



LVIII. On the voltaic decomposition of aqueous and alcoholic solutions

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axis in the same relation to it as that in which they approached it. From this we conclude, that the space round the optic axis within the ring is traversed by only one image, and therefore that there is only one sheet of the luminiferous surface in this place: the form of the two series of cones also favours this view. This indicates what may not inaptly be termed an eyelet-hole in one sheet, and a conical point in the other.

To determine the real nature of the refraction about the optic axes of biaxial crystals, will evidently require a good deal more of minute examination.

If any fellow-labourers should enter on the subject, I should be very glad to see their results in print, and am glad to be able to inform them that Messrs. Watkins and Hill have undertaken to fit up for sale crystals of arragonite, mounted in a mode so as to facilitate the examination of the refraction near the optic axes.

Queen's College, Cambridge, Feb. 13, 1841.

LVIII. *On the Voltaic Decomposition of Aqueous and Alcoholic Solutions.* By ARTHUR CONNELL, Esq., F.R.S.Ed., Professor of Chemistry in the United College of St. Salvador's and St. Leonard's, St. Andrew's.

[Continued from p. 249, and concluded.]

II. *Alcoholic Solutions.*

I SHALL content myself with simply referring to the experiments, by which I have shown that under voltaic agency water entering into the constitution of absolute alcohol is resolved into its elements, hydrogen being given off at the negative pole, and oxygen being engaged in producing secondary effects on the hydrocarbon of the alcohol, and to those demonstrating the extraordinary effect which the solution of the minutest quantities of alkalies, acids and saline bodies, have in promoting this action*.

This fact, that the water of absolute alcohol suffers decomposition under galvanic action, furnishes the key for solving all cases of the voltaic decomposition of alcoholic solutions, by assimilating them to those which occur in aqueous solutions. The analogy between the two cases is complete, with the difference merely, that in the former the appearances are less marked, from the smaller quantity of water present, the inferior conducting power of the solution, and the slight modi-

* Edinburgh Transactions, vol. xiii.; Jameson's Journal, 1835; and London, Edinburgh and Dubl. Phil. Mag., Dec. 1841.

fications of secondary action due to the presence of hydrocarbon. In short, as respects voltaic agency, an alcoholic solution may be regarded as an aqueous one, in which a foreign substance is present retarding the principal action, but affording an additional source of secondary agency.

Accordingly, when the alcoholic solution of an ordinary salt is acted on, the acid and alkali go to their proper poles, as in an aqueous solution, but much more slowly, and the hydrogen of the water of the alcohol is evolved at the negative pole, whilst the oxygen enters into secondary combination. When the base is of easy reduction, metal reduced by hydrogen appears at the negative; whatever substance is dissolved, if it is not of a nature to afford room for a secondary action with hydrogen, that element is given off in the same proportion as from water, due regard being had to some circumstances connected with the conducting power of the solution which have been formerly pointed out*. This fact was verified for alcoholic solutions of alkalies, haloid salts, and oxyacid salts.

It was also found, by experiments similar to those with aqueous solutions of hydracids and haloid salts, that when iodine appears at the positive pole in alcoholic solutions of hydriodic acid or of iodides, it is due to secondary action. Absolute alcohol was charged with dry hydriodic acid gas, and placed in A, fig. 2, (p. 243) and water in B and C, A being made negative, and C positive by seventy pairs of four-inch plates. Effervescence soon arose from both poles, but no discoloration was anywhere observed, nor acid in B or C until after the lapse of twenty minutes, when a slight brown discoloration from liberated iodine commenced in C with acid reaction. In half an hour the battery was reversed, when the hydriodic solution was instantly discoloured without elastic fluid from the pole in that solution, and with effervescence from the other. This experiment would of course have had more analogy to those with water, if B and C had contained alcohol; but the feeble conducting power of that liquid, and the risk of interfering with the reactions if any substance was dissolved in it, prevented its employment. The appearances are, however, best explained on the view that the water of the alcohol only suffers direct decomposition.

Analogous experiments led to the same view in regard to iodides.

The appearances with a positive pole of zinc led to the same conclusion. When a saturated solution of dry iodide of potassium in absolute alcohol was thus acted on by fifty

* Lond. Edinb. and Dubl. Phil. Mag., Dec. 1841.

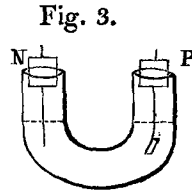
pairs of two-inch plates in the bent tube, fig. 3, oxide of zinc soon separated at *both poles* without any appearance of iodine, or of effervescence at the positive. The deposition of oxide at that pole is in conformity with the view of the direct decomposition of water.

