at 17°C .	366.0	„

By combustion with protoxide of copper the following results were obtained:

- I. 0.3990 gm. of substance gave:
 - 0.5590 „ „ carbonic acid, and
 - 0.2470 „ „ water.
- II. 0.2165 „ „ passed over ignited lime, dissolved in nitric acid and precipitated with nitrate of silver gave:
 - 0.4790 „ „ chloride of silver.

These numbers coincide with the formula :



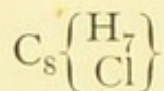
	Theory.		Experiment.
8 equiv. of Carbon . . .	600.0	37.8	38.2
8 ,, ,, Hydrogen . . .	100 0	6.3	6.8
2 ,, ,, Chlorine . . .	886.0	55.9	55.5
	1586.0	100.0	100.5

If we adopt, in this compound, a similar condensation of the elements, as in the oil of olefiant gas, the specific gravity of its vapour should be, 4.3837.

2 vol. of Carbon	1.6584
4 ,, ,, Hydrogen	0.2764
1 ,, ,, Chlorine	2.4489
			4.3837

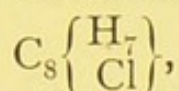
(with this number the result of experiment 4.426 closely coincides).

It would have been extremely interesting to have studied the comportment of this compound with an alcoholic solution of potash, since its analogy to chloride of elayl justifies the expectation that, in this case, chloride of potassium, and a compound corresponding to chloride of acetyl would have been formed, the latter being represented by the formula :



The small quantity of liquid at my disposal, unfortunately, did not allow me to pursue the subject any further. I must therefore confine myself to mentioning, that on heating an alcoholic solution of the compound with potash, a copious crystalline precipitate of chloride of potassium was formed, while the characteristic odour

of the compound was replaced by that of a very volatile liquid, having probably the formula :



which remaining dissolved in the alcoholic solution, was precipitated, on the addition of water, in small drops, which separating at the sides of the vessel, united only with difficulty; the liquid remaining milky for a considerable period.

By the action of chlorine, on the above carbo-hydrogen, with the fluid boiling at $123^\circ C.$ ($253^\circ.4 F.$), higher chlorinated products are formed, even when an excess of chlorine has been carefully avoided. The slow elevation of the boiling-point from $123^\circ C.$ ($253^\circ.4 F.$) to $160^\circ C.$ ($320^\circ F.$), at once intimates that we have, in this case, other substances richer in chlorine, which possibly might have been separated by fractional distillation of a larger quantity.

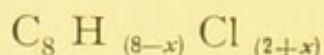
The combustion of 0.3620 gm. of the product, distilling at $132^\circ C.$ ($269^\circ.6 F.$), gave 0.4600 gm. of carbonic acid, and 0.1800 gm. water, corresponding to the following per-centage composition :

Carbon	.	.	34.6
Hydrogen	.	.	5.5

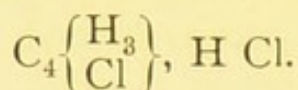
A compound still richer in chlorine is obtained by passing the gas through pentachloride of antimony, and distilling the substance thus produced. During the process of absorption, the mixture blackened, with the evolution of hydrochloric acid. The oily product obtained was purified by repeated distillation with water, dried over chloride of calcium, and subjected to analysis, when it exhibited the following per-centage composition :

Carbon	.	.	28.4
Hydrogen	.	.	4.0
Chlorine	.	.	68.2

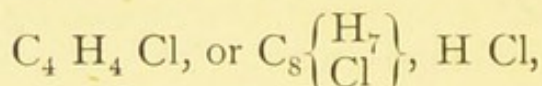
being evidently a mixture of different chlorinated compounds, whose composition may be represented by the general formula :



The opinions of chemists regarding the rational composition of the oil of olefiant gas, are, as is well known, still divided, as to whether it should be considered as the chlorine compound of a radical $C_2 H_2$, or whether its atomic weight should be doubled, in which case it would appear as the hydrochlorate of chloride of acetyl.



