

IV.—*On the Action of Voltaic Electricity on Pyroxylic Spirit, and Solutions in Water, Alcohol, and Ether.* By ARTHUR CONNELL, Esq. F. R. S. Ed.

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THE following paper contains a continuation of the experiments on the action of the voltaic pile on alcohol, and some other liquids, of which experiments a considerable number was described to the Royal Society in a former memoir.\* At present it is intended, in the first place, to shew the perfect analogy between the electric action on pyroxylic spirit, and on alcohol, thereby confirming the interesting analogy already known to exist between these fluids in other respects: in the second place, to adduce a few farther illustrations of secondary voltaic actions in aqueous solutions; in the third place, to examine the nature of the changes produced in alcoholic solutions, under galvanic agency; in the fourth place, to inquire whether electric action does not throw light on the state in which the haloid salts are dissolved by water; and, lastly, to endeavour to suggest as a general law, regulating the electric decomposition of solutions of binary combinations of elementary substances in the principal solvents, that the dissolved body is not directly decomposed, but only the solvent, if itself an electrolyte.

I. *Voltaic Action on Pyroxylic Spirit.*

Previous to the examination of this liquid by MM. DUMAS and PELIGOT, experiments had been made on it by several chemists, as by MM. MACAIRE and MARCET, Dr THOMSON, and others. The gaseous hydrate of methylene of DUMAS and PELIGOT, appears certainly to have been obtained, although in small quantity, by MACAIRE and MARCET, by distilling pyroxylic spirit, with three parts of sulphuric acid; but they mistook its nature, supposing it to be protocarburetted hydrogen, with a little hydrogen.† Still more important were the researches of Dr THOMSON, which led him distinctly to infer the existence of the carbohydrogen  $\text{CH}^2$ , which may be viewed as substituted in the pyroxylic series for  $\text{C}^2\text{H}^4$  in the alcohol series. By distilling a mixture of pyroxylic spirit and aqua regia, he

\* On the action of voltaic electricity on alcohol, ether, and aqueous solutions. Edinburgh Transactions, vol. xiii. Part II.

† Bib. Univer. xxiv. 128.

obtained a new inflammable gas, which, after freeing it from nitrous and azotic gases with which it was mixed, he inferred from his experiments to consist of 1 vol. carbon vapour + 1 vol. hydrogen +  $1\frac{1}{2}$  vol. chlorine; and to be a sesquichloride of the new carbo-hydrogen.\* Although Dr THOMSON, thus distinctly pointed out the existence of this carbo-hydrogen, he did not positively state that it existed in pyroxylic spirit, which indeed could hardly have been done at the time, as the existing analysis of the latter substance by MACAIRE and MARCET was inaccurate; but still he appears to have had some such idea in view.†

It is however undoubtedly to MM. DUMAS and PELIGOT, that we are indebted for an accurate view of the nature and constitution of this liquid, and for the full development of the highly interesting series of relative substances. Amidst the multitude of detached and isolated facts, which inorganic chemistry at present offers, presenting little interest from analogies, or often supported by merely imaginary ones, the development of the pyroxylic series, by unfolding a beautiful analogy with alcohol and the ethers, possesses with some other examples, a high degree of importance.

It was to be expected that a similar connection should be observed between pyroxylic spirit and alcohol, in their galvanic relations as in their composition and general properties; and experiment fully established this farther analogy.

The pyroxylic spirit employed, was obtained from Glasgow, and for a commercial article possessed a high degree of purity. Its colour had a slight yellow tinge. Its specific gravity and boiling point, (taken after it had been a year in my possession) were, the former .851 at 62° F., the latter, in contact with mercury, 160° F., under 30 inches of pressure. Heated with slaked lime there was no evolution of ammonia either in the cold or by heat. By a single distillation from powdered quicklime, it became quite colourless and transparent. After a second distillation from quicklime, its specific gravity was .808 at 62° F. A third distillation from recently ignited and powdered lime brought it down to .801 at 62° F. Its boiling point in contact with mercury was then found to be 148°, under a pressure of 29.5 inches.‡ It was with the product of this last distillation, that the galvanic experiments were made.

\* Transactions of the Royal Society of Edinburgh, vol. xi. p. 15.

† See Inorganic Chemistry, vol. ii. p. 295.

‡ The specific gravity of absolute Pyroxylic spirit is given by MM. DUMAS and PELIGOT as .798 at 68° F., and its boiling point 151.7° F. at 30 inches of the barometer. In the case of alcohol, the difference of temperature at which the specific gravity was taken by the French chemists and myself, would very nearly account for the difference of specific gravity, and I did not conceive it of any moment to attempt to rectify the pyroxylic spirit more highly, because in regard to alcohol I had found that far greater differences in the density had no material influence on the voltaic results; and the analogy of the action on the two fluids was complete, as will soon appear.

In examining the nature of the voltaic action on pyroxylic spirit, it was unnecessary to go into the same minuteness of investigation as in regard to alcohol for the analogy of the two cases became immediately apparent, and all that then was necessary was to seize the leading points of resemblance. It will be proper briefly to recapitulate the principal facts which I had observed in regard to alcohol, and the conclusions which I had drawn from them.

1st, It was found, that, under powerful voltaic agency, absolute alcohol yielded hydrogen from the negative pole, and no elastic fluid from the positive.

2d, By dissolving minute quantities of certain acid, alkaline and saline bodies in absolute alcohol, this voltaic agency was greatly favoured, through an increase of the conducting power of the liquid;  $\frac{1}{10,000}$ th part of potash having a marked effect.

3d, By particular arrangements, as by operating in metallic vessels, elastic fluid also appeared at the positive pole.

4th, The quantity of hydrogen obtained at the negative pole was found to be the same as that given off from water, under the influence of the same electric current.

5th, Besides elastic fluid, there were formed in the liquid acted on, certain products, the same as, or analogous to, those often resulting from the oxidation of alcohol; such as resinous matter, carbonic acid which combined with the dissolved potash, &c.

6th, From these various facts it was concluded, that water contained in the alcohol was the immediate subject of the voltaic agency, its hydrogen being evolved at the proper pole, and its oxygen being engaged in giving rise, by a secondary action, to the products of oxidation, dissolved in, or precipitated from, the liquid.

7th, As a general inference from the whole, it was farther concluded that, as the phenomena were obtained with absolute alcohol, that fluid must necessarily contain water as an essential constituent; a view which, although previously very generally adopted, had not, it was conceived, hitherto received any direct experimental proof.

Such were the leading facts and conclusions which it will be easy to shew are all equally applicable to pyroxylic spirit. In these investigations, it was found, that less powerful currents are capable of producing the same effects on pyroxylic spirit as on alcohol; a circumstance probably due to the greater absolute quantity, although not greater atomic proportion, of water, in a given weight of the former of these liquids.

A little more than a dram of the rectified pyroxylic spirit was exposed in a tube,\* with parallel platinum-foil poles, and adapted for collecting evolved elas-

\* See fig. 2 of plate in former memoir. Ed. Trans. xiii. pl. xiii.

tic fluid, to the action of seventy-two pairs of 4-inch plates.\* In a few minutes elastic fluid began to be evolved, and was collected over mercury; and the liquid after a time became warm, but did not boil. In order to favour the action, the foils were only about  $\frac{1}{8}$ th of an inch apart; which circumstance made it difficult to say with certainty, from the appearance alone, from which pole the gas came; but from the nature of the elastic fluid, as afterwards determined, as well as from the subsequent experiments, and the analogy of alcohol, little doubt could exist that it proceeded from the negative foil. After one and a-half hour's action, about one-third of a cubic inch was obtained, and, from the diminished action of the battery, the flow was a good deal slackened. This gas was analyzed in the voltaic eudiometer, and was found, as in the case of alcohol, to be hydrogen mixed with a little impurity, which was partly common air or its constituents, and partly a trace of vapour of the liquid acted on.

The pyroxylic spirit which had been acted on, when mixed with water and evaporated, shewed a little whitish matter mixed with it, and afforded a peculiar smell; and when the evaporation was carried to dryness, some yellowish-white resinous matter was left.

