VI. *Experimental Researches in Electricity.—Seventh Series.* By Michael Faraday, *D.C.L. F.R.S. Fullerian Prof. Chem. Royal Institution, Corr. Memb. Royal and Imp. Acadd. of Sciences, Paris, Petersburgh, Florence, Copenhagen, Berlin, &c. &c.*

§. 11. *On Electro-chemical Decomposition, continued.* ¶ iv. *On some general conditions of Electro-decomposition.* ¶ v. *On a new Measurer of Volta-electricity.* ¶ vi. *On the primitive or secondary character of bodies evolved in Electro-decomposition.* ¶ vii. *On the definite nature and extent of Electro-chemical Decompositions.* §. 13. *On the absolute quantity of Electricity associated with the particles or atoms of Matter.*

Preliminary.

661. THE theory which I believe to be a true expression of the facts of electrochemical decomposition, and which I have therefore detailed in a former series of these Researches, is so much at variance with those previously advanced, that I find the greatest difficulty in stating results, as I think, correctly, whilst limited to the use of terms which are current with a certain accepted meaning. Of this kind is the term pole, with its prefixes of positive and negative, and the attached ideas of attraction and repulsion. The general phraseology is that the positive pole *attracts* oxygen, acids, &c., or more cautiously, that it *determines* their evolution upon the surface; and that the negative pole acts in an equal manner upon hydrogen, combustibles, metals, and bases. According to my view, the determining force is *not* at the poles, but *within* the decomposing body; and the oxygen and acids are rendered at the *negative* extremity of that body, whilst hydrogen, metals, &c., are evolved at the *positive* extremity (518. 524.).

662. To avoid, therefore, confusion and circumlocution, and for the sake of greater precision of expression than I can otherwise obtain, I have deliberately considered the subject with two friends, and with their assistance and concurrence in framing them, I purpose henceforward using certain other terms, which I will now define. The poles, as they are usually called, are only the doors or ways by which the electric current passes into and out of the decomposing body (556.); and they of course, when in contact with that body, are the limits of its extent in the direction of the current. The term has been generally applied to the metal surfaces in contact with the decomposing substance; but whether philosophers generally would also apply it to the

surfaces of air (465. 471.) and water (493.), against which I have effected electro-chemical decomposition, is subject to doubt. In place of the term pole, I propose using that of *Electrode**, and I mean thereby that substance, or rather surface, whether of air, water, metal, or any other body, which bounds the extent of the decomposing matter in the direction of the electric current.

663. The surfaces at which, according to the common phraseology, the electric current enters and leaves a decomposing body, are most important places of action, and require to be distinguished apart from the poles, with which they are mostly, and the electrodes, with which they are always, in contact. Wishing for a natural standard of electric direction to which I might refer these, expressive of their difference and at the same time free from all theory, I have thought it might be found in the earth. If the magnetism of the earth be due to electric currents passing round it, the latter must be in a constant direction, which, according to present usage of speech, would be from east to west, or, which will strengthen this help to the memory, that in which the sun appears to move. If in any case of electro-decomposition we consider the decomposing body as placed so that the current passing through it shall be in the same direction, and parallel to that supposed to exist in the earth, then the surfaces at which the electricity is passing into and out of the substance would have an invariable reference, and exhibit constantly the same relations of powers. Upon this notion we purpose calling that towards the east the *anode*†, and that towards the west the *cathode*‡; and whatever changes may take place in our views of the nature of electricity and electrical action, as they must affect the natural standard referred to in the same direction, and to an equal amount with any decomposing substances to which these terms may at any time be applied, there seems no reason to expect that they will lead to confusion, or tend in any way to support false views. The *anode* is therefore that surface at which the electric current, according to our present expression, enters: it is the negative extremity of the decomposing body; is where oxygen, chlorine, acids, &c., are evolved; and is against or opposite the positive electrode. The *cathode* is that surface at which the current leaves the decomposing body, and is its positive extremity; the combustible bodies, metals, alkalies, and bases, are evolved there, and it is in contact with the negative electrode.

664. I shall have occasion in these Researches, also, to class bodies together according to certain relations derived from their electrical actions (822.); and wishing to express those relations without at the same time involving the expression of any hypothetical views, I intend using the following names and terms. Many bodies are decomposed directly by the electric current, their elements being set free; these I propose to call *electrolytes*§. Water, therefore, is an electrolyte. The bodies which,

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* ἤλεκτρον, and ὸδος *a way.*

† ἀνα *upwards,* ὸδος *a way*; the way which the sun rises.

‡ κατα *downwards,* ὸδος *a way*; the way which the sun sets.

§ ἤλεκτρον, and λυω *solvo.* N. Electrolyte, V. Electrolyze.

like nitric or sulphuric acids, are decomposed in a secondary manner (752. 757.), are not included under this term. Then for *electro-chemically decomposed*, I shall often use the term *electrolyzed*, derived in the same way, and implying that the body spoken of is separated into its components under the influence of electricity: it is analogous in its sense and sound to *analyze*, which is derived in a similar manner. The term *electrolytical* will be understood at once. Muriatic acid is electrolytical, boracic acid is not.

665. Finally, I require a term to express those bodies which can pass to the *electrodes*, or, as they are usually called, the poles. Substances are frequently spoken of as being *electro-negative*, or *electro-positive*, according as they go under the supposed influence of a direct attraction to the positive or negative pole. But these terms are much too significant for the use to which I should have to put them; for though the meanings are perhaps right, they are only hypothetical, and may be wrong; and then, through a very imperceptible, but still very dangerous, because continual, influence, they do great injury to science, by contracting and limiting the habitual views of those engaged in pursuing it. I propose to distinguish these bodies by calling those *anions** which go to the *anode* of the decomposing body; and those passing to the *cathode, cations†*; and when I have occasion to speak of these together, I shall call them *ions*. Thus, the chloride of lead is an *electrolyte*, and when *electrolyzed* evolves the two *ions*, chlorine and lead, the former being an *anion*, and the latter a *cation*.

666. These terms being once well defined, will, I hope, in their use enable me to avoid much periphrasis and ambiguity of expression. I do not mean to press them into service more frequently than will be required, for I am fully aware that names are one thing and science another‡.

667. It will be well understood that I am giving no opinion respecting the nature of the electric current now, beyond what I have done on a former occasion (283. 517.); and that though I speak of the current as proceeding from the parts which are positive to those which are negative (663.), it is merely in accordance with the conventional, though in some degree tacit, agreement entered into by scientific men, that they may have a constant, certain, and definite means of referring to the direction of the forces of that current.

¶ iv. *On some general conditions of Electro-chemical Decomposition.*

669. From the period when electro-chemical decomposition was first effected to the present time, it has been a remark, that those elements which, in the ordinary phenomena of chemical affinity, were the most directly opposed to each other, and combined with the greatest attractive force, were those which were the most readily evolved at the opposite extremities of the decomposing bodies (549.).

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* ἄνιον *that which goes up.* (Neuter participle.)   † κατιον *that which goes down.*

‡ Since this paper was read, I have changed some of the terms which were first proposed, that I might employ only such as were at the same time simple in their nature, clear in their reference, and free from hypothesis.

670. If this result was evident when water was supposed to be essential to, and was present, in almost every case of such decomposition (472.), it is far more evident now that it has been shown and proved that water is not necessarily concerned in the phenomena (474.), and that other bodies much surpass it in some of the effects supposed to be peculiar to that substance.

671. Water, from its constitution and the nature of its elements, and from its frequent presence in cases of electrolytic action, has hitherto stood foremost in this respect. Though a compound formed by very powerful affinity, it yields up its elements under the influence of a very feeble electric current; and it is doubtful whether a case of electrolyzation can occur, where, being present, it is not resolved into its first principles.

672. The various oxides, chlorides, iodides, and salts (402.), which I have shown are decomposable by the electric current when in the liquid state, under the same general law with water, illustrate in an equally striking manner the activity, in such decompositions, of elements directly and powerfully opposed to each other by their chemical relations.

673. On the other hand, bodies dependent on weak affinities very rarely give way. Take, for instance, glasses: many of those formed of silica, lime, alkali, and oxide of lead, may be considered as little more than solutions of substances one in another*. If bottle-glass be fused, and subjected to the voltaic pile, it does not appear to be at all decomposed (408.). If flint-glass, which contains substances more directly opposed, be operated upon, it suffers some decomposition; and if borate of lead glass, which is a definite chemical compound, be experimented with, it readily yields up its elements (408).