With a similar solution of dry chloride of lithium, oxide of zinc soon separated at the negative pole, with effervescence from that pole, but none from the positive; and it was somewhat uncertain whether any separation of oxide took place at the positive: but little doubt could exist that the oxide originated, as in the case of iodide of potassium, by the action of oxygen of the water of the alcohol on the zinc, and was subsequently dissolved and transferred to the negative pole.

The principal condition of the deposition of oxide of zinc at the positive pole, whether in aqueous or alcoholic solutions, appears to be a pretty rapid formation, from brisk action; and the less powerful the acid, and the less its quantity drawn to the positive side, the more of the oxide separates previous to solution and transference.

With respect to pyroxylic solutions, I have made few experiments; because if the general rule holds good in regard to alcohol, there can be little doubt that it will embrace pyroxylic spirit, since, as I formerly showed, the decomposition of its water is much more readily effected than that of alcohol. I found, experimentally, that when a solution of dry iodide of potassium in rectified pyroxylic spirit was placed in a tube A*, and water in a tube B, the two being connected by asbestos, and A made negative, and B positive by fifty pairs of two-inch plates, although iodine soon appeared in the neighbourhood of the positive pole in B, yet it was accompanied by acid passing into the water of B; and after forty minutes' action these appearances continued the same, only more decided, and without any appearance of iodine elsewhere. There is little doubt that the nature of the action was just the same as in aqueous and alcoholic solutions.

In the whole circumstances, although the evidence may not be of quite so decided a character in some of the cases of alcoholic solutions as in regard to those in water, still I think there need not be much hesitation in laying down as a still more general proposition than that above stated, that "When solutions of primary combinations of elementary substances, in water and in those liquids, such as alcohol and pyroxylic



* Fig. 1. (p. 243.)

spirit, which contain water as such as an essential constituent, are submitted to voltaic agency, the dissolved substance is not directly decomposed by the current, but only the water of the solvent."

III. *Æthereal Solutions*.—Rectified æther gives no symptom of decomposition, nor of conducting power, under the influence of powerful currents, such as that from 200 pairs of four-inch plates; and although $\frac{1}{10000}$ th of potash has a marked influence in promoting the voltaic decomposition of alcohol, the largest quantity of that alkali which æther is capable of dissolving has no effect in affording room for any galvanic agency. Neither do any of the ordinary substances soluble in æther, such as corrosive sublimate, chloride of platinum, or chromic acid, produce any such effect. Nor is an oxyacid salt, such as nitrate of uranium, when held in solution by it, resolved into its constituents under galvanic action. The conclusion drawn from all these experiments is, that æther does not like alcohol contain water as a constituent*.

Up to this point, then, æther and æthereal solutions resist all voltaic action. I have since, however, found that when rectified æther is saturated with dry muriatic acid gas, and then submitted to moderate galvanic action, hydrogen, retaining some æthereal vapour mixed with it, is liberated at the negative pole, and no gas from the positive, but the liquid acquires a yellow colour from dissolved chlorine.

When dry hydriodic acid gas was conducted into æther in a little Wolfe's apparatus, the liquid immediately separated into two layers, a lower dense and deep red, and an upper slightly coloured, which under voltaic agency yielded gas from the negative pole.

In regard to the latter of these experiments, there can be no doubt that in saturating the æther with hydriodic acid gas decomposition took place; and although the nature of this decomposition was not fully investigated, it seems probable that the lower liquid consisted principally of iodized hydriodic acid, resulting from the combination of oxygen derived from the æther with hydrogen of a portion of the hydriodic acid, on which view water of course would be formed, and become the subject of the subsequent voltaic action. During the saturation of æther with muriatic acid, no signs of decomposition were visible; but still it is not impossible that some internal changes may have taken place, and water resulted from the action united to muriatic acid. Unless such a view be adopted, I should be inclined to hold that there really was

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

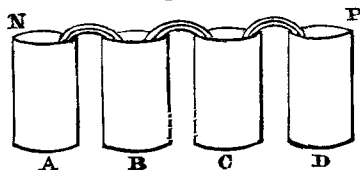
direct decomposition of the muriatic acid by the voltaic current; for when I recollect that pure æther resisted very powerful voltaic currents, and that even potash, which has so wonderful an effect in promoting the galvanic decomposition of the water in absolute alcohol, did not make æther more susceptible of electric agency, I cannot allow myself to suppose that the decomposition in the case of an æthereal solution of a hydracid is that of water entering into the constitution of æther, but adhere to the original view, that æther contains no water, and that alcohol consists of æther and of water.