This question must remain undecided as long as both views can still claim arguments of equal force. Now, whichever of these opinions may in future be found correct, it will evidently determine our views respecting the chemical constitution of the above chlorinated oil produced from ditetryl, or, in other words, it will decide whether we have to adopt the formula :



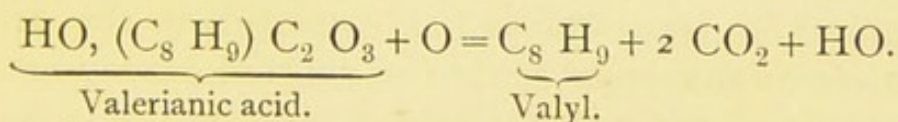
as the true exponent of its rational composition. This supposition once recognised will add new force in favour of the latter mode of representation, if we bring to bear upon this case the law of Kopp respecting the regularity displayed in the boiling points of *homologous* liquids, (to employ an expression lately introduced to designate the members of such series of bodies), which, like the alcohols or the fatty acids, are represented as being derived from a starting member by the addition of n times $C_2 H_2$, $C_4 H_2$, on any other carbo-hydrogen, experiment having (within certain limits) evinced the fact that the boiling points of homologous fluids rise $19^\circ C.$ ($34^\circ F.$) for each additional equivalent of the carbo-

hydrogen $C_2 H_2$. The chloride of ditetryl, $C_4 H_4 Cl$, which boils at $85^\circ C.$ ($185^\circ F.$), differing from chloride of elayl by one equivalent of the carbo-hydrogen $C_2 H_2$, should boil at $104^\circ C.$ ($219.2 F.$); on doubling, however, the atomic weight of the two bodies, (chloride of elayl $C_4 H_4 Cl_2$, and chloride of ditetryl $C_8 H_8 Cl_2$), their elementary difference becoming equal to 2 ($C_2 H_2$), the boiling point of the latter should be $123^\circ C.$ ($253.4 F.$), which is the temperature actually observed by experiment. Although this observation cannot be considered as a direct argument for the assumed molecular arrangement, I consider it nevertheless of sufficient weight to assist in the ultimate decision of the question regarding the atomic constitution of the two compounds.

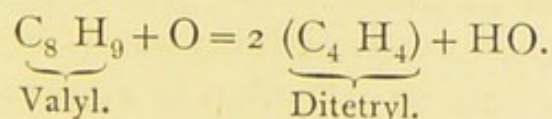
We find no difficulty in explaining the formation of the carbo-hydrogen $C_4 H_4$, or $C_8 H_8$, from valerianic acid; like the valerianate of the oxide of valyl, it is evidently a secondary product of the decomposition of valyl, and most probably formed by the action of the oxygen separating along with valyl, at the positive pole. We may assume that, under the influence of this oxygen, valyl is deprived of one equivalent of hydrogen, yielding one equivalent of ditetryl and one equivalent of water.

The action of electrolized oxygen, on a solution of valerianate of potash, therefore gives rise to three distinct phenomena :

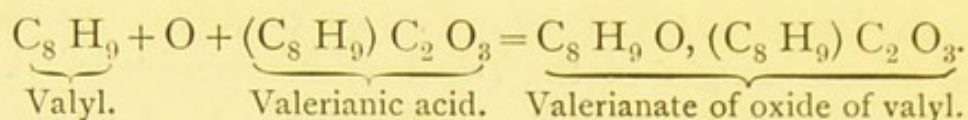
1st. A decomposition of the acid into valyl and carbonic acid :



2ndly. The decomposition of valyl into ditetryl and water :



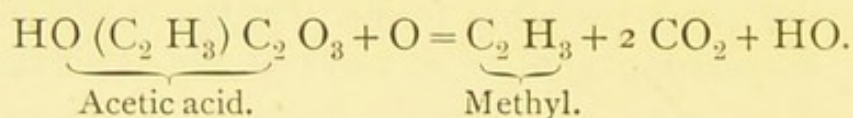
3rdly. A direct oxidation of valyl into oxide of valyl, which combines in the nascent state with free valerianic acid.