674. But the result which is found to be so striking in the instances quoted is not at all borne out by reference to other cases where a similar consequence might have been expected. It may be said, that my own theory of electro-chemical decomposition would lead to the expectation that all compound bodies should give way under the influence of the electric current with a facility proportionate to the strength of the affinity by which their elements, either proximate or ultimate, are combined. I am not sure that that follows as a consequence of the theory; but if the objection be supposed one presented by facts, I have no doubt it will be removed when we obtain a more intimate acquaintance with, and precise idea of, the nature of chemical affinity and the mode of action of an electric current over it (518. 524.) : besides which, it is just as directly opposed to any other theory of electro-chemical decomposition as the one I have propounded; for if it be admitted, as is generally the case, that the more directly bodies are opposed to each other in their attractive forces, the more powerfully do they combine, then the objection applies with equal force to any of the theories of electrolyzation which have been considered, and is an addition to those which I have taken against them.

* Philosophical Transactions, 1830, p. 49.

675. Amongst powerful compounds which are not decomposed, boracic acid stands prominent (408.). Then again, the iodide of sulphur, and the chlorides of sulphur, phosphorus, and carbon, are not decomposable under common circumstances, though their elements are of a nature which would lead to a contrary expectation. Chloride of antimony (402. 690.), the hydro-carbons, acetic acid, ammonia, and many other bodies undecomposable by the voltaic pile, would seem to be formed by an affinity sufficiently strong to indicate that the elements were so far contrasted in their nature as to sanction the expectation that the pile would separate them, especially as in some cases of mere solution (530. 544.), where the affinity must by comparison be very weak, separation takes place*.

676. It must not be forgotten, however, that much of this difficulty, and perhaps the whole, may depend upon the absence of conducting power, which, preventing the transmission of the current, prevents of course the effects due to it. All known compounds being non-conductors when solid, but conductors when liquid, are decomposed, with *perhaps* the single exception at present known of periodide of mercury (679. 691.) ; and even water itself, which so easily yields up its elements when the current passes, if rendered quite pure, scarcely suffers change, because it then becomes a very bad conductor.

677. If it should hereafter be proved that the want of decomposition in those cases where, from chemical considerations, it might be so strongly expected (669. 674. 672.), is due to the absence or deficiency of conducting power, it would also be proved, at the same time, that decomposition *depends* upon conduction, and not the latter upon the former (413.) ; and in water this seems to be very nearly decided. On the other hand, the conclusion is almost irresistible, that in electrolytes the power of transmitting the electricity across the substance is dependent upon their capability of suffering decomposition ; taking place only whilst they are decomposing, and being proportionate to the quantity of elements separated (821.). I may not, however, stop to discuss this point experimentally at present.

678. When a compound contains such elements as are known to pass towards the opposite extremities of the voltaic pile, still the proportions in which they are present appear to be intimately connected with capability in the compound of suffering or resisting decomposition. Thus, the protochloride of tin readily conducts, and is decomposed (402.), but the perchloride neither conducts nor is decomposed (406.). The protiodide of tin is decomposed when fluid (402.); the periodide is not (405.). The periodide of mercury when fused is not decomposed (691.), even though it does conduct. I was unable to contrast it with the protiodide, the latter being converted into mercury and periodide by heat.

679. These important differences induced me to look more closely to certain binary compounds, with a view of ascertaining whether a *law* regulating the *decomposability*

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* With regard to solution, I have met with some reasons for supposing that it will probably disappear as a cause of transference, and intend resuming the consideration at a convenient opportunity.

according to some *relation of the proportionals or equivalents* of the elements, could be discovered. The proto compounds only, amongst those just referred to, were decomposable; and on referring to the substances quoted to illustrate the force and generality of the law of conduction and decomposition which I discovered (402.), it will be found that all the oxides, chlorides, and iodides subject to it, except the chloride of antimony and the periodide of mercury, (to which may now perhaps be added corrosive sublimate,) are also decomposable, whilst many per compounds of the same elements, not subject to the law, were not so (405. 406.).

680. The substances which appeared to form the strongest exceptions to this gegeral result were such bodies as the sulphuric, phosphoric, nitric, arsenic, and other acids.

681. On experimenting with sulphuric acid, I found no reason to believe that it was by itself a conductor of, or decomposable by, electricity, although I had previously been of that opinion (552.). When very strong it is a much worse conductor than if diluted*. If then subjected to the action of a powerful battery, oxygen appears at the *anode*, or positive electrode, although much is absorbed (728.), and hydrogen and sulphur appear at the *cathode*, or negative electrode. Now the hydrogen has with me always been pure, not sulphuretted, and has been deficient in proportion to the sulphur present, so that it is evident that when decomposition occurred water must have been decomposed. I endeavoured to make the experiment with anhydrous sulphuric acid. It appeared to me that in that state, when fused, sulphuric acid was not a conductor, nor decomposed; but I had not enough of the dry acid in my possession to allow me to decide the point satisfactorily. My belief is, that when sulphur appears by the action of the pile on sulphuric acid, it is the result of a secondary action, and that the acid itself is not electrolyzable (757.).

682. Phosphoric acid is, I believe, also in the same condition; but I have found it impossible to decide the point, because of the difficulty of operating on fused anhydrous phosphoric acid. Phosphoric acid which has once obtained water cannot be deprived of it by heat alone. When heated, the hydrated acid volatilizes. Upon subjecting phosphoric acid, fused upon the ring end of a wire (401.), to the action of the voltaic apparatus, it conducted, and was decomposed; but gas, which I believe to be hydrogen, was always evolved at the negative electrode, and the wire was not affected as would have happened had phosphorus been separated. Gas was also evolved at the positive electrode. From all the facts, I conclude it was the water and not the acid which was decomposed.

683. *Arsenic acid.* This substance conducted, and was decomposed; but it contained water, and I was unable at the time to press the investigation so as to ascertain whether a fusible anhydrous arsenic acid could be obtained. It forms, therefore, at present no exception to the general result.

684. Nitrous acid, obtained by distilling nitrate of lead, and keeping it in contact

* DE LA RIVE.

with strong sulphuric acid, was found to conduct and decompose slowly. But on examination there were strong reasons for believing that water was present, and that the decomposition and conduction depended upon it. I endeavoured to prepare a perfectly anhydrous portion, but could not spare the time required to procure an unexceptionable result.

685. Nitric acid is a substance which I believe is not decomposed directly by the electric current. As I want the facts in illustration of the distinction existing between primary and secondary decomposition, I will merely refer to them in this place (752.).

686. That these mineral acids should confer facility of conduction and decomposition on water, is no proof that they are competent to favour and suffer these actions in themselves. Boracic acid does the same thing, though not decomposable. M. DE LA RIVE has pointed out that chlorine has this power also; but being to us an elementary substance, it cannot be due to its capability of suffering decomposition.

687. *Chloride of sulphur* does not conduct, nor is it decomposed. It consists of single proportionals of its elements, but is not on that account an exception to the rule (679.), which does not affirm that *all* compounds of single proportionals of elements are decomposable, but that such as are decomposable are so constituted.

688. *Protochloride of phosphorus* does not conduct nor become decomposed.

689. *Protochloride of carbon* does not conduct nor suffer decomposition. In association with this substance, I submitted the *hydro-chloride of carbon* from olefiant gas and chlorine to the action of the electric current; but it also refused to conduct or yield up its elements.

690. With regard to the exceptions (679.), upon closer examination, some of them disappear. Chloride of antimony (a compound of one proportional of antimony and one and a half of chlorine) of recent preparation was put into a tube (fig. 13.) (789.), and submitted when fused to the action of the current, the positive electrode being of plumbago. No electricity passed, and no appearance of decomposition was visible at first; but when the positive and negative electrodes were brought very near each other in the chloride, then a feeble action occurred and a feeble current passed. The effect altogether was so small (although quite amenable to the law before given), and so unlike the decomposition and conduction occurring in all the other cases, that I attribute it to the presence of a minute quantity of water, (for which this and many other chlorides have strong attractions, producing hydrated chlorides,) or perhaps of a true protochloride consisting of single proportionals (695. 796.).

691. *Periodide of mercury* being examined in the same manner, was found most distinctly to insulate whilst solid, but conduct when fluid, according to the law of *liquido-conduction* (402.); but there was no appearance of decomposition. No iodine appeared at the *anode*, nor mercury or other substance at the *cathode*. The case is, therefore, no exception to the rule, that only compounds of single proportionals are decomposable; but it is an exception, and I think the only one, to the statement, that

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all bodies subject to the law of liquido-conduction are decomposable. I incline, however, to believe, that a portion of protiodide of mercury is retained dissolved in the periodide, and that to its slow decomposition the feeble conducting power is due. Periodide would be formed, as a secondary result, at the *anode*; and the mercury at the *cathode* would also form, as a secondary result, protiodide. Both these bodies would mingle with the fluid mass, and thus no final separation appear, notwithstanding the continued decomposition.

692. When *perchloride of mercury* was subjected to the voltaic current, it did not conduct in the solid state, but it did conduct when fluid. I think, also, that in the latter case it was decomposed; but there are many interfering circumstances which require examination before a positive conclusion can be drawn.