IV. *On the state in which the Haloid Salts are dissolved by Water and Alcohol.*—The question whether haloid salts are dissolved by water as such, or decompose it and assume the state of hydracid salts, is one on which chemists are still divided. The action of voltaic electricity on such solutions appears to me to decide the matter: during such action it is frequently difficult, particularly in the case of iodides, to observe any acid reaction at the positive pole, when both poles are plunged directly into the solution, on account of the reducing action of oxygen on the acid formed; and even in those cases in which acid is observed, that circumstance will not of itself prove the haloid to be dissolved as a hydracid salt, because it might be held that acid is formed by secondary action at the negative pole, from whence it is drawn to the positive. In this way only, on the hypothesis of solution as a haloid, and direct voltaic decomposition of water alone, can the separation of reduced metal at the negative pole be accounted for. A doubt might also exist whether the acid reaction at the pole might not arise from an oxyacid formed by secondary action at the positive. All such objections are, however, obviated by placing the poles beyond the solution, so as to get quit of secondary actions; and if in such circumstances we can show that the acid and the base go to their proper poles, and that this acid is a hydracid, we have, I conceive, sufficient evidence that the salt has been dissolved as a hydracid salt; for even laying aside for a moment the experiments by which I have endeavoured to show that the haloids, if existing as such in water, are not directly decomposed, let us take the different views of the nature of the galvanic action which suggest themselves when both poles are plunged into the solution in the ordinary manner, and consider them on the supposition that haloids are dissolved as such. First, let us suppose that one or other of the two substances, water or haloid, it matters not which, is decomposed, it is evident that we cannot account for the production of acid where

secondary action is excluded. Next let us suppose that both substances are decomposed, and that either the elements going to the same pole unite on their journey, or by an interchange of elements the oxygen of water unites with the metal of the haloid, and the hydrogen of water with the electro-negative constituent of the haloid. The former of these alternations is contradicted by the fact, that the acid formed is a hydracid; and the latter, although it might account for the formation of acid and alkali, would not account for the liberation of the electro-negative constituent of the haloid at the positive pole, and of hydrogen in fixed and definite proportion at the negative, whatever be the strength of the solution. It appears to me then sufficient, in order to prove the aqueous solution of a haloid as a hydracid salt, to show the separation of the hydracid by voltaic action, under circumstances which exclude secondary action.

To exhibit this result the solution was placed in the tube B, fig. 2, (p. 243) and distilled water in A and C, A being made negative and B positive. When solutions of the chlorides of potassium and of calcium, and of the iodide of potassium were treated in this way by fifty pairs of two-inch plates, acid and alkali were speedily detected at their proper poles in C and A, and on the corresponding sides of the vessel B, and continued to increase whilst the action lasted. The acid collected in C was found in the case of the chlorides to be the muriatic. In the case of the iodide the nature of the acid was somewhat ambiguous with the above power, but when seventy pairs of four-inch plates were employed it was decidedly the iodic. There appeared, however, little doubt that this latter acid had originated in an oxidating action at the positive pole on reduced hydriodic acid; and this view was confirmed by connecting the tube B, containing a solution of iodide of potassium, with two other vessels, C and D, containing distilled water on the positive sides, as in fig. 4, and acting with seventy pairs of four-inch plates:—

Fig. 4.



when the acid produced in C was found to be the hydriodic, and that in D the iodic; in other words, the acid separated from B was the hydriodic, but on passing to the poles it was

reduced, and the iodine oxidated; thus both in the case of chlorides and of iodides, the acid separated proved to be the hydracid.

It must, however, always be remembered, that although such production can be readily shown in many cases of haloids, it does not necessarily follow that this would hold in all cases. We are of course best prepared to expect it in the case of haloids, of which the constituents have the strongest affinity for oxygen and hydrogen, such as the ordinary haloids of the bases of the alkalies and alkaline earths; and accordingly, I showed that it applied to chlorides and iodides of potassium and calcium. But further, it was found to hold good in regard to the ordinary haloids of the common metals, such as zinc. I was prepared, however, to consider it as doubtful what might be the result in regard to the noble metals. Accordingly, when a moderately strong solution of chloride of gold was placed in the tube B*, and connected by asbestos with the tubes A and C, which were filled with distilled water, A being made negative, and C positive by a power of fifty pairs of two-inch plates, no decided indications of the formation of acid were obtained during an hour's action; for although towards the end there was a slight acid reaction at the positive pole, it was not greater than distilled water itself might have yielded, and there was a trace of alkali at the negative. Before, however, deciding that chloride of gold in solution does not yield to voltaic action, it would be necessary to repeat the experiment with a more powerful current, because it may possibly only be a case of more difficult electric resolution. In such cases also atomic constitution may have a considerable, if not the principal influence, on the result.