The two latter processes appear to take place simultaneously, though perfectly independent of each other. I have not, however, succeeded in exactly ascertaining the circumstances which favour the formation of the one or the other.

ELECTROLYSIS OF ACETIC ACID.

The remarkable analogy of the series of acids $(C_2 H_2)_n + O_4$, induced me to believe that acetic acid would undergo a similar decomposition to valerianic acid, yielding, by absorption of one equivalent of oxygen, methyl and carbonic acid :



In a preliminary experiment, it was found that on decomposing a concentrated solution of acetate of potash, gaseous products only were evolved, consisting of carbonic acid, hydrogen, a combustible inodorous gas, and a compound possessing a peculiar ethereal odour, and absorbable by sulphuric acid. In the investigation of these gaseous products, I availed myself of the same decomposing apparatus as was employed in the decomposition of valerianic acid; the evolved gases were first passed through a series of bulb tubes containing potash, afterwards through a tube filled with sulphuric acid (for the absorption of the odorous gas), and finally made to pass through a tube containing pieces of fused hydrate of potash, previous to collection in a gas-holder. In this

operation it is necessary to employ a very concentrated solution of the potash salt perfectly free from chloride of potassium, the smallest trace of the latter giving rise to the formation of chloride of methyl, which is easily recognisable by the green-bordered flame with which it burns when inflamed in contact with the air.*

When the evolution of gas had continued for about an hour, and had entirely displaced all traces of atmospheric air contained in the system of tubes and the gasometer, I filled the latter by gradually raising the bell, the delivery tube dipping under the mercury. The apparatus being too small to allow a sufficient quantity of gas being collected for taking its specific gravity, for eudiometrical analysis, and for combustion with protoxide of copper, the bell-jar was again fixed before being completely filled, and the gas issuing from the tube *r* was collected in a flask, for the determination of the specific gravity.

The contents of the gasometer were now easily confined by tying the caoutchouc valves *p* and *v* over the inserted glass rods, after the collection of gas had ceased from the interruption of the galvanic current.

In determining the relative proportion of carbon and hydrogen, an ordinary combustion-tube, open at both ends, was employed; when filled with freshly ignited protoxide of copper, the anterior extremity was connected with the usual potash bulbs and chloride of calcium tube, the posterior end being attached by a caoutchouc tube to the gasometer. After opening the caoutchouc valve *v*, the silken cord was untied, and by gently de-

* In a similar manner various other secondary products are formed, a mixture of valerianate of potash and chloride of potassium, for example, produces in the place of valyl, a chlorinated, etherial compound; a disagreeably smelling compound is obtained by exposing a mixture of acetate of potash and sulphide of potassium to the action of a galvanic current, the anode being formed of a platinum plate.

pressing the bell-jar, a continuous stream of gas passed over the ignited protoxide of copper, until a sufficiency of carbonic acid and water had been collected, when the caoutchouc valve was again closed. The posterior tube connected with the gas-holder was now cut, in order to allow of the removal of the carbonic acid remaining in the apparatus.

The following are the numbers obtained :

Carbonic acid	0.2470
Water	0.2635

corresponding to a ratio of 1 equivalent of carbon to 2.06 equivs. of hydrogen, or of 1 volume of carbon vapour to 5.2 vols. of hydrogen.

The specific gravity of the gas collected in a small flask over mercury was found to be 0.403.

	Temp.	Pressure.	
Volume of gases in flask	19.3°C.	749.2 ^{mm}	211.3 cc.
Mercury column to be deducted	15.0 ,,	...
Weight of flask filled with gas	22.0°C.	749.0 ,,	46.669 gm.
Weight of flask filled with air	—	—	46.819 ,,

The further data for the composition of the gas were obtained by eudiometrical analysis, which exhibited the presence of a minute quantity of oxygen.