693. When the ordinary protoxide of antimony is subjected to the voltaic current in a fused state, it also is decomposed, although the effect from other causes soon ceases (402. 802.). This oxide consists of one proportional of antimony and one and a half of oxygen, and is therefore an exception to the general law assumed. But in working with this oxide and the chloride, I observed facts which lead me to doubt whether the compounds usually called the protoxide and the protochloride do not often contain other compounds, consisting of single proportions, which are the true proto compounds, and which, in the case of the oxide, might give rise to the decomposition above described.

694. The ordinary sulphuret of antimony is considered as being the compound with the smallest quantity of sulphur, and analogous in its proportions to the ordinary protoxide. But I find that if it be fused with metallic antimony, a new sulphuret is formed, containing much more of the metal than the former, and separating distinctly, when fused, both from the pure metal on the one hand, and the ordinary grey sulphuret on the other. In some rough experiments, the metal thus taken up by the ordinary sulphuret of antimony was equal to half the proportion of that previously in the sulphuret, in which case the new sulphuret would consist of *single* proportionals.

695. When this new sulphuret was dissolved in muriatic acid, although a little antimony separated, yet it appeared to me that a true protochloride, consisting of *single* proportionals, was formed, and from that, by alkalies, &c., a true protoxide, consisting also of *single* proportionals was obtainable. But I could not stop to ascertain this matter strictly by analysis.

696. I believe, however, that there is such an oxide; that it is often present in variable proportions in what is commonly called protoxide, throwing uncertainty upon the results of its analysis, and causing the electrolytic decomposition above described.

697. Upon the whole, it appears probable that all those binary compounds of elementary bodies which are capable of being electrolyzed when fluid, but not whilst solid, according to the law of liquido-conduction (394.), consist of single proportionals of their elementary principles; and it may be because of their departure from this

s implicity of composition, that boracic acid, ammonia, perchlorides, periodides, and many other direct compounds of elements, are indecomposable.

698. With regard to salts and combinations of compound bodies, the same simple relation does not appear to hold good. I could not decide this by bisulphates of the alkalies, for as long as the second proportion of acid remained, water was retained with it. The fused salt, therefore, conducted, and was decomposed; but hydrogen always appeared at the negative electrode.

699. A biphosphate of soda was prepared by heating, and ultimately fusing, the ammonia-phosphate of soda. In this case the fused bisalt conducted, and was decomposed; but a little gas appeared at the negative electrode, and though I believe the salt itself was electrolyzed, I am not quite satisfied that water was entirely absent.

700. Then a biborate of soda was prepared; and this, I think, is an unobjectionable case. The salt, when fused, conducted, and was decomposed, and gas appeared at both electrodes: even when the boracic acid was increased to three proportionals the same effect took place.

701. Hence this class of compound combinations does not seem to be subject to the same simple law as the former class of binary combinations. Whether we may find reason to consider them as mere solutions of the compound of single proportionals in the excess of acid, is a matter which, with some apparent exceptions occurring amongst the sulphurets, must be left for decision by future examination.

702. In any investigation of these points, great care must be taken to exclude water; for if present, secondary effects are so frequently produced as often seemingly to indicate an electro-decomposition of substances, when no true result of the kind has occurred (742. &c.).

703. It is evident that all the cases in which decomposition *does not occur may* depend upon the want of conduction (677. 413.); but that does not at all lessen the interest excited by seeing the great difference of effect due to a change, not in the nature of the elements, but merely in their proportions, especially in any attempt which may be made to elucidate and expound the beautiful theory put forth by Sir HUMPHRY DAVY[*], and illustrated by BERZELIUS and other eminent philosophers, that ordinary chemical affinity is a mere result of the electrical attractions of the particles of matter.

¶ v. *On a new Measurer of Volta-electricity.*

704. I have already said, when engaged in reducing common and voltaic electricity to one standard of measurement (377.), and again when introducing my theory of electro-chemical decomposition (504. 505. 510.), that the chemical decomposing action of a current *is constant for a constant quantity of electricity*, notwithstanding the greatest variations in its sources, in its intensity, in the size of the *electrodes* used, in the nature of the conductors (or non-conductors (307.)) through which it is

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[*] Philosophical Transactions, 1807, pp. 32, 39; also 1826, pp. 387, 389.

passed, or in other circumstances. The conclusive proofs of the truth of these state-
ments shall be given almost immediately (783. &c.).

705. I endeavoured upon this law to construct an instrument which should measure
out the electricity passing through it, and which, being interposed in the course of the
current used in any particular experiment, should serve at pleasure, either as a *com-
parative standard* of effect, or as a *positive measurer* of this subtile agent.

706. There is no substance better fitted, under ordinary circumstances, to be the
indicating body in such an instrument than water; for it is decomposed with facility
when rendered a better conductor by the addition of acids or salts; its elements may
in numerous cases be obtained and collected without any embarrassment from secon
dary action, and, being gaseous, they are in the best physical condition for separation
and measurement. Water, therefore, acidulated by sulphuric acid, is the substance
I shall generally refer to, although it may become expedient in peculiar cases or forms
of experiment to use other bodies (843.).

707. The first precaution needful in the construction of the instrument was to
avoid the recombination of the evolved gases, an effect which the positive electrode
has been found so capable of producing (571.). For this purpose various forms of
decomposing apparatus were used. The first consisted of straight tubes, each con-
taining a plate and wire of platina soldered together by gold, and fixed hermetically
in the glass at the closed extremity of the tube (Plate I. fig. 5.). The tubes were
about eight inches long, 0·7 of an inch in diameter, and graduated. The platina plates
were about an inch long, as wide as the tubes would permit, and adjusted as near to
the mouths of the tubes as was consistent with the safe collection of the gases evolved.
In certain cases, where it was required to evolve the elements upon as small a surface
as possible, the metallic extremity, instead of being a plate, consisted of the wire bent
into the form of a ring (fig. 6.). When these tubes were used as measurers, they were
filled with the dilute sulphuric acid, and inverted in a basin of the same liquid (fig. 7.),
being placed in an inclined position, with their mouths near to each other, that as
little decomposing matter should intervene as possible; and also, in such a direction
that the platina plates should be in vertical planes (720.).

708. Another form of apparatus was that delineated (fig. 8.). The tube is bent in
the middle; one end is closed; in that end is fixed a wire and plate, *a*, proceeding so
far downwards, that, when in the position figured, it shall be as near to the angle as
possible, consistently with the collection, at the closed extremity of the tube, of all the
gas evolved against it. The plane of this plate is also perpendicular (720.). The
other metallic termination, *b*, is introduced at the time decomposition is to be effected,
being brought as near the angle as possible, without causing any gas to pass from it
towards the closed end of the instrument. The gas evolved against it is allowed to
escape.

709. The third form of apparatus contains both electrodes in the same tube; the
transmission, therefore, of the electricity, and the consequent decomposition, is far

more rapid than in the separate tubes. The resulting gas is the sum of the portions evolved at the two electrodes, and the instrument is better adapted than either of the former as a measurer of the quantity of voltaic electricity transmitted in ordinary cases. It consists of a straight tube (fig. 9.) closed at the upper extremity, and graduated, through the sides of which pass the platina wires (being fused into the glass), which are connected with two plates within. The tube is fitted by grinding into one mouth of a double-necked bottle. If the latter be one half or two thirds full of the dilute sulphuric acid, it will, upon inclination of the whole, flow into the tube and fill it. When an electric current is passed through the instrument, the gases evolved against the plates collect in the upper portion of the tube, and are not subject to the recombining power of the platina.

710. Another form of the instrument is given at fig. 10.

711. A fifth form is delineated (fig. 11.). This I have found exceedingly useful in experiments continued in succession for days together, and where large quantities of indicating gas were to be collected. It is fixed on a weighted foot, and has the form of a small retort containing the two electrodes: the neck is narrow, and sufficiently long to deliver gas issuing from it into a jar placed in a small pneumatic trough. The electrode chamber, sealed hermetically at the part held in the stand, is five inches in length, and 0·6 of an inch in diameter; the neck about nine inches in length, and 0·4 of an inch in diameter internally. The figure will fully indicate the construction.

712. It can hardly be requisite to remark, that in the arrangement of any of these forms of apparatus, they, and the wires connecting them with the substance, which is collaterally subjected to the action of the same electric current, should be so far insulated as to ensure a certainty that all the electricity which passes through the one shall also be transmitted through the other.

713. Next to the precaution of collecting the gases, if mingled, out of contact with the platinum, was the necessity of testing the law of a *definite electrolytic* action, upon water at least, under all varieties of condition; that, with a conviction of its certainty, might also be obtained a knowledge of those interfering circumstances which would require to be practically guarded against.