Whenever we have obtained a decided instance of the formation of acid in the above circumstances, we may conclude, with every probability, that all haloids, of the same nature and atomic constitution, of metals, of equal or more powerful affinities, are in the same situation. Thus having verified the rule for chloride of zinc, we may conclude that all protochlorides of more electro-positive metals, such as manganese, cerium, magnesium, barium, potassium, &c., are dissolved as muriates. On the other hand, for the whole series of metals of less powerful affinities, as well as for all haloids of more complex atomic constitution, the matter will still require to be investigated, and I purpose making some further researches on the subject.

* Fig. 2. (p. 243.)

In regard to sal-ammoniac, I found that it was resolved into acid and alkali in the above circumstances, a result showing that in solution at least it is simple muriate of ammonia, and cannot justly be regarded as chloride of ammonium. The same reasoning above applied to the results with common haloids, can be readily extended to the hypothetical chloride of ammonium; and to complete the evidence on this point, I found that a solution of muriate of ammonia yielded the definite quantity of hydrogen from the negative pole.

The experiments with a positive zinc pole lead to the same result, at least when taken in conjunction with those showing that the haloids, if viewed as existing as such in solution, are not directly decomposed. The oxide of zinc which is dissolved and transferred, must have been taken up by acid which had been previously drawn to the positive side.

The analogy of the action with a positive zinc pole in alcoholic solutions of haloid salts, as formerly described, leads by similar reasoning to the view, that in moderately strong solutions of that description also, such as that of chloride of lithium, iodide of potassium, and moderately saturated alcoholic solutions of chloride of calcium, the haloid decomposes the water of the alcohol, and exists in solution as an oxy-salt. Many phenomena of the voltaic action on such solutions will thus receive a more ready explanation than on the idea of these salts being dissolved as haloids; such as the appearance of alkalies and earths at the negative pole, which will thus result directly from the decomposition of a hydracid, instead of supposing the secondary action of the hydrogen and reaction of the metal on water.

We cannot easily get the same evidence on this subject by the method applied to aqueous solutions, of placing the poles in water beyond the solution, because, from the inferior conducting power of the alcoholic solution, less acid will be separated if it truly exist in the liquid, and we cannot distinguish whether it may not come from the point of junction of the alcoholic solution with the water in which the poles are placed.

If alcohol dissolves haloid salts as hydracid salts, there can be little doubt that pyroxylic spirit does the same: I incline to think that the greater solvent powers of the latter fluid than the former in regard to some substances, such as barytes, are due to its greater absolute quantity of water, although not greater atomic proportion.

V. *On the Conducting Powers of Solutions.*—Without going the length of holding that the additional conducting powers

bestowed on water by dissolved substances is exactly proportional to the degree of chemical change under voltaic action resulting from the dissolved body, there seems in every instance in which increased conducting power is bestowed some chemical change, or at least voltaic transference, attending the increase of conduction. This chemical change may result either from the direct action of the current or from secondary agencies; and both circumstances lend their aid, where they occur, in augmenting conducting power.

In the case of salts the voltaic separation of acid and alkali at once explains the result, and in many of such cases we have an additional effect from secondary action at one or both poles.

Acids alone in solution, as is now generally known, and as I have myself verified experimentally for sulphuric acid and the hydracids, undergo transference to their proper pole, which circumstance appears to be the principal cause of their promoting conduction. In some instances secondary action at the poles also contributes to the result.

To ascertain whether alkalis have a similar action by suffering transference, a moderately strong solution of caustic potash was placed in a tube B*, connected by asbestos moistened with distilled water, with two tubes, A and C, containing the latter fluid, A being made negative, and C positive by seventy-two pairs of four-inch plates. The whole tubes were covered with a close glass covering, a piece of turmeric paper having been introduced into the liquids A and C between the asbestos and the poles. In a few minutes alkali was indicated at the negative pole, and went on increasing during half an hour, whilst the test paper in C was not discoloured, showing that the effect in A was not owing to capillary action. The experiment was then stopped, when the water in A, although not alkaline to test paper throughout, became decidedly so by concentration, whilst that in C showed no alkali even after concentration.