	Observed.	Temp. C.	Bar.	Height of mercury column.	Corrected vol. 0° C. and 1 ^{mm} pressure.
Volume of gas employed (moist).	137.3	19.3	747.2 ^{mm}	31.5 ^{mm}	89.6
After absorption of oxygen (moist).					
	132.0	19.0	740.0 ,,	35.9 ,,	86.9

The quantity of oxygen, therefore, amounts to 3 per cent. The residuary gas was transferred into a larger eudiometer, and detonated with oxygen in experiments II *a* and II *b*, the following numbers were obtained :

II *a*.

	Observed vol.	Temp. C°.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 760 mm pressure.
Volume of gas employed (moist).	200.0	18.0	749.0 ^{mm}	373.4 ^{mm}	67.6
After admis- sion of oxygen (moist).	475.9	17.4	751.2 ,,	92.3 ,,	287.6
After combus- tion (moist).	345.6	18.0	751.1 ,,	225.6 ,,	165.4
After absorp- tion of carbonic acid (dry).	283.2	17.7	748.8 ,,	288.6 ,,	122.3
After admis- sion of hydro- gen (dry).	574.5	17.8	747.5 ,,	6.0 ,,	399.0
After combus- tion (moist).	114.2	17.4	748.9 ,,	460.2 ,,	29.4

II *b*.

Volume of gas employed (moist).	91.8	18.9	740.2 ,,	476.3 ,,	21.26
After admis- sion of oxygen (moist).	410.2	19.0	740.3 ,,	153.7 ,,	218.7
After combus- tion (moist).	366.2	19.0	740.4 ,,	197.1 ,,	180.43
After absorp- tion of carbonic acid (dry).	341.4	18.0	744.0 ,,	222.1 ,,	167.15

	Vol. of gases used.	Oxygen consumed.	Carbonic acid generated.
Experiment II <i>a</i>	67.6	97.7	43.1
Experiment II <i>b</i>	21.26	30.3	13.3

In calculating these numbers for a mixture of hydrogen and methyl, we find that in both experiments a smaller quantity of oxygen has disappeared than is required for the perfect combustion of such a mixture.

This circumstance appears to point out the presence of oxide of methyl, which accompanies methyl itself in pretty constant proportion. In designating the quantity of combustible gas employed by *A*, the oxygen which has disappeared by *B*, the carbonic acid produced in combustion by *C*; and further, the quantity of oxygen, methyl, and of oxide of methyl, respectively by *x*, *y*, and *z*, we arrive at the following equation,

$$\begin{aligned}x + y + z &= A \\ \frac{1}{2}x + 3\frac{1}{2}y + 3z &= B \\ 2y + 2z &= C\end{aligned}$$

by which we obtain for *x*, *y*, and *z*, the following values :

$$\begin{aligned}x &= \frac{2A - C}{2} \\ y &= \frac{4B - 2A - 5C}{2} \\ z &= A + 3C - 2B.\end{aligned}$$

If we now substitute for *A*, *B*, and *C*, the numerical values found, we arrive at the following composition for the two consumed volumes of gas (Exp. II *a* and II *b*):

	Experiment II <i>a</i> .	Experiment II <i>b</i> .
Hydrogen	46.1	14.60
Methyl	20.0	6.10
Oxide of methyl	1.5	0.56
	<hr/>	<hr/>
Total volume	67.6	21.26

Hence, from experiments I. and II., results the following per-centage composition of the mixed gases :

Oxygen . . .	3.0		3.0
Hydrogen . . .	66.0		66.6
Methyl . . .	28.8		27.8
Oxide of methyl . . .	2.2		2.6
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	100.0		100.0

The specific gravity of a gaseous mixture of this composition would be 0.4123 which closely coincides with the numbers found by experiment, 0.403. This composition receives further confirmation from the relative proportions of carbon and hydrogen, obtained by combustion with protoxide of copper.

		Carbon vapour.	Hydrogen.
28.8 vol. Methyl contain		28.8 vol.	86.4 vol.
2.2 ,, Oxide methyl ,,		2.2 ,,	6.6 ,,
66.0 ,, Hydrogen ,,		— ,,	66.0 ,,
		<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
The gaseous mixture .		31.0	159.0 ,,

Being the ratio of 31.0 vol. of carbon vapour to 159.0 vol. of hydrogen, or of 1 vol. of carbon vapour to 5.13 vol. of hydrogen, very closely coinciding with the above experimental ratio of 1 : 5.21.