714. The first point investigated was the influence or indifference of extensive variations in the size of the electrodes, for which purpose instruments like those last described (709. 710. 711.) were used. One of these had plates 0·7 of an inch wide, and nearly four inches long; another had plates only 0·5 of an inch wide, and 0·8 of an inch long; a third had wires 0·02 of an inch in diameter, and three inches long; and a fourth similar wires only half an inch in length. Yet when these were filled with dilute sulphuric acid, and, being placed in succession, had one common current of electricity passed through them, very nearly the same quantity of gas was evolved in all. The difference was sometimes in favour of one, and sometimes on the side of another; but the general result was that the largest quantity of gases was evolved upon the smaller surface of the wires.

715. Experiments of a similar kind were made with the single-plate, straight tubes (707.), and also with the curved tubes (708.), with similar consequences; and when these, with the former tubes, were arranged together in various ways, the result, as to the equality of action of large and small metallic surfaces when delivering and receiving the same current of electricity, was constantly the same. As an illustration, the following numbers are given. An instrument with two wires evolved 74·3 volumes of mixed gases; another with plates 73·25 volumes; whilst the sum of the oxygen and hydrogen in two separate tubes amounted to 73·65 volumes. In another experiment the volumes were 55·3, 55·3, and 54·4.

716. But it was observed in these experiments, that in single-plate tubes (707.) more hydrogen was evolved at the negative electrode than was proportionate to the oxygen at the positive electrode; and generally, also, more than was proportionate to the oxygen and hydrogen in a double-plate tube. Upon more minutely examining these effects, I was led to refer them, and also the differences between wires and plates (714.), to the solubility of the gases evolved, especially at the positive electrode.

717. When the positive and negative electrodes are equal in surface, the bubbles which rise from them in dilute sulphuric acid are always different in character. Those from the positive plate are exceedingly small, and separate instantly from every part of the surface of the metal, in consequence of its perfect cleanliness (633.); whilst in the liquid they give it a hazy appearance, from their number and minuteness; are easily carried down by currents; and therefore not only present far greater surface of contact with the liquid than larger bubbles would do, but are retained a much longer time in mixture with it. But the bubbles at the negative surface, though they constitute twice the volume of the gas at the positive electrode, are nevertheless very inferior in number. They do not rise so universally from every part of the surface, but seem to be evolved at different points; and though so much larger, they appear to cling to the metal, separating with difficulty from it, and when separated, instantly rising to the top of the liquid. If, therefore, oxygen and hydrogen had equal solubility in, or powers of combining with, water under similar circumstances, still under the present conditions the oxygen would be far the most liable to solution; but when to these is added its well known power of forming a compound with water, it is no longer surprising that such a compound should be produced in small quantities at the positive electrode; and indeed the bleaching power which some philosophers have observed in a solution at this electrode, when chlorine and similar bodies have been carefully excluded, is probably due to the formation there, in this manner, of oxy-water.

718. That more gas was collected from the wires than from the plates, I attribute to the circumstance, that as equal quantities were evolved in equal times, the bubbles at the wires having been more rapidly produced, in relation to any part of the surface, must have been much larger; have been therefore in contact with the fluid by a much

smaller surface, and for a much shorter time than those at the plates; hence less solution and a greater collection.

719. There was also another effect produced, especially by the use of large electrodes, which was both a consequence and a proof of the solution of part of the gas evolved there. The collected gas, when examined, was found to contain small portions of nitrogen. This I attribute to the presence of air dissolved in the acid used for decomposition. It is a well-known fact, that when bubbles of a gas but slightly soluble in water or solutions pass through them, the portion of this gas which is dissolved displaces a portion of that previously in union with the liquid: and so, in the decompositions under consideration, as the oxygen dissolves, it displaces a part of the air, or at least of the nitrogen, previously united to the acid; and this proceeds *most extensively* with large plates, because the gas evolved at them is in the most favourable condition for solution.

720. With the intention of avoiding this solubility of the gases as much as possible, I arranged the decomposing plates in a vertical position (707. 708.), that the bubbles might quickly escape upwards, and that the downward currents in the fluid should not meet ascending currents of gas. This precaution I found to assist greatly in producing constant results, and especially in experiments to be hereafter referred to, in which other liquids than dilute sulphuric acid, as for instance solution of potash, were used.

721. The irregularities in the indications of the measurer proposed, arising from the solubility just referred to, are but small, and may be very nearly corrected by comparing the results of two or three experiments. They may also be almost entirely avoided by selecting that solution which is found to favour them in the least degree (728.); and still further by collecting the hydrogen only, and using that as the indicating gas; for being much less soluble than oxygen, being evolved with twice the rapidity and in larger bubbles (717.), it can be collected more perfectly and in greater purity.

722. From the foregoing and many other experiments, it results that *variation in the size of the electrodes causes no variation in the chemical action of a given quantity of electricity upon water.*

723. The next point in regard to which the principle of constant electro-chemical action was tested, was *variation of intensity.* In the first place, the preceding experiments were repeated, using batteries of an *equal* number of plates, *strongly* and *weakly* charged; but the results were alike. They were then repeated, using batteries sometimes containing forty, and at other times only five pairs of plates; but the results were still the same. *Variations therefore in the intensity,* caused by difference in the strength of charge, or in the number of alternations used, *produced no difference as to the equal action of large and small electrodes.*

724. Still these results did not prove that variation in the intensity of the current was not accompanied by a corresponding variation in the electro-chemical effects,

since the actions at *all* the surfaces might have increased or diminished together. The deficiency in the evidence is, however, completely supplied by the former experiments on different-sized electrodes; for with variation in the size of these, a variation in the intensity must have occurred. The intensity of an electric current traversing conductors alike in their nature, quality, and length, is probably as the quantity of electricity passing through a given sectional area perpendicular to the current, divided by the time (360. *note*); and therefore when large plates were contrasted with wires separated by an equal length of the same decomposing conductor (714.), whilst one current of electricity passed through both arrangements, that electricity must have been in a very different state, as to *tension*, between the plates and between the wires; yet the chemical results were the same.

725. The difference in intensity, under the circumstances described, may be easily shown practically, by arranging two decomposing apparatus as in fig. 12, where the same fluid is subjected to the decomposing power of the same current of electricity, passing in the vessel A. between large platina plates, and in the vessel B. between small wires. If a third decomposing apparatus, such as that delineated fig. 11. (711.), be connected with the wires at *a b*, fig. 12, it will serve sufficiently well, by the degree of decomposition occurring in it, to indicate the relative state of the two plates as to intensity; and if it then be applied in the same way, as a test of the state of the wires at *a′ b′*, it will, by the increase of decomposition within, show how much greater the intensity is there than at the former points. The connexions of P and N with the voltaic battery are of course to be continued during the whole time.

726. A third form of experiment in which difference of intensity was obtained, for the purpose of testing the principle of equal chemical action, was to arrange three volta-electrometers, so that after the electric current had passed through one, it should divide into two parts, which, after traversing each one of the remaining instruments, should reunite. The sum of the decomposition in the two latter vessels was always equal to the decomposition in the former vessel. But the *intensity* of the divided current could not be the same as that it had in its original state; and therefore *variation of intensity has no influence on the results if the quantity of electricity remain the same.* The experiment, in fact, resolves itself simply into an increase in the size of the electrodes (725.).

727. The *third point*, in respect to which the principle of equal electro-chemical action on water was tested, was *variation of the strength of the solution used.* In order to render the water a conductor, sulphuric acid had been added to it (707.); and it did not seem unlikely that this substance, with many others, might render the water more subject to decomposition, the electricity remaining the same in quantity. But such did not prove to be the case. Diluted sulphuric acid, of different strengths, was introduced into different decomposing apparatus, and submitted simultaneously to the action of the same electric current (714.). Slight differences occurred, as before, sometimes in one direction, sometimes in another; but the final result was, that

exactly the same quantity of water was decomposed in all the solutions by the same quantity of electricity, though the sulphuric acid in some was seventyfold what it was in others.   The strengths used were of specific gravity 1·495, and downwards.

728. When an acid having a specific gravity of about 1·336 was employed, the results were most uniform, and the oxygen and hydrogen (716.) most constantly in the right proportion to each other.   Such an acid gave more gas than one much weaker acted upon by the same current, apparently because it had less solvent power.   If the acid were very strong, then a remarkable disappearance of oxygen took place; thus, one made by mixing two measures of strong oil of vitriol with one of water, gave forty-two volumes of hydrogen, but only twelve of oxygen.   The hydrogen was very nearly the same with that evolved from acid of the specific gravity 1·232.   I have not yet had time to examine minutely the circumstances attending the disappearance of the oxygen in this case, but imagine it is due to the formation of oxywater, which THÉNARD has shown is favoured by the presence of acid.

729. Although not necessary for the practical use of the instrument I am describing, yet as connected with the important point of constant electro-chemical action upon water, I now investigated the effects produced by an electric current passing through aqueous solutions of acids, salts, and compounds, exceedingly different from each other in their nature, and found them to yield astonishingly uniform results.   But many of them which are connected with a secondary action will be more usefully described hereafter (778.).