A minute quantity of pure caustic potash, when dissolved in the liquid, had, as in the case of alcohol, a wonderful effect in promoting the voltaic action. A similar quantity of the spirit, as in the last experiment, containing in solution  $\frac{1}{30}$  of pure caustic potash, was acted on in the same apparatus by thirty-six pairs of 4-inch plates, the platinum foil poles being parallel to one another, and from one-eighth to one-tenth of an inch apart. Elastic fluid was immediately evolved, and from the greater distance of the foils it was easy to see that it proceeded entirely from the negative pole. The action was so intense that the liquid soon boiled. A cubic inch of permanently elastic fluid was collected over mercury in a quarter of an hour; and when two cubic inches had been obtained, the process was stopped, although gas was still coming over. A portion of this gas was analyzed as before, and found to be hydrogen in a state of nearly perfect purity.

The liquid during the action did not perceptibly change in colour. A little flocky matter had precipitated, but it did not appear to be carbonate of potash. Some of the liquid was mixed with water, and after being a good deal concentrated by heat, it became slightly muddy, and a pungent aromatic smell arose, and some brownish matter was left on evaporating to dryness.

When a little of the spirit containing about  $\frac{1}{30}$  of potash was acted on in a watch-glass by fifty pairs of 2-inch plates, the platinum-foil poles being simply approached to one another horizontally, elastic fluid was evolved, as in the preceding experiment, from the negative pole, and none from the positive foil; but

\* All the batteries employed in the experiments in this paper were, as formerly, on Cruickshanks' construction.

when a platinum capsule was substituted for the watch-glass, gas arose from both poles, as had also been observed in the case of alcohol, holding a similar minute quantity of potash in solution.

A small quantity of chloride of calcium, when dissolved in the spirit, had also the effect of increasing the action, gas appearing at the negative pole, and none at the positive in glass vessels.

The most minute quantity of potash which could be employed was found to have the effect of increasing the action. When only  $\frac{1}{10000}$ th part was dissolved, the evolution of elastic fluid at the negative pole could be distinctly observed in a watch-glass with fifty pairs of 2-inch plates; the pure spirit itself, under such circumstances, scarcely shewing the slightest action.\*

Although no distinct formation of carbonate of potash was observed when small quantities only of potash were held in solution, the case was different when a strong solution of the alkali in pyroxylic spirit was acted on. A small quantity of such a solution was exposed to the agency of thirty-six pairs of 4-inch plates in a tube, with parallel platinum-foil poles placed at the distance from one another of about  $\frac{1}{10}$ th of an inch. In this case a copious evolution of elastic fluid took place from the negative pole as usual; but gas also arose, although in less quantity, from the positive, owing to the greatly increased action from the concentration of the liquid, and also to the *now* notable quantity of water in the hydrate of potash dissolved. The liquid boiled in a few minutes, and soon acquired a red colour; and a good deal of white matter was deposited, which proved to be carbonate of potash. The red liquid acquired a strong peculiar odour, and when mixed with water became muddy, and got a yellow tint, evidently from the separation of oily or etherial matter which had been formed during the action.

The true nature of the voltaic action in all the experiments which have been detailed appears to be sufficiently obvious. Water is decomposed, as was the case when alcohol was employed instead of pyroxylic spirit. Its hydrogen is evolved at the negative pole, whilst its oxygen is employed in giving rise by a secondary action to the formation of small quantities of resinous, oily, or etherial matter, and also carbonic acid when the action is energetic. In the last described experiment, the quantity of gas generated at the positive pole being larger than in the

\* If any one should imagine that the water of the hydrate of potash employed has any effect on these experiments, he is at liberty to calculate the quantity of water in  $\frac{1}{10000}$ th part of potash, held in solution by a few drops of spirit contained in a watch-glass. Again, the quantity of spirit acted on in the experiment in the preceding page, contained .16 of a grain of hydrate of potash, which contains .03 of water, equivalent to .154 of a cubic inch of hydrogen. But above two cubic inches of hydrogen were collected, and the process was stopped while the evolution was going on. Similar observations apply to the experiments with alcohol. The true action of the potash in these cases is just the same as when it is dissolved in water itself. It increases the conducting power of the liquid, aided, in the case of alcohol and pyroxylic spirit, by a circumstance to be noticed immediately.

others, the excess beyond what was required for the secondary action was liberated. This fact was more particularly determined in regard to a strong alcoholic solution of potash, as will be afterwards noticed, and the analogy was sufficiently obvious. The resinous, oily, or etherial matters were never found in sufficient quantity to admit a more particular examination of them; an observation which applies equally to the formerly detailed experiments with alcohol.

The extraordinary extent to which dissolved potash promotes the voltaic action on alcohol and pyroxylic spirit, appears to be in part due to its *disposing* affinity for the resinous or acid secondary products.

As a farther proof that water was the true subject of the direct voltaic action, an experiment was made with the volta-electrometer, as had been done in the case of alcohol. The current from thirty-six pairs of 4 inch plates was passed through pyroxylic spirit containing  $\frac{3}{10}$  part of potash dissolved, and also through water containing the same quantity of potash, in the apparatus fig. 6. of former memoir, the pyroxylic solution being placed in the bent tube sealed at the negative end. Gas was evolved from all the poles except the positive of the spirit solution, and at the end of 1 hour 5<sup>m</sup> there was found in

N of the pyroxylic solution	.10	cub. in.
N of the aqueous solution	.12	— —
P of the aqueous solution	.05	— —

Thus the quantities of hydrogen evolved from the two negative poles were sufficiently similar in amount to confirm the view, that water in both cases was the subject of decomposition.

It being thus in the whole circumstances sufficiently clear, that when pyroxylic spirit is submitted to voltaic agency, water contained in the liquid is resolved into its elements by the direct operation of the current, it is conceived that experimental proof is thus afforded that pyroxylic spirit, like alcohol, contains water as an essential constituent. When allowance is made for the difference of temperature at which the specific gravity of the spirit was taken by MM. DUMAS and PELIGOT and myself, the observed densities probably hardly differ; and no material variation on the nature of the action occurred in the case of alcohol, under much more considerable diversities of specific gravity.

Since the substance in the pyroxylic series, corresponding to ether in the alcohol series, bears the gaseous form, I did not attempt to submit it to voltaic action; but I can hardly doubt that, had it been a liquid, the same analogy would have been shewn in its electric relations, with respect to ether, as pyroxylic spirit exhibited in regard to alcohol. Following out the general analogy between the two series, I am inclined to adopt the same view in regard to the constitution of the two liquids of the one series as with respect to those of the other; and as it appears to be sufficiently proved that pyroxylic spirit is a hydrate, it may be re-

garded as a hydrate of pyroxylic ether, in the same way that alcohol was viewed as a hydrate of sulphuric ether. In my former experiments, I had found that sulphuric ether resisted the action of the most powerful voltaic battery which I had at my command, nor could I discover any substance which, when dissolved, led under voltaic agency to any appearance which countenanced the idea that it contained water, as such, as a constituent; and I therefore concluded that water, as such, did not enter into its constitution. On those views, the formula of pyroxylic ether will be  $H^6 C^2 O$ , and that of pyroxylic spirit  $H^6 C^2 O + H^2 O$ . In this way no hypothetical radicle is assumed as the basis of which pyroxylic ether is considered as the oxide, the latter being viewed, like sulphuric ether, merely as a ternary combination of its constituent elements.\* Neither am I acquainted with any experiment which proves the existence of the hydro-carbon  $H^2 C$ , as such, in the pyroxylic series, any more than that of the hydro-carbon  $H^4 C^2$  in the alcohol series. Indeed, the former hydro-carbon has not yet been obtained in a separate form in a state of purity, so that even its own existence is still in some measure hypothetical. It may be questioned, therefore, whether we have really made much greater progress towards a knowledge of the existence of the hydro-carbon  $H^2 C$  in combination as such, in consequence of the discovery of the pyroxylic combinations, than when we only knew of the sesqui-chloride of Dr THOMSON. If we content ourselves with saying, that throughout the pyroxylic series certain elements are substituted for certain other elements throughout the alcohol series, we do little more than express a matter of fact, with scarcely any theory. The elements so substituted appear to me to be 6 atoms of hydrogen and 2 atoms of carbon in the pyroxylic series, for 10 atoms of hydrogen and 4 atoms of carbon in the alcohol compounds, and the analogy between the two series appears to be nearly as well preserved on this view as on any other. I have in contemplation some voltaic experiments on the compound ethers of both series, which may possibly throw some light on the nature of the combinations.