I have before mentioned, that the gases evolved in the electrolysis of acetic acid, contain a gas which is absorbable by sulphuric acid. Independently of the remarkable odour of acetate of methyl which this gas possesses, the supposition that acetate of methyl is actually obtained among the products of the decomposition of acetic acid, receives some support from the analogous decomposition of valerianic acid. With the view of ascertaining the

per-centage of this body in the mixture of gases, and to study its nature, I repeated the above experiments with a portion of gas which had not previously been passed through sulphuric acid, and which consequently still contained the odorous principle; it burned like the other, with a feebly luminous, bluish flame.

An indefinite volume being passed from the gas-holder over ignited protoxide of copper, gave:

0.249 gm. of carbonic acid, and
0.247 ,, ,, water.

Corresponding to the ratio of:

1 vol. of carbon vapour, and
4.851 vols. of hydrogen.

The specific gravity of the mixture was found to be 0.4373, as is seen by the following experiment:

	Temp. C.	Pressure.	
Volume of gas in flask	18.0°	741.0 ^{mm}	211.7 cc.
Weight of flask filled with gas	19.0°	749.0 ,,	42.4065 gm.
Weight of flask filled with air	—	—	42.5500 ,,

To ascertain the per-centage of free oxygen and of the odorous constituent, I first determined, in a measured volume, (experiment III), the quantity of the latter by absorption with a coke ball saturated with sulphuric acid, and subsequently the amount of oxygen, by introducing a ball of phosphorus. The remaining portion of combustible gas was then detonated with oxygen in a large eudiometer, (experiment IV).

III.

	Observed vol.	Temp. C.	Bar.	Height of mercury column.	Corrected vol. 0° C. and 1 ^m pressure.
Volume of gas used (moist).	116.4	17.8	747.2 ^{mm}	21.2 ^{mm}	77.67
After absorp- tion with sul- phuric acid (dry).	113.8	17.9	746.0 ,,	24.8 ,,	77.03
After absorp- tion of oxygen (dry).	113.0	17.6	746.0 ,,	25.1 ,,	76.5

IV.

Volume of gas free from oxygen and odorous con- stituent (moist).	190.6	17.8	746.0 ,,	378.2 ,,	63.1
After admis- sion of oxygen (moist).	373.9	17.9	744.7 ,,	192.4 ,,	188.4
After combus- tion (moist).	208.6	18.0	743.8 ,,	339.6 ,,	72.17
After absorp- tion of carbonic acid (dry).	105.3	18.2	745.9 ,,	465.7 ,,	27.66
After admis- sion of hydro- gen (dry).	311.5	18.0	750.6 ,,	255.7 ,,	144.63
After combus- tion (dry).	182.6	18.1	750.6 ,,	386.5 ,,	62.35

According to the latter experiment, it follows that 63.1 vols. of gas previously treated with sulphuric acid and

phosphorus, require for combustion 97.4 volumes of oxygen, giving rise to the formation of 44.51 vols. of carbonic acid. If we now calculate these numbers according to the above equation for hydrogen, methyl, and oxide of methyl, we find that the original 63.1 vols. contained 40.85 vols. of hydrogen, 20.9 vols. of methyl, and 1.35 vol. of oxide of methyl. From these data, and likewise from the results of experiment III, we obtain the following per-centage composition of the mixture, in which the gas absorbable by sulphuric acid is enumerated as acetate of methyl.

Oxygen	0.7
Hydrogen	63.8
Methyl	32.6
Oxide of methyl	2.1
Acetate of methyl	0.8
	100.0

The specific gravity of such a mixture should be 0.4430, which does not far differ from experimental results, the number obtained being 0.4370.