730. When solutions of caustic potassa or soda, or sulphate of magnesia, or sulphate of soda, were acted upon by the electric current, just as much oxygen and hydrogen was evolved from them as from the diluted sulphuric acid, with which they were compared.   When a solution of ammonia, rendered a better conductor by sulphate of ammonia (554.), or a solution of subcarbonate of potassa was experimented with, the *hydrogen* evolved was in the same quantity as that set free from the diluted sulphuric acid with which they were compared.   Hence *changes in the nature of the solution do not alter the constancy of electrolytic action upon water.*

731. I have already said, respecting large and small electrodes, that change of order caused no change in the general effect (715.).   The same was the case with different solutions, or with different intensities; and however the circumstances of an experiment might be varied, the results came forth exceedingly consistent, and proved that the electro-chemical action was still the same.

732. I consider the foregoing investigation as sufficient to prove the very extraordinary and important principle with respect to WATER, *that when subjected to the influence of the electric current, a quantity of it is decomposed exactly proportionate to the quantity of electricity which has passed,* notwithstanding the thousand variations in the conditions and circumstances under which it may at the time be placed; and further, that when the interference of certain secondary effects (742. &c.), together with the solution or recombination of the gas and the evolution of air, are guarded against,

the products of the decomposition may be collected with such accuracy, as to afford a very excellent and valuable measurer of the electricity concerned in their evolution.

733. The forms of instrument which I have given, figg. 9, 10, 11. (709. 710. 711.), are probably those which will be found most useful, as they indicate the quantity of electricity by the largest volume of gases, and cause the least obstruction to the passage of the current. The fluid which my present experience leads me to prefer, is a solution of sulphuric acid of specific gravity about 1·336, or from that to specific gravity 1·25; but it is very essential that there should be no organic substance, nor any vegetable acid, nor other body, which, by being liable to the action of the oxygen or hydrogen evolved at the electrodes (773. &c.), shall diminish their quantity, or add other gases to them.

734. In many cases when the instrument is used as a *comparative standard*, or even as *a measurer*, it may be desirable to collect the hydrogen only, as being less liable to absorption or disappearance in other ways than the oxygen; whilst at the same time its volume is so large, as to render it a good and sensible indicator. In such cases the first and second form of apparatus have been used, figg. 7, 8. (707. 708.). The indications obtained were very constant, the variations being much smaller than in those forms of apparatus collecting both gases; and they can also be procured when solutions are used in comparative experiments, which, yielding no oxygen or only secondary results of its action, can give no indications if the educts at both electrodes be collected. Such is the case when solutions of ammonia, muriatic acid, chlorides, iodides, acetates, or other vegetable salts, &c., are employed.

735. In a few cases, as where solutions of metallic salts liable to reduction at the negative electrode are acted upon, the oxygen may be advantageously used as the measuring substance. This is the case, for instance, with sulphate of copper.

736. There are therefore two general forms of the instrument which I submit as a measurer of electricity. One, in which both the gases of the water decomposed are collected (709. 710. 711.); and the other, in which a single gas, as the hydrogen only, is used (707. 708.). When referred to as a *comparative instrument*, (a use I shall now make of it very extensively,) it will not often require particular precaution in the observation; but when used as an *absolute measurer*, it will be needful that the barometric pressure and the temperature be taken into account, and that the graduation of the instruments should be to one scale; the hundredths and smaller divisions of a cubical inch are quite fit for this purpose, and the hundredth may be very conveniently taken as indicating a DEGREE of electricity.

737. It can scarcely be needful to point out further than has been done how this instrument is to be used. It is to be introduced into the course of the electric current, the action of which is to be exerted anywhere else, and if 60° or 70° of electricity are to be measured out, either in one or several portions, the current, whether strong or weak, is to be continued until the gas in the tube occupies that number of divisions or hundredths of a cubical inch. Or if a quantity competent to produce a certain

effect is to be measured, the effect is to be obtained, and then the indication read off. In exact experiments it is necessary to correct the volume of gas for changes in temperature and pressure, and especially for moisture*. For the latter object the volta-electrometer (fig. 11.) is most accurate, as its gas can be measured over water, whilst the others retain it over acid or saline solutions.

738. I have not hesitated to apply the term *degree*, in analogy with the use made of it with respect to another most important imponderable agent, namely, heat; and as the definite expansion of air, water, mercury, &c., is there made use of to measure heat, so the equally definite evolution of gases is here turned to a similar use for electricity.

739. The instrument offers the only *actual measurer* of voltaic electricity which we at present possess. For without being at all affected by variations in time or intensity, or alterations in the current itself, of any kind, or from any cause, or even of intermissions of action, it takes note with accuracy of the quantity of electricity which has passed through it, and reveals that quantity by inspection ; I have therefore named it a VOLTA-ELECTROMETER.

740. Another mode of measuring volta-electricity may be adopted with advantage in many cases, dependent on the quantities of metals or other substances evolved either as primary or as secondary results; but I refrain from enlarging on this use of the products, until the principles on which their constancy depends have been fully established (791. 843.).

741. By the aid of this instrument I have been able to establish the definite character of electro-chemical action in its most general sense; and I am persuaded it will become of the utmost use in the extensions of the science which these views afford. I do not pretend to have made its detail perfect, but to have demonstrated the truth of the principle, and the utility of the application.

¶ vi. *On the primary or secondary character of the bodies evolved at the Electrodes.*

742. Before the *volta-electrometer* could be employed in determining, as a *general law*, the constancy of electro-decomposition, it became necessary to examine a distinction, already recognised among scientific men, relative to the products of that action, namely, their primitive or secondary character; and, if possible, by some general rule or principle, to decide when they were of the one or the other kind. It will appear hereafter that great mistakes respecting electro-chemical action and its consequences, have arisen from confounding these two classes of results together.

743. When a substance under decomposition yields at the electrodes those bodies uncombined and unaltered which the electric current has separated, then they may be considered as primary results, even though themselves compounds. Thus the oxygen and hydrogen from water are primary results; and so also are the acid and alkali (themselves compound bodies) evolved from sulphate of soda. But when the sub-

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* For a simple table of correction for moisture, I may take the liberty of referring to my Chemical Manipulation, edition of 1830, p. 376.

stances separated by the current are changed at the electrodes before their appearance, then they give rise to secondary results, although in many cases the bodies evolved are elementary.

744. These secondary results occur in two ways, being sometimes due to the mutual action of the evolving substance and the matter of the electrode, and sometimes to its action upon the substances contained in the decomposing conductor itself. Thus, when carbon is made the positive electrode in dilute sulphuric acid, carbonic oxide and carbonic acid appear there instead of oxygen; for the latter, acting upon the matter of the electrode, produces these secondary results. Or if the positive electrode, in a solution of nitrate or acetate of lead, be platina, then peroxide of lead appears there, equally a secondary result with the former, but now depending upon an action of the oxygen on a substance in the solution. Again, when ammonia is decomposed by platina electrodes, nitrogen appears at the *anode**; but though an *elementary* body, it is a *secondary* result in this case, being derived from the chemical action of the oxygen electrically evolved there, upon the ammonia in the surrounding solution (554.). In the same manner when aqueous solutions of metallic salts are decomposed by the current, the metals evolved at the *cathode*, though elements, are *always* secondary results, and not immediate consequences of the decomposing power of the electric current.

745. Many of these secondary results are extremely valuable; for instance, all the interesting compounds which M. Becquerel has obtained by feeble electric currents are of this nature; but they are essentially chemical, and must, in the theory of electrolytic action, be carefully distinguished from those which are directly due to the action of the electric current.

746. The nature of the substances evolved will often lead to a correct judgement of their primary or secondary character, but is not sufficient alone to establish that point. Thus, nitrogen is said to be attracted sometimes by the positive and sometimes by the negative electrode, according to the bodies with which it may be combined (554. 555.), and it is on such occasions evidently viewed as a primary result†; but I think I shall show, that, when it appears at the positive electrode, or rather at the *anode*, it is a secondary result (748.). Thus, also, Sir Humphry Davy ‡, and with him the great body of chemical philosophers, (including myself,) have given the appearance of copper, lead, tin, silver, gold, &c., at the negative electrode, when their aqueous solutions were acted upon by the voltaic current, as proofs that the metals, as a class, were attracted to that surface; thus assuming the metal in each case to be a primary result. These however, I expect to prove, are all secondary results; the mere consequence of chemical action, and no proofs of the attraction or the law announced §.

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* Annales de Chimie, 1804, tom. li. p. 167.   † Ibid. tom. li. p. 172.

‡ Elements of Chemical Philosophy, pp. 144. 161.