## II.—*Voltaic Action on Aqueous Solutions.*

In my former paper I endeavoured to show that an electric current of sufficient intensity to decompose distilled water, did not cause the appearance of chlorine or iodine in aqueous solutions of the corresponding hydracids and haloid salts, where the evolution of oxygen at the positive pole did not actually take place in the solution, but in distilled water connected with that solution by as-

\* Even should we assume that pyroxylic ether and sulphuric ether unite with acids after the manner of *bases*, this circumstance will not, I conceive, prove them to be oxides, consisting of radicles *as such* and oxygen, any more than the same circumstance proves the vegetable alkalies, although undoubtedly *bases*, to be *oxides*, or than the circumstance that the vegetable acids unite with alkalies, shews that they consist of radicles and of oxygen.

bestus ; and that chlorine or iodine only appeared after a considerable time in the positive water, when acid had passed over into it, so as to afford room for a secondary action.\* These experiments were made with such moderate voltaic powers, as 50 pairs of 2 inch plates, but still sufficiently energetic to decompose distilled water, and, therefore, far more capable of producing the ordinary appearances in solutions, of hydracids and haloid salts, when both poles were placed in the solution : and I have since had occasion fully to confirm the results, with stronger powers. The consequence of employing more powerful batteries is just what might have been anticipated. The chlorine, and particularly the iodine, make their appearance sooner, and why ? because acid is sooner carried over into the positively electrified distilled water, as shown by test-paper, and because the reducing energy of the battery from evolved oxygen is increased.

Thus, when muriatic acid diluted with between twice and thrice its bulk of water was placed in a tube A, Fig. 1, Plate II, of the capacity of  $1\frac{1}{2}$  dram, connected with the negative side of a battery of 72 pairs of 4 inch plates, and distilled water in a similar tube B, connected with the positive side, the tubes being connected with one another by a bundle of asbestos about  $\frac{1}{4}$ th inch thick, acid was detected at the positive pole within three or four minutes, with effervescence from both poles, and in six minutes a very doubtful trace of the smell of chlorine was discernible, but when test-paper was dipped into the liquids, no trace of bleaching was observed. After half an hour's action, the smell of chlorine in B was still slight, and the liquid in it showed an acid reaction, but no bleaching ; whilst the liquid of the other tube neither had any smell of chlorine, nor did it bleach. The battery was now reversed without replenishing it ; the platinum foil, which was in the water, and had formerly been positive, being now connected with the negative side of the battery, and the foil in the muriatic acid being now made the positive pole. An instant pungent smell of chlorine arose from the now positive tube, with brisk effervescence from the negative pole, and rather less from the positive ; and test-paper was bleached at the positive pole as soon as the reaction was tried, which was in less than one minute.

When a moderately strong solution of hydriodic acid was next substituted for the muriatic acid, all other circumstances being exactly the same as in the commencement of the preceding experiment, and the voltaic power being the same and in fresh action, a commencement of browning, as from the formation of iodine, was observed, in about five minutes, in the liquid B, with effervescence from both poles, and at the same time a slight acid reaction was observed on the asbestos close to the same place. This browning went on increasing, and the acid reaction became quite obvious at the positive pole, the effervescence still continuing there, although considerably less than at the negative pole. In about

\* Edinr. Trans. xiii., 339, et seq.



twenty minutes the battery was reversed as before described; instantly the positive foil was covered with red matter, without any evolution of gas from that pole, and dense red liquid continued to fall from it, a brisk effervescence going on at the same time at the negative pole.

In these experiments it is evident that the appearance of chlorine or iodine at the positive pole before reversal, is dependent on acid passing over into the positive water; and the appearance is sooner observed and much more marked in the case of iodine than in that of chlorine, because hydriodic acid is a much weaker and more easily reduceable combination than muriatic acid, although the reaction of the latter acid on the positive side is much more marked than that of the former. On reversal, chlorine or iodine alone appears at the positive pole, and that instantly, the oxygen being entirely employed in reducing the corresponding acid. In the experiments formerly detailed, when weaker powers were employed, the chlorine or iodine was much longer of appearing previous to reversal, just because acid was longer of being carried over in sufficient quantity to make its secondary decomposition visible under the less energetic oxidating agency. In this point of view moderate powers are perhaps best calculated for such experiments, because the apparent contrast between the results at the positive pole before and after reversal is more striking, although the appearances with more powerful batteries are, on a very slight reflection, equally indicative of a secondary action.

The experiment with hydriodic acid was varied by connecting two glass-cups, of the capacity of a quarter of an ounce containing water, with the tube A of  $1\frac{1}{2}$  dram measure containing the acid, the acid being made negative by a battery of 72 pairs of 4 inch plates, and one of the water-glasses C positive; the other B, being intermediate, and all the three vessels being connected by asbestos, as in Fig. 2. Slight effervescence was observed at both poles, in one or two minutes. During the first fifty minutes not the least discoloration of any of the liquids was observed. A few minutes afterwards the positive liquid in C began to acquire a very slight brown tint, with slight acid reaction at the positive pole; and in ten minutes more the brown tint throughout the liquid in C was quite decided, without the slightest discoloration of that of B or A; and acid was also observed on the asbestos between B and C. The battery was then reversed, when the usual instant discoloration ensued at the positive pole without effervescence, while gas arose from the negative. Here, again, the iodine which appeared in the positive liquid before reversal, evidently owed its origin to a secondary action on the acid, which had travelled to the positive pole through the liquid in B.

A moderately strong solution of chloride of potassium was now placed in A, fig. 1, connected with the negative side of seventy-two pairs of 4-inch plates, and distilled water in B, connected with the positive side, asbestos being interposed as usual. In two or three minutes acid appeared at the positive pole, and near the

positive extremity of the asbestos, with effervescence from both poles; and in about eight minutes a slight odour of chlorine was observed, and also acid reaction at the positive side of the liquid in A. In a quarter of an hour test-paper was not bleached when dipped into either tube. After upwards of twenty minutes, no smell of chlorine could be distinguished in A, and when the action was then suspended the odour in B was still only slight. The battery was now reversed as before described. An instant smell of chlorine arose, with effervescence from the positive pole, and test-paper was bleached there within one minute. Effervescence also from the negative pole.

A moderately strong solution of iodide of potassium was now substituted for chloride of potassium, all other circumstances, including the voltaic power, being the same as at the commencement of the preceding experiment. In five minutes there was acid reaction at the positive side of the liquid in A; and about the same time browning was observed to be just beginning in the positive liquid near the termination of the asbestos, and extending to the positive foil. This browning went on increasing in the positive liquid, with acid reaction on the neighbouring asbestos and positive side of the negative liquid. The colour of the negative liquid was not changed. In this particular experiment the battery was not reversed; but in numerous others with the smaller powers, it was always found that the reversal caused immediate production of iodine at the positive pole without effervescence, whilst gas arose from the negative.

These results are quite conformable to those with the hydracids. Chlorine or iodine appears in virtue of acid passing to the positive side and suffering a secondary action. The degree of observed secondary action is proportional to the facility with which the corresponding acid is decomposed by nascent oxygen, and not to the absolute quantity of acid which appears at the positive side, the secondary action being strongest in the case of iodide of potassium, whilst the quantity of acid on the positive side is much smaller than in the case of chloride of potassium. I shall afterwards describe an experiment similar to that with hydriodic acid and two other vessels of water, in confirmation of these views. I shall then also state the grounds which have led me to infer from the appearances under galvanic agency, that haloid salts do not exist in solution as such, but as *hydracid salts*; in other words, that when dissolved they decompose water.