	Volume per-cent.	Specific gravity.	Weight.
Oxygen	0.7	$\times 1.1092$	$= 0.7647$
Hydrogen	63.8	$\times 0.0691$	$= 4.4086$
Methyl	32.6	$\times 1.0365$	$= 33.7899$
Oxide of methyl	2.1	$\times 1.5893$	$= 3.3375$
Acetate of methyl	0.8	$\times 2.5567$	$= 2.0454$
			$\frac{44.3461}{100} = 0.443$

If we calculate the relative volumes of carbon and

hydrogen contained in this mixture of gases, we obtain the following numbers :

		Carbon vapour.	Hydrogen.
63.8 vol. H	containing	—	63.8 vol.
32.6 „ C ₂ H ₃	„	32.6 vol.	97.8 „
2.1 „ C ₂ H ₃ O	„	2.1 „	6.3 „
0.8 „ C ₂ H ₃ O, \bar{A}	„	1.2 „	2.4 „
		—————	—————

Being a proportion of . 35.9 to 170.3 „

or of one volume of carbon vapour to 4.74 vols. of hydrogen, which coincides with the results obtained by combustion with protoxide of copper, viz.: 1 vol. of carbon vapour to 4.85 vol. of hydrogen. The per-centage composition gains additional support by the eudiometrical analysis of the same gas, which still contained the odorous principle, but which was previously freed from oxygen.

The following numbers were obtained :

	Observed vol.	Temp. C.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1 ^m pressure.
Volume of gas used (moist).	138.0	18.2	750.5 ^{mm}	432.6 ^{mm}	39.11
After admission of oxygen (moist).	360.6	18.3	750.2 „	206.4 „	178.5
After combustion (moist).	263.9	18.2	750.1 „	303.9 „	106.8
After absorption of carbonic acid (dry).	213.9	18.2	748.4 „	354.0 „	78.9

In the combustion of 39.1 vols. of this gas 60.5 vols. of oxygen are consumed, giving rise to the formation of

27.9 vols. of carbonic acid. By now calculating the quantity of oxygen necessary for the combustion of 63.8 vols. of hydrogen, 32.6 vols. of methyl, 2.1 vols. of oxide of methyl, and 0.8 vol. of acetate of methyl, and likewise taking into consideration the amount of carbonic acid produced, we arrive at results but slightly differing from the numbers obtained by experiment :

Vols.		Oxygen vols.	Carbonic acid vols.
63.8 H	requiring for combustion	31.9	and producing —
32.6 C ₂ H ₃	„ „	114.1	„ 65.2
2.1 C ₂ H ₃ O	„ „	6.3	„ 4.2
0.8 C ₂ H ₃ O, A	„ „	2.8	„ 2.4
<hr/>		<hr/>	<hr/>
99.3 mixed gases	=	155.1	71.8

or that 39.1 vols. require for combustion 61.0 vols. of oxygen (experimental result, 60.5 vols.), producing 28.2 vols. of carbonic acid (experimental result, 27.9).

These facts sufficiently prove that the quantity of the compound imparting the peculiar ethereal odour to the gases, which are evolved in the electrolytical decomposition of acetate of potash, is so small, that if, as experiment seems to point out, it actually consists of acetate of methyl, it becomes almost impossible to condense it by a low temperature. An experiment made with this view was, indeed, perfectly unsuccessful. The ready absorption of this body, by sulphuric acid, agrees with the comportment of acetate of methyl; the acid employed in the experiment assumed a yellowish tint, and darkened on the application of heat, with the evolution of acetic and sulphurous acid vapours.

The above experiments had been completed, when I became aware that a gaseous mixture, consisting of one-third methyl and two-thirds of hydrogen, possesses the same specific gravity as is exhibited by a mixture of two-

thirds of marsh-gas, and one-third of hydrogen, and moreover, both mixtures contain the same relative amounts of carbon and hydrogen, and consequently consume, not only an equal volume of oxygen in their combustion, but produce the same quantity of carbonic acid; and hence the facts observed in the electrolysis of acetic acid might lead to the assumption, that the gases evolved in its electrolytical decomposition consist of hydrogen and marsh-gas. With the view of removing all doubt on this point, I have endeavoured to prepare methyl in a state of purity: I availed myself for this purpose, of the decomposing apparatus already described, which allows us to collect with facility the products liberated at either pole.