§ It is remarkable that up to 1804 it was the received opinion that the metals were reduced by the nascent hydrogen. At that date the general opinion was reversed by Hisinger and Berzelius (Annales de Chimie,

747. But when we take to our assistance the law of *constant electro-chemical action* already proved with regard to water (732.), and which I hope to extend satisfactorily to all bodies (821.), and consider the *quantities* as well as the *nature* of the substances set free, a generally accurate judgement of the primary or secondary character of the results may be formed : and this important point, so essential to the theory of electro-decomposition, since it decides what are the particles directly under the influence of the current, (distinguishing them from such as are not affected,) and what are the results to be expected, may be established with such degree of certainty as to remove innumerable ambiguities and doubtful considerations from this branch of the science.

748. Let us apply these principles to the case of ammonia, and the supposed determination of nitrogen to one or the other *electrode* (554. 555.). A pure strong solution of ammonia is as bad a conductor, and therefore as little liable to electro-decomposition, as pure water ; but when sulphate of ammonia is dissolved in it, the whole becomes a conductor ; nitrogen *almost* and occasionally *quite* pure is evolved at the *anode*, and hydrogen at the *cathode* ; the ratio of the volume of the former to that of the latter varying, but being as 1 to about 3 or 4. This result would seem at first to imply that the electric current had decomposed ammonia, and that the nitrogen had been determined towards the positive electrode. But when the electricity used was measured out by the volta-electrometer (707. 736.), it was found that the hydrogen obtained was exactly in the proportion which would have been supplied by decomposed water, whilst the nitrogen had no certain or constant relation whatever. When, upon multiplying experiments, it was found that, by using a stronger or weaker solution, or a more or less powerful battery, the gas evolved at the *anode* was a mixture of oxygen and nitrogen, varying both in proportion and absolute quantity, whilst the hydrogen at the *cathode* remained constant, no doubt could be entertained that the nitrogen at the *anode* was a secondary result, depending upon the chemical action of the nascent oxygen, determined to that surface by the electric current, upon the ammonia in solution. It was the water, therefore, which was electrolyzed, not the ammonia. Further, the experiment gives no real indication of the tendency of the element nitrogen to either one electrode or the other ; nor do I know of any experiment with nitric acid, or other compounds of nitrogen, which shows the tendency of this element, under the influence of the electric current, to pass in either direction along its course.

749. As another illustration of secondary results, the effects on a solution of acetate of potassa may be quoted. When a very strong solution was used, more gas was evolved at the *anode* than at the *cathode*, in the proportion of 4 to 3 nearly : that from the *anode* was a mixture of carbonic oxide and carbonic acid ; that from the *cathode* pure hydrogen. When a much weaker solution was used, less gas was evolved at the *anode* than at the *cathode* ; and it now contained carburetted hydrogen, as well as carbonic oxide and car-

1804, tom. li. p. 174.), who stated that the metals were evolved directly by the electricity : in which opinion it appears, from that time, DAVY coincided (Philosophical Transactions, 1826, p. 388.).

bonic acid. This result of carburetted hydrogen at the positive electrode has a very anomalous appearance, if considered as an immediate consequence of the decomposing power of the current. It, however, as well as the carbonic oxide and acid, is only a *secondary result*; for it is the water alone which suffers electro-decomposition, and it is the oxygen eliminated at the *anode* which, reacting on the acetic acid, in the midst of which it is evolved, produces those substances that finally appear there. This is fully proved by experiments with the volta-electrometer (707.); for then the hydrogen evolved from the acetate at the *cathode* is always found to be definite, being exactly proportionate to the electricity which has passed through the solution, and, in quantity, the same as the hydrogen evolved in the volta-electrometer itself. The appearance of the carbon in combination with the hydrogen at the positive electrode, and its non-appearance at the negative electrode, are in curious contrast with the results which might have been expected from the law usually accepted respecting the final places of the elements.

750. If the salt in solution be an acetate of lead, then the results at both electrodes are secondary, and cannot be used to estimate or express the amount of electro-chemical action, except by a circuitous process (843.). In place of oxygen, or even the gases already described (749.), peroxide of lead now appears at the positive, and lead itself at the negative electrode. When other metallic solutions are used, containing, for instance, peroxides, as that of copper, combined with this or any other decomposable acid, still more complicated results will be obtained; which, viewed as direct results of the electro-chemical action, will, in their proportions, present nothing but confusion, but will appear perfectly harmonious and simple if they be considered as secondary results, and will accord in their proportions with the oxygen and hydrogen evolved from water by the action of a definite quantity of electricity.

751. I have experimented upon many bodies, with a view to determine whether the results were primary or secondary. I have been surprised to find how many of them, in ordinary cases, are of the latter class, and how frequently water is the only body electrolyzed in instances where other substances have been supposed to give way. Some of these results I will give in as few words as possible.

752. *Nitric acid.*—When very strong, it conducted well, and yielded oxygen at the positive electrode. No gas appeared at the negative electrode; but nitrous acid, and apparently nitric oxide, were formed there, which, dissolving, rendered the acid yellow or red, and at last even effervescent, from the spontaneous separation of nitric oxide. Upon diluting the acid with its bulk or more of water, gas appeared at the negative electrode. Its quantity could be varied by variations, either in the strength of the acid or of the voltaic current: for that acid from which no gas separated at the *cathode*, with a weak voltaic battery, did evolve gas there with a stronger; and that battery which evolved no gas there, with a strong acid, did cause its evolution with an acid more dilute. The gas at the *anode* was always oxygen; that at the *cathode* hydrogen. When the quantity of products was examined by the volta-electro-

meter (707.), the oxygen, whether from strong or weak acid, proved to be in the same proportion as from water. When the acid was diluted to specific gravity 1·24, or less, the hydrogen also proved to be the same in quantity as from water. Hence I conclude that the nitric acid does not undergo electro-chemical decomposition, but the water only; that the oxygen at the *anode* is always a primary result, but that the products at the *cathode* are often secondary, and due to the reaction of the hydrogen upon the nitric acid.

753. *Nitre.*—A solution of this salt yields very variable results, according as one or other form of tube is used, or as the electrodes are large or small. Sometimes the whole of the hydrogen of the water decomposed may be obtained at the negative electrode; at other times, only a part of it, because of the ready formation of secondary results. The solution is a very excellent conductor of electricity.

754. *Nitrate of ammonia,* in aqueous solution, gives rise to secondary results very varied and uncertain in their proportions.

755. *Sulphurous acid.*—Pure liquid sulphurous acid does not conduct nor suffer decomposition by the voltaic current *, but, when dissolved in water, the solution acquires conducting power, and is decomposed, yielding oxygen at the *anode*, and hydrogen and sulphur at the *cathode*.

756. A solution containing sulphuric acid in addition, was a better conductor. It gave very little gas at either electrode: that at the *anode* was oxygen, that at the *cathode* pure hydrogen. From the *cathode* also rose a white turbid stream, consisting of diffused sulphur, which soon rendered the whole solution milky. The volumes of gases were in no regular proportion to the quantities evolved from water in the volta-electrometer. I conclude that the sulphurous acid was not at all affected by the electric current in any of these cases, and that the water present was the only body electro-chemically decomposed; that, at the *anode*, the oxygen from the water converted the sulphurous acid into sulphuric acid, and, at the *cathode*, the hydrogen electrically evolved decomposed the sulphurous acid, combining with its oxygen, and setting its sulphur free. I conclude that the sulphur at the negative electrode was only a secondary result; and, in fact, no part of it was found combined with the small portion of hydrogen which escaped when weak solutions of sulphurous acid were used.

757. *Sulphuric acid.*—I have already given my reasons for concluding that sulphuric acid is not electrolyzable, i. e. not decomposable directly by the electric current, but occasionally suffering by a secondary action at the *cathode* from the hydrogen evolved there (681.). In the year 1800, DAVY considered the sulphur from sulphuric acid as the result of the action of the nascent hydrogen †. In 1804, HISINGER and BERZELIUS stated that it was the direct result of the action of the voltaic pile ‡; an opinion which from that time DAVY seems to have adopted, and which has since been

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* See also DE LA RIVE, Bibliothèque Universelle, tom. xl. p. 205 ; or Quarterly Journal of Science, vol. xxvii. p. 407.

† Nicholson's Quarterly Journal, vol. iv. pp. 280, 281.   ‡ Annales de Chimie, 1804, tom. li. p. 173.

commonly received by all. The change of my own opinion requires that I should correct what I have already said of the decomposition of sulphuric acid in a former series of these Researches (552.) : I do not now think that the appearance of the sulphur at the negative electrode is an immediate consequence of electrolytic action.

758. *Muriatic acid.*—A strong solution gave hydrogen at the negative electrode, and chlorine only at the positive electrode ; of the latter, a part acted on the platina and a part was dissolved. A minute bubble of gas remained ; it was not oxygen, but probably air previously held in solution.

759. It was an important matter to determine whether the chlorine was a primary result, or only a secondary product, due to the action of the oxygen evolved from water at the *anode* upon the muriatic acid ; i. e. whether the muriatic acid was electrolyzable, and if so, whether the decomposition was *definite*.