It was shewn a few years ago by M. DE LA RIVE, that when a mixed solution of bromide of iodine and starch in water was acted on voltaically, iodine appeared at the positive pole, and formed the usual blue combination with the dissolved starch.\* By an experiment conducted on similar principles with those just described, I have been led to conclude, that the action is here also a secondary one. The mixed solution placed in a tube was connected with the positive side of fifty

\* Annales de Chim. et de Phys. xxviii. p. 160.

pairs of 2-inch plates, and a solution of starch in another similar tube was connected with the negative side, asbestos intervening as usual. Effervescence speedily ensued from both poles, but after forty minutes' action not a trace of any blue colour was observed in either tube. The battery was then reversed. Within two minutes, the blue combination appeared round the negative foil now in the mixed solution, the effervescence ceasing at that pole, but continuing at the positive pole. Had the bromide been directly decomposed, iodine ought to have been liberated, and the blue colour produced in one or other of the tubes before reversal; but as this change did not occur till after reversal, the effect was due to nascent hydrogen at the negative pole. This hydrogen must have combined with bromine if the bromide is dissolved as such, as is usually held, or with oxygen if the whole or a part of it decomposes water, forming hydrobromic and iodic acids.\* It is plain, however, that the experiment is equally effectual on this view as on any other for the purpose to which M. DE LA RIVE applied it, that of detecting iodine in bromine. It does not, however, prove that bromine when in combination with iodine is carried to the positive pole; but on passing the current from thirty-six pairs of 4-inch plates through liquid bromide of iodine, neither water nor starch being present, I found the galvanometer to be decidedly, although not powerfully, affected; and although in the course of a few minutes' action I could not notice the appearance of either bromine or iodine at the respective poles, yet the quantities carried to the poles may have been too minute for observation, or they may have been redissolved by the bromide as soon as carried to the extremities.

### III.—*Voltaic Action on Alcoholic Solutions.*

In my former voltaic experiments on alcohol, the object was merely to promote the action by dissolving such minute quantities of different substances as served to increase the conducting power of the liquid. At present, it is intended to examine the nature of the changes produced by electric agency on alcoholic solutions of greater strength.

The appearances presented by solutions of acid, alkaline, and saline substances in alcohol under voltaic action have, generally speaking, a great resemblance to those offered by the corresponding aqueous solutions; and when we consider that water as such enters into the constitution of alcohol, and suffers its ordinary electric decomposition, it is not surprising that this resemblance in the phenomena should take place; the principal difference being, that oxygen is hardly ever

\* I am quite aware that when both the poles are introduced directly into the mixed solution, the voltaic power being in fresh action, there is effervescence at both poles, along with the appearance of iodine at the negative; but in this case I apprehend that a *part*, although not the whole, of the hydrogen enters into the new combination.

evolved at its proper pole, being employed in there producing secondary effects either on the solvent or the dissolved body.

When an ordinary oxy-acid salt, of a powerful base, such as nitrate of lime, is dissolved in absolute alcohol, the acid and base go to their proper poles under voltaic agency, as in a similar aqueous solution, but much more slowly, effervescence taking place at the negative pole, and little or none at the positive. Where the base is not of difficult reduction, as in nitrate of zinc, the evolution of gas at the negative pole is diminished, and metal reduced by hydrogen separates at that pole, mixed with oxide.

When an acid whose elements are strongly united, as boracic acid, or an alkali, as potash, is held in solution, effervescence appears at the negative pole, but none at the positive, unless in the case of a strong solution of a hydrated alkali, when a slight evolution of gas also occurs at the positive pole; and in these cases, appearances do not indicate any decomposition of the dissolved body. When an alcoholic solution of a haloid salt is acted on, no gas is evolved from the positive pole; but in the case of an iodide there is immediate separation of iodine at that pole, which is dissolved by the solution, giving it a deep red colour. When the metal of the haloid salt is one of powerful affinities, as potassium, calcium, or magnesium, there is brisk evolution of hydrogen, and more or less appearance of the oxide of the metal at the negative pole; metal appearing in that case to be first reduced by a portion of the nascent hydrogen, which combines with the electro-negative element of the haloid, and then to react on the water of the alcohol; and a portion of the oxide, when it is soluble in alcohol, being also drawn from the positive pole, where it has been formed by another secondary action. Where the metal is of more easy reduction, as in the case of zinc, the effervescence at the negative is diminished, although it does not cease, and metal separates there, apparently in consequence of a part of the hydrogen combining with the electro-negative constituent of the haloid salt.

When absolute alcohol, holding in solution chloride of magnesium, prepared by LIEBIG'S process, is acted on in a close tube, magnesia separates, after a few hours' action, as a transparent and colourless crystalline layer, covering the negative platinum-foil, and much resembling the native hydrate of magnesia.\*

I formerly stated the changes produced by voltaic agency on alcohol, containing very small quantities of potash in solution; I shall now shew the action on a strong solution.

Rather more than an ounce measure of a saturated solution of hydrate of potash in alcohol was submitted to the action of thirty-six pairs of 4-inch plates, by parallel platinum-foil poles, placed at the distance of one-sixth or one-seventh

\* When this transparent substance was heated, it gave off moisture, so that it appeared either to be a hydrate or an alcoate of magnesia, but the experiment had afforded too little to determine this point.

of an inch from one another. A brisk effervescence ensued from the negative pole, and considerably less from the positive, and the mixed gases were collected over mercury. After twenty to thirty minutes' action, the liquid began to deepen in colour, and when the foils were examined after nearly an hour's action, the positive foil was found to be fringed with white matter, which was afterwards ascertained to be carbonate of potash. In seven and a-half hours, after which time a moderate effervescence was still going on from the negative pole, and none from the positive, the liquid had acquired the colour of Port wine, and after twenty-two hours' action, when a feeble effervescence was still observed, the colour had become a very dark red; and carbonate of potash was collected at the bottom of the liquid, having doubtless gradually fallen from the positive foil, which was found to be still fringed with that salt. When the red solution was evaporated nearly to dryness, re-dissolved in water, and saturated with muriatic acid, an abundant precipitation of resinous matter ensued.\*

The hydrogen which was collected during the second quarter of an hour of the preceding experiment, was found to contain about  $\frac{1}{2}$  of oxygen, which had come from the positive pole, the difference between this proportion and that in water, having been employed in producing the secondary action, from which the resinous matter resulted.

I formerly shewed that when the same electric current was passed through absolute alcohol containing a small quantity of potash, iodide of potassium, or chloride of calcium, and through water either containing the same proportion of the same substance, or simply acidulated with sulphuric acid, the quantity of hydrogen evolved at the negative pole from both solutions was the same.† I

\* It would appear that DÖBEREINER had observed the formation of resinous matter in small quantities, in a galvanized solution of potash in alcohol (Pog. Annal. xxiv. 609), but he says nothing of any evolution of elastic fluid at either pole; and although he regarded the formation of resinous matter as an effect of oxidation, he gives no more explicit opinion as to the source of the oxygen or nature of the action. On the other hand, M. LÜDERSDORF (*Id.* xix. 77), like Dr RITCHIE, had observed that absolute alcohol, holding nothing in solution, gave off, under strong voltaic agency, elastic fluid from the negative pole; but he did not state that it was hydrogen, and, on the contrary, seems to have thought that it was not hydrogen, from the colour of its flame. I have found that the hydrogen evolved from pyroxylic spirit under electric action, when it contained a little of the vapour of the spirit mixed with it, burned with a blue flame, but when freed from that vapour, by being washed with solution of potash, it burned with a pale whitish flame. In analyzing, by the voltaic eudiometer, the gases obtained in such experiments, deceptive appearances, if we are not on our guard, may arise from the production of small quantities of carbonic acid, proceeding from the presence of vapour of the spirit which has passed over. I had read both DÖBEREINER's and LÜDERSDORF's observations, when first published, but in the two or three intervening years they had escaped my memory, until again recalled to it by allusions to them which I met with in the course of my reading, subsequent to the publication of my former paper; and even if I had remembered them at an earlier period, they could not have superseded any part of my researches.