The interior cell containing the platinum plate was closed for this purpose with the cork, which besides the platinum wire for producing contact, contained, moreover, the delivery tube through which the generated gases were evolved, in order to be conducted through two bulb-tubes filled with concentrated solution of potash, and afterwards through a similar vessel containing sulphuric acid (for the absorption of water and acetate of oxide of methyl) and subsequently collected in the gas-holder. After every trace of atmospheric air had been expelled, the collected gas contained, nevertheless, a small quantity of carbonic acid, the two potash bulbs not having been sufficient to absorb the carbonic acid, which had been evolved from the separated cell in much larger proportion than in the former arrangement, because, in the former experiment, the simultaneous liberation of acetic acid at the positive pole effectually prevented the formation of a carbonate.

The eudiometrical analysis of the mixture which, as special experiment had proved, did not contain free oxygen, gave the following results:

VI.

	Observed vol.	Temp. C.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1 ^m pressure.
Volume of gas used (moist).	121.9	17.3	738.6 ^{mm}	18.2 ^{mm}	80.9
After absorp- tion of carbonic acid (dry).	90.9	17.2	744.8 ,,	44.9 ,,	59.86

VII.

Gas used (moist).	114.1	17.5	744.9 ^{mm}	457.4 ^{mm}	29.23
After admis- sion of oxygen (moist).	452.0	17.5	745.2 ,,	115.7 ,,	261.1
After combus- tion (moist).	374.0	17.6	745.2 ,,	192.5 ,,	188.9
After absorp- tion of carbonic acid (dry).	293.5	17.5	746.0 ,,	273.6 ,,	130.5

According to these observations the gaseous mixture contains 26.0 of carbonic acid, and 74.0 of combustible gas, of which (experiment VII) 29.23 vols. require 101.37 vols. of oxygen for complete combustion, producing 58.4 vols. of carbonic acid, which closely corresponds with the ratio, $1 : 3\frac{1}{2} : 2$; hence it appears that the gas evolved with carbonic acid, at the positive pole, is actually methyl, containing not even a trace of marsh-gas, which requires the double volume of oxygen for its complete combustion, and produces only an equal volume of carbonic acid.

The experimental numbers correspond with the following per-centage :

Carbonic acid . . .	26.0
Methyl . . .	69.3
Oxide of methyl . . .	4.7
	100.0

The specific gravity of such a mixture is 1.188, a number closely coinciding with the result of experiment, which gave 1.172, as the following data will shew :

	Temp.	Barometer.	
Volume of gas in flask	17.3°	717.6	212 C. C.
Weight of flask filled with gas	17.2°	738.6	53.826 gm.
„ „ air	—	—	53.796 „

The gas remaining after the absorption of carbonic acid (experiment VI), which is methyl mixed with traces of oxide of methyl, possesses the following properties : it is inodorous * and tasteless, insoluble in water, and burns with a bluish non-luminous flame ; alcohol dissolves an equal volume, absorbing it without residue ; neither sulphuric acid nor pentachloride of antimony dissolve it, and hence it corresponds, in all its properties, to the gas obtained from cyanide of ethyl. †

Methyl may be distinguished from marsh-gas, to which it is in some respects very similar, both by its solubility in alcohol, and its comportment with an excess of chlorine gas, by which methyl is converted into sesquichloride of carbon, while marsh-gas is transformed into the bichloride.

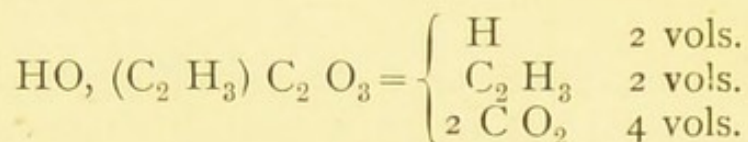
In conclusion, I may observe, that on employing two

* The feebly etherial odour of the gas prepared from cyanide of ethyl evidently arises from traces of cyanide of ethyl.