In the experiments also already detailed, in which acid and alkali were separately drawn to the poles in distilled water from saline solutions, the alkali usually reached the pole as soon as the acid.

There can thus be no doubt, that by voltaic action, the alkali in an aqueous solution is transferred to the negative pole.

Water coloured by bromine gives sensibly more effervescence under galvanic action, showing a superior conducting power of the solution.

The manner in which such simple substances increase the

* Fig. 2. (p. 243.)

conducting power of water requires a little investigation. Chlorine, bromine, and iodine are generally admitted to be non-conductors themselves; and even if a little doubt may exist as to iodine in a state of fusion, it is scarcely possible that the minute quantity in an aqueous solution can operate in that way.

To ascertain whether such substances were capable of transference in solution, an aqueous solution of bromine, with a little undissolved bromine at the bottom, to maintain a state of saturation, was placed in the tube B, the arrangement being in all other respects the same as in the last-described experiment with a solution of potash; and after an hour's action of seventy-two pairs of four-inch plates no discoloration from transference of bromine could be observed in the water either of A or of C; and the latter had only a scarcely perceptible smell of bromine, which I believe was due to the secondary decomposition of a trace of hydrobromic acid drawn into C, as both the liquids B and C showed some degree of acid reaction.

An aqueous solution of iodine was then substituted in B for that of bromine, a little iodine being also left at the bottom, and all other circumstances the same, and the battery recharged. After an hour's action there was no appearance of iodine either in A or C.

From these experiments, it is obvious that neither of these substances are transferred in solution by voltaic agency. We must therefore look for some other explanation of the increased conducting power, and that which readily occurs is a secondary action at the negative pole, by the union of hydrogen with the dissolved substance. To determine the accuracy of this view, the current from fifty pairs of two-inch plates was passed at the same time through a solution of bromine and diluted sulphuric acid, and the hydrogen evolved from the two negative poles collected, when after half an hour thirteen cubic inches were collected from the sulphuric solution, and only a bubble, the size of a pea, from the bromine solution: the difference had evidently combined with bromine.

When an aqueous solution of iodine, which had previously been purified by sublimation, solution in alcohol and precipitation by water, was substituted for that of bromine, the action was much more feeble. In a quarter of an hour only a small bubble of gas was collected from each negative pole, and in two hours and a quarter .1 cubic inch from the sulphuric solution, and .077 from the iodic.

It is thus evident, that both in the case of bromine and iodine the action is increased by the combination of the dissolved substance with hydrogen of the decomposed water, but

that, as is to be expected, this circumstance occurs to a much larger extent in the case of bromine than of iodine*.

On connecting the rules regulating the voltaic decomposition of solutions and the transference of substances held dissolved, we observe that no substance, when in a state of transference, suffers direct voltaic decomposition. Acids and alkalies suffer transference, but not direct decomposition. On the other hand, salts, whether oxyacid or hydracid, are not transferred, but are resolved into their constituent acid and alkali.

We cannot, however, say that every substance which is not transferred is directly decomposed. Thus we can hardly doubt that such compounds as bromide of iodine do not suffer voltaic transference, seeing that their constituent elements are not transferred; and we have further seen that this combination is not directly decomposed in solution. Probably also some cases of chlorides exist, in which, from peculiarity of atomic constitution, or other circumstances, there is neither transference nor direct decomposition.

Erratum in the former part of this paper in No. 117: page 247, line 44, for non-negative read now negative.

LIX. *On the Natural Arrangement of the Consonantal Sounds.* By H. WEDGWOOD, Esq.

To the Editors of the Philosophical Magazine and Journal.

GENTLEMEN,

SEEING from your last (February) Number, p. 124, that you do not consider speculation on such a subject foreign to the plan of your publication, I am induced to send you a scheme of all the simple consonantal sounds, exhibiting, in a tabular form, a complete synopsis of their relations with each other.

The first point to be settled is the list of the sounds that are to be the subject of arrangement, which are far from coinciding with those represented by the consonants of the English alphabet. In our mode of writing many simple consonantal sounds are represented by a combination of letters, and conversely, some of our simple consonants are used to represent compound sounds, while others are used on different occasions as the representatives of more than one simple or compound sound.

* Long after these experiments were made and conclusions drawn, I observed that M. Becquerel had also found that bromine and iodine in solution unite with hydrogen under voltaic action.—*Institut, Juin, 1840.*