† Edinb. Trans. xiii. 327, et seq.

have since compared, in the same way, some other alcoholic and aqueous solutions. Thus, absolute alcohol, containing  $\frac{1}{20}$  of dry nitrate of lime, was placed in the bent tube A, Fig. 6, of former memoir, and water acidulated with  $\frac{1}{12}$  of sulphuric acid in the tubes and evaporating basin B, the positive pole of the one solution, and the negative of the other, being in metallic connection. The current from thirty-six pairs of 4-inch plates was passed through both solutions, and in an hour and forty minutes there was collected from the negative pole of the alcoholic solution .0375 of a cubic inch of hydrogen, and .039 from the negative pole of the aqueous solution, lime appearing at the same time at the negative pole of the alcoholic solution, and acid at the positive. The quantities of gas were thus very small from the feeble conducting power of the solution, but sufficiently similar in amount to shew that in both solutions water had been decomposed. The same experiment was now made, substituting an alcoholic solution of  $\frac{1}{20}$  of boracic acid for the nitrate of lime solution, all other circumstances, including the voltaic power, being the same. The conducting power of this alcoholic solution was still more feeble than that of the other, insomuch so, that for some time I thought there would not have been any sufficient action to afford room for a comparison; although when an alcoholic solution of boracic acid is acted on in a tube with parallel platinum foil poles, the action is immediately seen. In three hours the charge of the battery was renewed, and the whole left for eighteen hours farther. No deposit was, during the whole time, formed on either foil in the boracic solution, nor was any gas evolved from the positive pole in it. At the end of the above mentioned time, there was collected from the negative pole in the alcoholic solution .025 of a cubic inch, and from that in the aqueous solution .035. Thus this result, from the very feeble conducting power of the solution, was much less regular than in any former trial; but still I think it will be admitted that it at least does not interfere with the conclusion, that in this case, as was evident in all the other cases, water was the subject of the voltaic agency; and there were no other appearances which indicated that boracic acid had been decomposed.

It will I hope be granted from the various phenomena, which have been described now and formerly, that when alcoholic solutions of acids, alkalies, and oxyacid salts are submitted to voltaic agency, the water of the alcohol is the subject of direct electric action, and that the dissolved body, with the exception of oxyacid salts, is not decomposed. In regard to alcoholic solutions of haloid salts, however, it might perhaps be held from the electro-negative constituent actually appearing, at least in the case of iodides, at the positive pole, that it is really the haloid salt which is directly decomposed, and that the definite quantity of hydrogen at the negative pole, arises from the reaction of the metal of the decomposed haloid, on the constituent water of the alcohol; a view which, of course, would afford

equally satisfactory evidence as the other, of the existence of water as such in absolute alcohol. I have now, however, to describe a variety of experiments analogous to those made with aqueous solutions of haloid salts, from which I conceive it follows that water is directly decomposed in alcoholic solutions of such bodies, as well as in those of other substances, and that the appearance of iodine at the positive pole in such solutions, is a secondary effect; and I hope I shall be pardoned for some minuteness of detail, with a view to the general conclusion alluded to in the commencement of the paper.

Absolute alcohol containing in solution as much dry and pounded iodide of potassium as it took up in three quarters of an hour's digestion, at a temperature of about  $130^{\circ}$ , which was about  $\frac{1}{10}$ th, was placed, when cold, in a glass tube A fig. 1. of the capacity of  $1\frac{1}{2}$  dram, connected with the negative side of a battery of fifty pairs of 2-inch plates; and distilled water in a tube B of similar capacity connected with the positive side, a bunch of asbestos of about  $\frac{1}{4}$ th inch thick, and moistened with alcohol, being interposed between the tubes. In one or two minutes gas began to be evolved from both poles. In five minutes a little brown matter like iodine began to be deposited in the positive water, in the immediate neighbourhood of the positive pole; and at the same moment an acid reaction was observed on the asbestos at its extremity on the positive side, and an alkaline at the negative pole, as well as on the positive side of the negative liquid. Both the browning and the acid reaction went on encreasing; as well as the effervescence at the negative pole, that at the positive continuing but not encreasing.\* In about half an hour, in which time the positive liquid had become pretty brown, whilst the negative was not at all discoloured, the battery was reversed as before described, and without renewing the charge. The positive pole now in the alcoholic solution was immediately covered with reddish brown matter, and a red liquid continued to fall from it, there being no evolution of gas from that pole, but an effervescence from the negative, and in a few minutes alkali was detected at the negative pole.

In some previous experiments, with a similar arrangement and the same voltaic power, the principal differences being, that the connecting bunch of asbestos was not so thick, and the positive pole perhaps a little farther from the asbestos, the acid reaction could not be detected, although the browning appeared after a certain time, and these experiments, as well as the circumstance that iodine usually appeared at an earlier period with an alcoholic than with an aqueous solution, at first led me to think that iodide of potassium in solution in alcohol was really directly decomposed under voltaic agency; but the detecting acid

\* It was necessary from time to time to add a little alcohol to the negative liquid, to prevent its level getting too low, an observation which applies to all the subsequently detailed experiments with alcoholic solutions.

as above stated, as well as more decidedly when stronger powers were employed,—that acid also appearing proportionally sooner in the positive liquid when alcoholic than when aqueous solutions were employed—soon shewed me the true nature of the action, and that the acid was not detected in the instances alluded to, merely from its having been formed in smaller quantity, and having suffered that decomposition to which it is so subject, as soon as it passed to the positive side. *Whence* the acid comes I shall explain presently.

When a power of seventy-two pairs of 4-inch plates was employed, all the other arrangements being exactly the same as in the beginning of the experiment described in the preceding page, acid was detected in five minutes not only at the positive end of the asbestos, but on the positive side of the negative alcoholic solution, with alkali at the negative pole; browning having begun to appear about a minute before, and effervescence at both poles still earlier. The browning went on increasing, without any discoloration having occurred in the negative tube in a quarter of an hour. The battery was then reversed, when the usual instant discoloration ensued at the positive pole.

In these experiments, therefore, the appearance of iodine at the positive pole before reversal of the battery, is really dependent on hydriodic acid being drawn to that side, and decomposed by nascent oxygen, as in the case of aqueous solutions of iodide of potassium. The hydriodic acid comes, I conceive, principally from the point where the alcoholic solution is *in contact with water*, and where it becomes an aqueous one of hydriodate of potash, which salt is resolved into its constituent acid and alkali by the voltaic agency.

Another source of the acid seems to be the secondary action of hydrogen at the negative pole, in virtue of which acid and alkali appear to be there formed as formerly stated, the acid being immediately afterwards carried towards the positive pole; and accordingly, in one of the preceding experiments, where the stronger power was employed, acid was detected in the alcoholic liquid,—the affinity of potassium for the oxygen of the water of the alcohol of course forming this secondary action.

There is another arrangement which shows, I think, still more clearly the secondary nature of the action, in virtue of which iodine appears.

The usual alcoholic solution of iodide of potassium was placed in a tube A, fig. 2. of the same size as before, and connected on the one side with the negative side of seventy-two pairs of 4-inch plates, and on the other by asbestos, with a glass cup B of the capacity of  $\frac{1}{4}$ th of an ounce containing water, which, in its turn, was connected by the same means with another glass cup C, also containing water, which was made positive. Within the first quarter of an hour, acid was detected at various places on the intermediate asbestuses, and at the positive pole;



with alkali at the negative, and effervescence at both poles; but in that time no discoloration of any of the liquids was visible. In twenty-five minutes the water in C had acquired a uniform although slight brown tint; and in forty minutes this brown colour had become much more decided. The liquid in B had been acid for some time, and was quite colourless, with the exception of the slightest possible yellow tint which its upper layer had acquired, and which was not only confined entirely to the upper part, but was far less deep than the brown colour which the whole of C had acquired. The liquid in A was not at all discoloured.

This experiment was repeated with the same arrangement and same power, the only difference being, that the three tubes were all of the size of  $1\frac{1}{2}$  dram. In fifteen minutes a slight browning commenced near the positive pole in C, with acid on both sides of the liquid in B, and on the asbestos between B and C. In forty minutes C was brown throughout, and neither A nor B at all discoloured; and when in fifty minutes the process was stopped, the liquid in C smelt like a strong solution of iodine, whilst that in A and B was still without the least change of tint.