† Ann. der Chem. und Pharm. Bd. LXV. S. 269.

decomposing cells, the gas evolved at the positive pole does not contain carbonic acid, but consists of pure hydrogen.

According to the observations I have communicated, acetic acid, when decomposed in the circuit of the voltaic current, is decomposed into methyl and carbonic acid, both being liberated at the positive pole, whilst at the negative pole, pure hydrogen only is evolved. It further appears, that a small quantity of methyl is converted into the oxide. On leaving out of consideration the small quantity of the latter, one equivalent of acetic acid should accordingly yield 2 vols. of hydrogen, 2 vols. of methyl, and 4 vols. of carbonic acid, as is shown in the following equation :



The gases evolved from the decomposing cell, in the decomposition of acetate of potash, should therefore consist of equal volumes of methyl and hydrogen; as, however, experiments II, IV, and V, show that nearly double the amount of hydrogen is evolved, without an equivalent proportion of oxygen being liberated, we are led to the conclusion, that together with the above-mentioned transformations a simultaneous decomposition of water takes place, whose oxygen (considerably surpassing the amount contained in the oxide of methyl) evidently oxidizes a portion of the liberated methyl completely into carbonic acid and water; from this fact, however, it would follow, that carbonic acid would be produced in much larger proportion compared with methyl, than is indicated by the foregoing formula. With the view of deciding this question, I have investigated the mixture of carbonic acid and methyl, evolved at the

positive pole, which had been previously freed from acetic vapours which might have been carried over, by passing the gas through a bulb-tube containing water.

VIII.

	Observed vol.	Temp. C.	Barom.	Mercury column.	Corrected vol. 0° C. and 1 ^m pressure.
Volume of gas (moist).	110.2	17.0	764.0 ^{mm}	25.3 ^{mm}	73.27
After absorp- tion of carbonic acid (dry).	35.3	15.8	753.3 „	99.0 „	21.96

The gaseous mixture under investigation was found to contain 21.96 vols. of methyl and 51.31 vols. of carbonic acid; or, in other words, for every volume of the former, there are 2½ volumes of the latter, instead of 2 volumes, as indicated by the above equation.

These observations appear sufficient to prove, that in the electrolysis of acetic acid, even when employed in the form of a concentrated solution of its potash salt, a simultaneous decomposition of water takes place, which may perhaps be partially or entirely avoided by modifying the electrical current.

ON THE ELECTROLYSIS OF ACETIC
ACID.*

HAVING twenty years ago resolved acetic acid into carbonic acid and methyl, by the electrolysis of the aqueous solution of its potassium salt, I further examined the behaviour of free acetic acid towards

* [From The Journal of the Chemical Society of London, Vol. 21 (1868), pp. 195-196.]

oxygen evolved by electrolysis, in the hope of thereby oxidising it to glycollic or dioxyacetic acid.

I have lately resumed these experiments, using as the electrolyte, glacial acetic acid, mixed with just enough water and sulphuric acid to render it capable of conducting the galvanic current. For electrodes, I used two platinum plates, which were immersed in the liquid without any separating diaphragm, and the liquid was kept cool during the electrolysis.

If, after the action of the current has been continued for twelve hours, the liquid be freed from sulphuric acid by baryta-water, and then evaporated, there remains a small quantity of a viscid non-volatile substance, which exhibits strong acid properties, and crystallises slowly over oil of vitriol.

My expectation that this acid might be glycollic acid has not been realised. Its behaviour, and more especially the properties of its salts, are quite distinct from those of glycollic acid, and yet its calcium salt has exactly the composition of glycollate of calcium.

The quantity of this acid obtained being always very small, I have not hitherto been able to analyse any of its other salts.

If the further investigation of this interesting acid should establish its isomerism with glycollic acid, the result might, perhaps, tend to support the assumption that the four hydrogen atoms of marsh gas, or the three hydrogen atoms of methyl, are not of equal value.

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