760. The muriatic acid was gradually diluted. One part with six of water gave only chlorine at the *anode*. One part with eight of water gave only chlorine ; with nine of water, a little oxygen appeared with the chlorine : but the occurrence or non-occurrence of oxygen at these strengths depended, in part, on the strength of the voltaic battery used. With fifteen parts of water, a little oxygen, with much chlorine, was evolved at the *anode*. As the solution was now becoming a bad conductor of electricity, sulphuric acid was added to it : this caused more ready decomposition, but did not sensibly alter the proportion of chlorine and oxygen.

761. The muriatic acid was now diluted with 100 times its volume of dilute sulphuric acid. It still gave a large proportion of chlorine at the *anode*, mingled with oxygen ; and the result was the same, whether a voltaic battery of 40 pairs of plates or one containing only 5 pairs were used. With acid of this strength, the oxygen evolved at the *anode* was to the hydrogen at the *cathode*, in volume, as 17 is to 64 ; and therefore the chlorine would have been 30 volumes, had it not been dissolved by the fluid.

762. Next, with respect to the quantity of elements evolved. On using the volta-electrometer, it was found that, whether the strongest or the weakest muriatic acid were used, whether chlorine alone or chlorine mingled with oxygen appeared at the *anode*, still the hydrogen evolved at the *cathode* was a constant quantity, i. e. exactly the *same* as the hydrogen which the *same quantity of electricity* could evolve from water.

763. This constancy does not decide whether the muriatic acid is electrolyzed or not, although it proves that if so, it must be in definite proportions to the quantity of electricity used. Other considerations may, however, be allowed to decide the point. The analogy between chlorine and oxygen, in their relations to hydrogen, is so strong, as to lead almost to the certainty, that, when combined with that element, they would perform similar parts in the process of electro-decomposition. They both unite with it in single proportional or equivalent quantities ; and, the number of proportionals appearing to have an intimate and important relation to the decomposability of a

body (697.), those in muriatic acid, as well as in water, are the most favourable, or those, perhaps even necessary, to decomposition. In other binary compounds of chlorine also, where nothing equivocal depending on the simultaneous presence of it and oxygen is involved, the chlorine is directly eliminated at the *anode* by the electric current. Such is the case with the chloride of lead (395.), which may be justly compared with protoxide of lead (402.), and stands in the same relation to it as muriatic acid to water. The chlorides of potassium, sodium, barium, &c., are in the same relation to the protoxides of the same metals, and present the same results under the influence of the electric current (402.).

764. From all the experiments, combined with these considerations, I conclude that muriatic acid is decomposed by the direct influence of the electric current, and that the quantities evolved are, and therefore the chemical action is, *definite for a definite quantity of electricity*. For though I have not collected and measured the chlorine, in its separate state, at the *anode*, there can exist no doubt as to its being proportional to the hydrogen at the *cathode*; and the results are therefore sufficient to establish the general law of *constant electro-chemical action* in the case of muriatic acid.

765. In the dilute acid (761.), I conclude that a part of the water is electro-chemically decomposed, giving origin to the oxygen, which appears mingled with the chlorine at the *anode*. The oxygen *may* be viewed as a secondary result; but I incline to believe that it is not so: for, if it were, it might be expected in largest proportion from the stronger acid, whereas the reverse is the fact. This consideration, with others, also leads me to conclude that muriatic acid is more easily decomposed by the electric current than water; since, even when diluted with eight or nine times its quantity of the latter fluid, it alone gives way, the water remaining unaffected.

766. *Chlorides.*—On using solutions of chlorides in water,—for instance, the chlorides of sodium or calcium,—there was evolution of chlorine only at the positive electrode, and of hydrogen, with the oxide of the base, as soda or lime, at the negative electrode. The process of decomposition may be viewed as proceeding in two or three ways, all terminating in the same results. Perhaps the simplest is to consider the chloride as the substance electrolyzed, its chlorine being determined to and evolved at the *anode*, and its metal passing to the *cathode*, where, finding no more chlorine, it acts upon the water, producing hydrogen and an oxide as secondary results. As the discussion would detain me from more important matter, and is not of immediate consequence, I shall defer it for the present. It is, however, of *great consequence* to state, that, on using the volta-electrometer, the hydrogen in both cases was definite; and if the results do not prove the definite decomposition of chlorides, (which shall be proved elsewhere,—789. 794. 814.,) they are not in the slightest degree opposed to such a conclusion, and *do* support the *general law*.

767. *Hydriodic acid.*—A solution of hydriodic acid was affected exactly in the same manner as muriatic acid. When strong, hydrogen was evolved at the negative electrode, in definite proportion to the quantity of electricity which had passed, i. e. in

the same proportion as was evolved by the same current from water; and iodine with out any oxygen was evolved at the positive electrode. But when diluted, small quantities of oxygen appeared with the iodine at the *anode*, the proportion of hydrogen at the *cathode* remaining undisturbed.

768. I believe the decomposition of the hydriodic acid in this case to be direct, for the reasons already given respecting muriatic acid (763. 764.).

769. *Iodides.*—A solution of iodide of potassium being subjected to the voltaic current, iodine appeared at the positive electrode (without any oxygen), and hydrogen with free alkali at the negative electrode. The same observations as to the mode of decomposition are applicable here as were made in relation to the chlorides when in solution (766.).

770. *Hydro-fluoric acid and fluorides.*—Solution of hydro-fluoric acid did not appear to be decomposed under the influence of the electric current : it was the water which gave way apparently. The fused fluorides were electrolyzed (417.); but having during these actions obtained *fluorine* in the separate state, I think it better to refer to a future series of these Researches, in which I purpose giving a fuller account of the results than would be consistent with propriety here.

771. *Hydro-cyanic acid* in solution conducts very badly. The definite proportion of hydrogen (equal to that from water) was set free at the *cathode*, whilst at the *anode* a small quantity of oxygen was evolved and apparently a solution of cyanogen formed. The action altogether corresponded with that on a dilute muriatic or hydriodic acid. When the hydro-cyanic acid was made a better conductor by sulphuric acid, the same results occurred.

Cyanides.—With a solution of the cyanide of potassium, the result was precisely the same as with a chloride or iodide. No oxygen was evolved at the positive electrode, but a brown solution formed there. For the reasons given when speaking of the chlorides (766.), and because a fused cyanide of potassium evolves cyanogen at the positive electrode*, I incline to believe that the cyanide in solution is *directly* decomposed.

772. *Ferro-cyanic acid* and the *ferro-cyanides*, as also *sulpho-cyanic acid* and the *sulpho-cyanides*, presented results corresponding with those just described (771.).

773. *Acetic acid.* Glacial acetic acid, when fused (405.), is not decomposed by, nor does it conduct, electricity. On adding a little water to it, still there were no signs of action; on adding more water, it acted slowly and about as water alone would do. Dilute sulphuric acid was added to it in order to make it a better conductor ; then the definite proportion of hydrogen was evolved at the *cathode,* and a mixture of oxygen in very deficient quantity, with carbonic acid, and a little carbonic oxide, at the *anode.* Hence it appears that acetic acid is not electrolyzable, but that a portion of it is decomposed by the oxygen evolved at the *anode,* producing secondary results,

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* It is a very remarkable thing to see carbon and nitrogen in this case determined powerfully towards the positive surface of the voltaic battery; but it is perfectly in harmony with the theory of electro-chemical decomposition which I have advanced.

varying with the strength of the acid, the intensity of the current, and other circum-stances.

774. *Acetates.*—One of these has been referred to already, as affording only se-condary results relative to the acetic acid (749.). With many of the metallic acetates the results at both electrodes are secondary (746. 750.).

Acetate of soda fused and anhydrous is directly decomposed, being, as I believe, a true electrolyte, and evolving soda and acetic acid at the *cathode* and *anode*. These, however, have no sensible duration, but are immediately resolved into other sub-stances; charcoal, sodiuretted hydrogen, &c., being set free at the former, and as far as I could judge under the circumstances, acetic acid mingled with carbonic oxide, carbonic acid, &c., at the latter.

775. *Tartaric acid.*—Pure solution of tartaric acid is almost as bad a conductor as pure water. On adding sulphuric acid to it, it conducted well, the results at the positive electrode being primary or secondary in different proportions, according to variations in the strength of the acid and the power of the electric current (752.). Alkaline tartrates gave a large proportion of secondary results at the positive elec-trode. The hydrogen at the negative electrode remained constant unless certain me-tallic salts were used.

776. Solutions of salts containing other vegetable acids, as the benzoates; of sugar, gum, &c., dissolved in dilute sulphuric acid; of resin, albumen, &c., dissolved in alkalies, were in turn submitted to the electrolytic power of the voltaic current. In all these cases, secondary results to a greater or smaller extent were produced at the positive electrode.