It seems clear, that in these two experiments iodine appeared in the positive tube C, only in virtue of hydriodic acid having been drawn through the water in B into that in C, and there decomposed by nascent oxygen. The very trivial discoloration of the hydriodic liquid in the upper layer of B in the former of these experiments, was, I conceive, merely accidental, and arose from some subordinate secondary action, caused probably by the evolution of a few bubbles of oxygen, at some of the intermediate points on the asbestos. Some similar instances will afterwards occur, and in these experiments we ought always to bear in mind how extremely susceptible of decomposition hydriodic acid is. The *main* secondary action was plainly that in C. This was made still clearer by an examination of the aqueous liquids in B and C, after the close of the experiments. When the liquid in B was examined, both before and after concentration by heat, it was found to be a weak solution of hydriodic acid. On the other hand, when the liquid in C was concentrated by heat till the free iodine had been all expelled, it was found to be a weak solution of *iodic* acid; in other words, the hydriodic acid passing from B to C, as shown by the acid reaction on the asbestos between them, had not only been decomposed, and its iodine set free, but *a part* of that iodine had been oxidated by the excess of oxygen at the positive pole. If any doubt remained as to the existence of a secondary action, these facts, I think, would suffice to remove them.

I have mentioned, that in these experiments iodine appeared sooner on the positive side than with aqueous solutions. This circumstance arises from acid appearing sooner on the positive side of the asbestos in the former case than in

the latter, apparently owing to an action of the nature of endosmose; in which way a little of the salt itself may also be carried over, so as to augment the secondary action.

Alcoholic solutions of chlorides are less well adapted for such experiments than those of iodides, because if chlorine were evolved in an alcoholic liquid, we know that it would immediately react on the alcohol, giving rise to muriatic acid and other products. Still, if such a solution were connected in the usual way with water, some portion of the chlorine, if directly produced, might perhaps escape this reaction. It is at least proper to state the result actually observed, when it will appear that nothing contrary to the idea of a secondary action was noticed.

Absolute alcohol containing  $\frac{1}{12}$ th of recently ignited chloride of calcium was placed in a tube A of one and a half dram capacity, and connected by asbestos with water in a similar tube B, as in Fig. 2, the former liquid being made negative and the latter positive, by a power of 72 pairs of 4-inch plates. In four minutes acid appeared at the positive pole, and an alkaline reaction at the negative, with effervescence from both poles, but no smell of chlorine was perceived. After half an hour's action, there was still no smell of chlorine in either tube, nor any bleaching action, whilst the positive liquid was acid, and the negative showed an alkaline reaction, and the negative foil was coated with lime. On reversal, no chlorine was disengaged in the positive liquid, because it immediately reacted on the alcohol, which in consequence soon became strongly acid. In short, this experiment, if it affords no positive evidence in favour of a secondary action, is at least perfectly explicable on that idea.

Before proceeding to draw these general conclusions as to the nature of the voltaic decomposition of solutions in different solvents, to which I alluded in the outset of this paper, I think it better to describe those experiments which appear to illustrate the states in which haloid salts exist in solution in alcohol and in water, because additional evidence will be, in the course of them, afforded of the secondary origin of the electro-negative constituent of such salts in the electric decomposition of their solutions, and because we shall be better able to draw the conclusions referred to when the nature of such solutions has been examined.

#### IV.—*Voltaic Experiments illustrative of the state in which Haloid Salts are dissolved by water.*

The question, whether chlorides and other analogous salts are dissolved as such by water, or decompose it, and exist in solution as muriates, &c. remained after the old theory of the nature of chlorine had been abandoned, and the simple nature of that substance had been universally acknowledged. At the present

day this remnant of that celebrated controversy still, in some measure, divides the chemical world, although undoubtedly the view that chlorides exist as such in solution has latterly gained ground very considerably, and numbers amongst its supporters many of the most distinguished British and foreign chemists. Before, therefore, venturing to state those galvanic experiments which appear to me to lead to the opposite opinion, I would wish, first, to advert very briefly to some of those arguments which have been adduced within the last few years in support of the existence of chlorides in aqueous solutions, for the purpose of inquiring whether any of them is of such force as to admit of no answer, and consequently may induce us to presume some fallacy in views leading to a contrary conclusion.

M. DUMAS has argued, that because ether can separate the chlorides of iodine, of gold, of mercury, &c. from water, they must therefore exist in water in the same state in which they are dissolved in ether, *i. e.* as chlorides\*. To this argument, the answer which BERZELIUS suggests for the use of the advocates of the opposite doctrine, although not himself a supporter of it, seems sufficient; the affinity of ether for the chloride may determine the decomposition of the muriate and the formation of water†.

MATTEUCCI supposed, because he found that a weak voltaic power, which was incapable of decomposing acidulated water, produced, in aqueous solutions of metallic chlorides and iodides, metal at the negative pole, and chlorine or iodine at the positive, that, therefore, the chlorides and iodides had existed as such in solution. ‡ This result is easily explained, on the view of a secondary action consistently with the solution of a muriate and hydriodate. The affinity of hydrogen for the oxygen of the oxide, and of oxygen for the hydrogen of the acid, leads to the voltaic decomposition of water in these circumstances, although, in the ordinary case, it might not occur with the power used; and a secondary production of metal and chlorine or iodine ensues.

An argument much more effective than either of the preceding, is one brought forward by BERZELIUS, in noticing that of DUMAS.§ A solution of chloride of sodium evaporates at common temperatures, and leaves dry chloride of sodium. If a muriate was dissolved, then the tension of the water formed from the oxygen of the base, and hydrogen of the acid of the muriate, has come into play before its elements were united as such; or if it be said that this view involves no impossibility, still such tension must be admitted to be weaker than that of ready formed water; and yet chloride of sodium begins to be deposited by a saturated solution whilst water still remains. Considering the ingenuity of this argument, as well as the authority from which it comes, it is with hesitation that I at-

\* An. Ch. et Phy. xlv. 271.

† An. de Ch. et Phy. xlv. 324.

‡ Jahrsbericht, xi. 56.

Jahrsbericht, xi. 57.

tempt to answer it ; but I confess it appears to me to admit of a reply. The influence which water has on a variety of chemical phenomena has been shewn by M. PELOUZE, and that of quantity and cohesive force was long ago pointed out by BERTHOLLET ; and in regard to the phenomena of solution, the operation of quantity is generally acknowledged. By the aid of such principles, the appearances under consideration seem to admit of explanation. Since every substance is dissolved, in consequence of a chemical affinity between it and the solvent, it follows, that if a chloride is dissolved as a muriate, the affinity of water for the muriate has a considerable share in determining the union of the metal with oxygen, and of the chlorine with hydrogen. Now, when the water of such a solution has evaporated away to such an extent as to leave a completely saturated solution, the affinity of the oxygen and hydrogen of the muriate for one another is resisted by the attraction of a much smaller quantity of water for the muriate than formerly, and is now aided by the incipient cohesive attraction of the salt in the act of crystallization, joined to the powerful affinity of chlorine and sodium for one another. The affinity of the elements of water, therefore, *under the circumstances in which they now come to be placed*, and not its tension before its existence, I should humbly think is the cause of the union of these elements ; and this affinity may very well come into play *under the circumstances mentioned*, before the vaporizing tendency of the remaining actual water takes full effect ; and it farther seems probable, that the affinity of the remaining muriate for water will aid this union of the oxygen and hydrogen of the salt in the act of crystallization, the water formed by the union of the oxygen and hydrogen of the salt probably uniting with the dissolved muriate before its dissipation by evaporation.

In so far, therefore, as I am able to judge, it does not appear that any of these arguments foreclose the inquiry ; and we may still be at liberty to bring forward illustrations on the other side.

Let us assume for a moment, that chlorides and iodides are dissolved as such in absolute alcohol, and as muriates and hydriodates in water. Let us next suppose these alcoholic and aqueous solutions exposed to voltaic agency, *under circumstances in which no secondary action can take place at the poles from evolved oxygen and hydrogen*. What ought to happen in the two cases of alcoholic solution and of aqueous solution ? Surely this. In the alcoholic solution, since it has been shewn, I hope successfully, that water only is directly decomposed, then neither constituent of the chloride or iodide, nor any acid, ought to be produced in that solution ; whilst in the aqueous solution, the salt composed, ex hypothesi, of acid and alkali, ought to be resolved into its elements, conformably to the general law of the electric decomposition of ordinary salts, and acid and alkali, without chlorine or iodine, should appear in the solution, each on its proper side travelling towards the poles, which, by the supposition, are placed beyond the bounds of that

solution. Let us see how far this result, which we thus predict, is supported by experiment.

Absolute alcohol, with about  $\frac{1}{40}$  of iodide of potassium in solution, was placed in a glass tube of  $1\frac{1}{2}$  dram measure, and on each side a glass cup containing a quarter of an ounce of water was connected with it by means of asbestos moistened with alcohol, one of these cups being made negative and the other positive by fifty pairs of 2-inch plates. The arrangement is represented in Fig. 3, B containing the alcoholic solution and A and C the water. In eight minutes iodine began to appear in C round the positive pole, with effervescence at both poles. After forty minutes' action, not a trace of acid or of alkali could be detected in the alcoholic solution in B, nor had either been observed all along in that liquid. On the other hand, alkali had been noticed soon after the commencement, and all along at the negative pole in A; but no acid reaction was any where observed.\* At the conclusion of the experiment, in forty minutes, free iodine was very manifest in C both by the colour and smell; but not a trace of it was observed either in B or in A.

This experiment was repeated with a power of seventy-two pairs of 4-inch plates, and three tubes, each of the size of  $1\frac{1}{2}$  dram, all other circumstances being the same. Iodine began to appear in C in about four minutes, with bubbles at both poles. In eighteen minutes neither acid nor alkali could be detected in the alcoholic solution in B; but a trace of acid was noticed on the asbestos above the surface of the positive water in C, and alkali had appeared before this at the negative pole. In three quarters of an hour there was still no acid nor alkali in B, whilst the acid reaction was strong at the place where it had previously appeared. There was then much free iodine in C; and in B only an insignificant trace of that partial discoloration to which I formerly alluded as probably proceeding from some subordinate and trifling secondary action.

Let us now contrast these results with those obtained with an aqueous solution.

Water containing  $\frac{1}{40}$  of iodide of potassium was substituted in B for the alcoholic solution, all other circumstances, including the size of the vessels and voltaic power, being exactly the same as in the former of the two preceding experiments. The first decided acid reaction which was now observed was on the positive side of the solution in B, with alkali on the asbestos between A and B, and these in about fifteen minutes, effervescence having been in the mean time going on at both poles. During forty minutes only slight traces of acid appeared at the positive pole and on the asbestos between B and C, whilst a strong acid reaction continued in the liquid in B, with alkali at the negative pole, and on the asbestos between A and B. A slight discoloration of the water in C had just commenced at the end of this time, without any change of tint in A or B.

In explanation of the non-appearance of acid in the water in this experiment, see p. 15, 16.

This experiment was repeated with a strong aqueous solution of iodide of potassium, the water containing one-third of its weight of the salt, and being placed in B, all other circumstances being the same as before. In five minutes there was a trace of acid on the asbestos between B and C, with alkali at the negative pole. In fifteen minutes there was also a trace of acid at the positive side of the solution in B, and this was quite decided in twenty minutes, and more so than that on the asbestos, whilst at the positive pole there was still no acid. In forty minutes the acid reaction at the positive side of B was powerful, whilst all the other acid reactions were slight or doubtful. On the negative side of B, and from that to the negative pole, alkali was observed. A slight discoloration appeared in C, and none in A or B.

With a power of seventy-two pairs of 4-inch plates, and the strong solution of iodide in B, and water in A and C, the three vessels being glass cups, each of the capacity of one-fourth of an ounce, there was slight acid at the positive pole in five minutes, and strong acid at the positive side of B in fifteen, with alkali at the negative pole and on the adjoining asbestos. During the forty minutes which the experiment lasted, the acid reaction in B continued to increase and became very powerful, whilst that at all other places where it was noticed continued slight. A discoloration of the water in C had been noticed in fifteen minutes, with none in B or A then or for half-an-hour, and in forty minutes the liquid in C had assumed a pretty deep red throughout, and smelt strongly of iodine, whilst in B there was only a slight yellow tint confined to a single spot on the positive side of its upper layer, and no smell of iodine at all.

When the liquid in C was concentrated by heat till it was colourless, it was found, when the larger voltaic power had been used, to contain a trace of iodic acid; but where the smaller had been employed the nature of the acid in C was rather ambiguous. As the iodic acid was, to all appearance, referable to a secondary action, and it was of some consequence, with a view to the true explanation of the phenomena, to ascertain with certainty that the acid formed in B under the voltaic influence was hydriodic acid and not iodic acid, the following experiment was made.

Water containing  $\frac{1}{3}$ d of iodide of potassium was placed in the tube B, and pure water in the tubes A, C, and D, Fig. 4, the whole being connected by asbestos, and A made negative and D positive by 72 pairs of 4 inch plates. In ten minutes there was slight acid at the positive side of B, and on the asbestos between C and D, and at the positive pole in D, but none in the liquid in C. In twenty minutes the acid reaction on the positive side of B was strong, with a less marked on the asbestos between C and D, and alkali on the negative side of B. In fifty minutes the liquid in D had acquired a uniform pretty deep brown, whilst those in C and A were not at all discoloured; and in B there was merely a pale yellow

tint confined to the positive side of the surface. The liquids in C and D were then concentrated by heat, when the former was found to contain a trace of hydriodic acid, whilst the latter contained a trace of iodic acid. Hydriodic acid had thus been drawn, first, into C, and then into D, where it was decomposed by nascent oxygen, and a part of the liberated iodine oxidated.

A comparison was next instituted between alcoholic and aqueous solutions of the chlorides of calcium and of zinc.

Absolute alcohol containing  $\frac{1}{4}$ th of recently ignited chloride of calcium was placed in B, Fig. 3, and water in A and C, A being made positive and B negative by a power of 72 pair of 4-inch plates. In a quarter of an hour acid was detected at the positive pole, and on the adjoining asbestos, immediately above the surface of the liquid in C, but not a trace of it in B. In half an hour there was still no trace of acid in the liquid in B, but there was a trace of it on the asbestos at the positive side of B, having evidently spread from the other side of the same asbestos, where it was before observed, and where as well as at the positive pole it was now strong. In three quarters of an hour there was a just perceptible trace of acid in the liquid in B on the positive side, and strong acid all along the asbestos to the positive pole. This very trifling trace of acid in B had thus evidently spread from the asbestos, as just mentioned, and had not been *produced* in B. An alkaline reaction was observed at the negative pole. No smell of chlorine or bleaching action was any where noticed. When the experiment was concluded, the liquid in C was found to be a weak solution of muriatic acid, with a just perceptible trace of the smell of chlorine; this acid being too strong a combination to be so readily decomposed by nascent oxygen as hydriodic acid.

When a moderately strong aqueous solution of chloride of calcium was substituted in B for the alcoholic solution, and a power of fifty pairs of 2-inch plates employed, there was decided acid on the positive side of B in less than twenty minutes, with a slight trace at the positive pole, and none on the intermediate asbestos. In half an hour the acid in B was powerful, whilst there were still merely traces at the positive pole and on the asbestos, with alkaline reaction at the negative pole. No trace of chlorine was observed, although the action was continued above two hours.

With a pretty strong solution of recently ignited chloride of zinc in absolute alcohol in B, and water in A and C, the same voltaic power being employed as in last experiment, there was no acid reaction in B after forty minutes' action, whilst a trace of acid had appeared at an early period on the asbestos above the surface of the positive liquid in C. On the other hand, when an aqueous solution of chloride of zinc was substituted in B for the alcoholic, all other circumstances being the same, there was strong acid in B in ten minutes, with none at the positive pole, and only a trace on the intermediate asbestos. In neither experiment was

any smell of chlorine observed after action, for three quarters of an hour. In the latter experiment a little metallic zinc was deposited on the negative foil, from a small quantity of the solution having passed into A by capillary action, as was ascertained by reactives.

With aqueous solutions of chloride of potassium of various strengths in B, and water in A and C, there was, after a time, strong acid reaction in the solution in B, whilst at the positive pole, and on the intermediate asbestos, the reaction continued slight, and there was no bleaching action or decided smell of chlorine any where after an hour's action.

In all cases in which the acid which had passed into C, where solutions of chlorides were acted on, was examined, it was found to be muriatic.

The leading *facts* which have thus been observed are these: *First*, When alcoholic solutions of chlorides and iodides are acted on in the circumstances mentioned, no acid is observed to be produced in the alcoholic solutions. *Secondly*, When aqueous solutions of these substances are employed, the corresponding hydracids are produced in the solutions. *Thirdly*, When alcoholic solutions are used, the corresponding hydracids are produced at the point of contact between the alcoholic solutions and the water with which they are connected. *Fourthly*, The hydracids arising in both these ways, are carried to the positive pole situated in the water.

Such apparently being the facts, let us see whether they are capable of explanation on the idea of chlorides and iodides being dissolved as such in water; and let us take the different cases which may be assumed. Let us first suppose that water only is directly decomposed in the aqueous solution, and that, according to the usual and most approved view of electric action, a series of decompositions and recompositions of the directly decomposed body ensues, until its elements arrive at their respective poles. On this view we evidently cannot explain the production of acid in the aqueous solution under the described circumstances of the experiment. Let us next suppose that the chloride or iodide alone is directly decomposed, and that its elements proceed in the above way to their proper poles. Precisely the same objection applies to this view. Lastly, Let us suppose that both water and chloride or iodide suffer decomposition, and that either the elements going to the same pole unite on their journey, or, by a mutual interchange, the electro-negative constituent of the water unites with the electro-positive of the salt, and the electro-positive of the water with the electro-negative of the salt. The former of these alternatives is contradicted by the fact, that the acid passing to the positive pole is the hydracid and not the oxyacid; and the second is not only at variance with the usual view, that the elements of substances under voltaic decomposition follow the road *of themselves* to their proper poles, by a series of decompositions and recompositions; but is not in accordance with



the circumstance that no acid is observed to be produced under the described arrangement in the alcoholic solution; for alcohol contains water, and that water, as I trust it has been sufficiently proved, suffers voltaic decomposition, and thus an alcoholic as well as an aqueous solution presents the condition for a double decomposition, if such a double decomposition really can occur.

The observed appearances thus seem to be at variance on any reasonable mode of interpretation, with the idea that chlorides and iodides are dissolved as such in water. Let us take the other view, that they are dissolved as muriates and hydriodates, and what a contrast is observed. Not only are the phenomena easily explained, but they appear to be the necessary consequences of the supposition adopted. For if a salt composed of acid and alkali is dissolved in water, its constituents ought to go to their proper poles under voltaic agency; and in the experiments detailed, acid ought to be produced in the solution at its positive side, and to accumulate in that solution, if faster produced than carried over into the positive water, which experiment shews to be the case.\*

The observation lately made by Dr MOHR of Coblenz, that no electric stream is produced by the union of a hydracid and an alkali,† finds its readiest explanation in the views above advocated; because such a union is thus placed in the same case with that of an oxyacid and an alkali, which, according to Mr FARADAY, produces no voltaic current.

Although I have thus stated the conclusion on this point which appears to follow from the phenomena as observed, yet I am too well aware of the great subtlety of the subject, and have too much deference for the opinions of the many eminent men who have held different views, to wish to be understood as speaking dogmatically upon it. If any errors of observation, or mistakes in point of reasoning, affecting the conclusion which has been drawn, can be pointed out, I shall always be happy to acknowledge them, if they cannot be explained.

#### V.—*General Conclusions respecting the Voltaic Decomposition of Solutions in Water, Alcohol, and Ether.*

It is to Mr FARADAY that we are indebted for experimental evidence in numerous cases of aqueous solutions, that the direct agency of the electric current is exerted upon the water of the solution only, and that the other appearances of decomposition in these instances are due to secondary actions.‡ Amongst the

\* It will be readily understood, that when the poles are actually *in the solution*, the acid should first appear at the positive pole, and *thence* spread into the liquid when it has accumulated, as was shewn by M. DE LA RIVE; but when the poles are *beyond* the solution, the acid must make its way from the solution to the pole through the interposed water, and unless carried through the water as fast as it is produced, it must accumulate in the solution.

† Pog. Annal. xxxix. 134.

‡ Experimental Researches, seventh series.

most important of these cases are aqueous solutions of the oxyacids, as that of sulphuric acid; and embracing, as I fully do, his opinion, that the appearance of sulphur at the negative pole in such a case is a secondary result due to nascent hydrogen, I may be allowed to add, that this view seems well illustrated and confirmed by the experiment which I formerly described, in which the iodine of an aqueous solution of iodic acid appeared at the negative pole, under circumstances in which the secondary nature of the action was quite obvious.

Mr FARADAY, however, made an important exception in the case of aqueous solutions of the hydracids; but I shall here merely refer to the evidence so fully detailed now\* and formerly, which has led me to infer, that in solutions of the hydracids, as well as in those of the oxyacids, water only, and not the dissolved acid, is directly decomposed. I have also to refer to the experiment with an aqueous solution of bromide of iodine, from which it appeared that that compound was not directly decomposed when in solution, but only the water.† It would appear, therefore, that we at present know of no combination of two elementary substances with one another, which, when in solution in water, is directly decomposed by the electric current; but have every reason to believe, that in such solutions the water only suffers direct decomposition.

Farther, I have endeavoured to shew that in alcoholic solution of acids, alkalies, and haloid salts, the water of the alcohol alone is directly decomposed.

The conformity between these views and the results obtained with ethereal solutions is remarkable. I formerly stated that no evidence whatever was obtained from electric phenomena that ether contained water; and what was the farther observed result? When ethereal solutions of potash, of chromic acid, of chloride of platinum, and of corrosive sublimate, were acted on by fifty pairs of 2-inch plates, there neither were any symptoms of decomposition, nor was the galvanometer affected.‡ Thus, whilst in aqueous and alcoholic solutions, water and not the dissolved body is decomposed, in ethereal solutions, where there is no water present, no decomposition takes place at all.

In this way we are arrived within a few steps of the following general conclusion, which I cannot help thinking, if it shall be fully supported, is one of considerable interest, and not I believe hitherto anticipated: "That when solutions of binary combinations of elementary substances, in water, alcohol, or ether, are submitted to voltaic agency, the dissolved substance is not directly decomposed; but only the solvent, if itself an electrolyte."

In laying down any general law, which must, if well founded, comprehend a vast multitude of facts, one of course feels the necessity of having proceeded on an extensive induction; or at least of having established the leading analogies

\* P. 7, et seq.

† P. 10.

‡ Edinburgh Transactions, vol. xiii. p. 331.

comprehended within the bounds of the proposed law, for it rarely happens that the inductive process actually embraces every particular, its imperfection in point of logic being usually supplied by the necessary connections of the individual cases. All I can say is, that I am at present acquainted with no exception to the proposed law, and that all the experiments which I have yet made, go to support it; but still as there are some cases comprehended in it, which may and ought to be experimentally investigated, I shall not yet take upon me to give it as established in its utmost generality, but shall probably in a future communication state the farther results obtained.

This rule is of course entirely confined to compounds of elementary bodies. Every one knows that an ordinary salt dissolved in water, is resolved into its constituent acid and alkali under voltaic agency. The same observation I have found to apply to alcoholic solutions of such salts. With respect to their ethereal solutions, it would seem that it does not hold, in so far as reliance can be placed on a single experiment with a moderate voltaic power. A solution of nitrate of uranium in rectified ether was submitted in a close tube to the action of fifty pairs of 2-inch plates, without any appearance of the constituents of the salt at their respective poles, or action on the galvanometer formerly described.

#### ERRATA in former Memoir in Vol. XIII. of Edinburgh Transactions.

Page 316 (p. 2 of separate Memoir), line 20, for *liquid* read *solution*

— 334 (p. 20 — — — ), — 8, — *ether* — *alcohol*

— 337 (p. 23 — — — ), note, line 4, for *effects* read *quantities*

— 346 (p. 32 — — — ), lines 8 and 9 for *positive* read *negative*, and for *negative* read *positive*