777. In concluding this division of these Researches, it cannot but occur to the mind that the final result of the action of the electric current upon substances placed between the electrodes, instead of being simple may be very complicated. There are two modes by which these substances may be decomposed, either by the direct force of the electric current, or by the action of bodies which that current may evolve. There are also two modes by which new compounds may be formed, i. e. by combi-nation of the evolving substances whilst in their nascent state (658.), directly with the matter of the electrode; or else their combination with those bodies, which being contained in, or associated with, the decomposing conductor, are necessarily present at the *anode* and *cathode*. The complexity is rendered still greater by the circumstance that two or more of these actions may occur simultaneously, and also in variable pro-portions to each other. But it may in a great measure be resolved by attention to the principles already laid down (747.).

778. When *aqueous* solutions of bodies are used, secondary results are exceedingly frequent. Even when the water is not present in large quantity, but is merely that of combination, still secondary results often ensue: for instance, it is very possible that in Sir HUMPHRY DAVY's decomposition of the hydrates of potassa and soda, a part of the potassium produced was the result of a secondary action. Hence, also, a frequent

cause for the disappearance of the oxygen and hydrogen which would otherwise be evolved: and when hydrogen does *not* appear at the *cathode* in an *aqueous solution*, it perhaps always indicates that a secondary action has taken place there. No exception to this rule has as yet occurred to my observation.

779. Secondary actions are *not confined to aqueous solutions*, or cases where water is present. For instance, various chlorides acted upon, when fused (402.), by platina electrodes, have the chlorine determined electrically to the *anode*. In many cases, as with the chlorides of lead, potassium, barium, &c., the chlorine acts on the platina and forms a compound with it, which dissolves; but when protochloride of tin is used, the chlorine at the *anode* does not act upon the platina, but upon the chloride already there, forming a perchloride which rises in vapour (790. 804.). These are, therefore, instances of secondary actions of both kinds, produced in bodies containing no water.

780. The production of boron from fused borax (402. 417.) is also a case of secondary action; for boracic acid is not decomposable by electricity (408.), and it was the sodium evolved at the *cathode* which, reacting on the boracic acid around it, took oxygen from it and set boron free in the experiments formerly described.

781. Secondary actions have already, in the hands of M. BECQUEREL, produced many interesting results in the formation of compounds; some of them new, others imitations of those occurring naturally*. It is probable they may prove equally interesting in an opposite direction, i. e. as affording cases of analytic decomposition. Much information regarding the composition, and perhaps even the arrangement of the particles of such bodies as the vegetable acids and alkalies, and organic compounds generally, will probably be obtained by submitting them to the action of nascent oxygen, hydrogen, chlorine, &c., at the electrodes; and the action seems the more promising, because of the thorough command which we possess over attendant circumstances, such as the strength of the current, the size of the electrodes, the nature of the decomposing conductor, its strength, &c., all of which may be expected to have their corresponding influence upon the final result.

782. It is to me a great satisfaction that the extreme variety of secondary results have presented nothing opposed to the doctrine of a constant and definite electrochemical action, to the particular consideration of which I shall now proceed.

¶ vii. *On the definite nature and extent of Electro-chemical Decomposition.*

783. In the third series of these Researches, after proving the identity of electricities derived from different sources, and showing, by actual measurement, the extraordinary quantity of electricity evolved by a very feeble voltaic arrangement (371. 376.), I announced a law, derived from experiment, which seemed to me of the utmost importance to the science of electricity in general, and that branch of it denominated electro-chemistry in particular. The law was expressed thus: *The chemical power of*

* Annales de Chimie, tom. xxxv. p. 113.

a current of electricity is in direct proportion to the absolute quantity of electricity which passes (377.).

784. In the further progress of the successive investigations, I have had frequent occasion to refer to the same law, occasionally in circumstances offering powerful corroboration of its truth (456. 504. 505.) ; and the present series already supplies numerous new cases in which it holds good (704. 722. 726. 732.). It is now my object to consider this great principle more closely, and to develope some of the consequences to which it leads. That the evidence for it may be the more distinct and applicable, I shall quote cases of decomposition subject to as few interferences from secondary results as possible, effected upon bodies very simple, yet very definite in their nature.

785. In the first place, I consider the law as so fully established with respect to the decomposition of *water*, and under so many circumstances which might be supposed, if anything could, to exert an influence over it, that I may be excused entering into further detail respecting that substance, or even summing up the results here (732). I refer, therefore, to the whole of the subdivision of this series of Researches which contains the account of the *volta-electrometer*.

786. In the next place, I also consider the law as established with respect to *muriatic acid* by the experiments and reasoning already advanced, when speaking of that substance, in the subdivision respecting primary and secondary results (758, &c.).

787. I consider the law as established also with regard to *hydriodic acid* by the experiments and considerations already advanced in the preceding division of this series of Researches (767. 768.).

788. Without speaking with the same confidence, yet from the experiments described, and many others not described, relating to hydro-fluoric, hydro-cyanic, ferro-cyanic, and sulpho-cyanic acids (770. 771. 772.), and from the close analogy which holds between these bodies and the hydro-acids of chlorine, iodine, bromine, &c., I consider these also as coming under subjection to the law, and assisting to prove its truth.

789. In the preceding cases, except the first, the water is believed to be inactive ; but to avoid any ambiguity arising from its presence, I sought for substances from which it should be absent altogether ; and, taking advantage of the law of conduction already developed (380. &c.), soon found abundance, amongst which *protochloride of tin* was first subjected to decomposition in the following manner. A piece of platina wire had one extremity coiled up into a small knob, and having been carefully weighed, was sealed hermetically into a piece of bottle-glass tube, so that the knob should be at the bottom of the tube within (fig. 13.). The tube was suspended by a piece of platina wire, so that the heat of a spirit-lamp could be applied to it. Recently fused proto-chloride of tin was introduced in sufficient quantity to occupy, when melted, about one half of the tube ; the wire of the tube was connected with a volta-electrometer (711.), which was itself connected with the negative end of a voltaic battery ; and a platina wire connected with the positive end of the same battery was dipped into the

fused chloride in the tube; being, however, so bent, that it could not by any shake of the hand or apparatus touch the negative electrode at the bottom of the vessel. The whole arrangement is delineated fig. 14.

790. Under these circumstances the chloride of tin was decomposed: the chlorine evolved at the positive electrode formed bichloride of tin (779.), which passed away in fumes, and the tin evolved at the negative electrode combined with the platina, forming an alloy, fusible at the temperature to which the tube was subjected, and therefore never occasioning metallic communication entirely through the decomposing chloride. When the experiment had been continued so long as to yield a reasonable quantity of gas in the volta-electrometer, the battery connexion was broken, the positive electrode removed, and the tube and remaining chloride allowed to cool. When cold, the tube was broken open, the rest of the chloride and the glass being easily separable from the platina wire and its button of alloy. The latter when washed was then reweighed, and the increase gave the weight of the tin reduced.

791. I will give the particular results of one experiment, in illustration of the mode adopted in this and others, the results of which I shall have occasion to quote. The negative electrode weighed at first 20 grains; after the experiment it, with its button of alloy, weighed 23·2 grains. The tin evolved by the electric current at the *cathode* weighed, therefore, 3·2 grains. The quantity of oxygen and hydrogen collected in the volta-electrometer = 3·85 cubic inches. As 100 cubic inches of oxygen and hydrogen, in the proportions to form water, may be considered as weighing 12·92 grains, the 3·85 cubic inches would weigh 0·49742 of a grain; that being, therefore, the weight of water decomposed by the same electric current as was able to decompose such weight of protochloride of tin as could yield 3·2 grains of metal. Now 0·49742 : 3·2 :: 9 the equivalent of water is to 57·9, which should therefore be the equivalent of tin, if the experiment had been made without error, and if the electro-chemical decomposition *is in this case also definite*. In some chemical works 58 is given as the chemical equivalent of tin, in others 57·9. Both are so near to the result of the experiment, and the experiment itself is so subject to slight causes of variation (as from the absorption of gas in the volta-electrometer (716.), &c.), that the numbers leave little doubt of the applicability of the *law of definite action* in this and all similar cases of electro-decomposition.

792. It is not often I have obtained an accordance in numbers so near as that I have just quoted. Four experiments were made on the protochloride of tin, the quantities of gas evolved in the volta-electrometer being from 2·05 to 10·29 cubic inches. The average of the four experiments gave 58·53 as the electro-chemical equivalent for tin.

793. The chloride remaining after the experiment, was pure protochloride of tin; and no one can doubt for a moment that the equivalent of chlorine had been evolved at the *anode*, and having formed bichloride of tin as a secondary result, had passed away.

794. *Chloride of lead* was experimented upon in a manner exactly similar, except that a change was made in the nature of the positive electrode; for as the chlorine evolved at the *anode* forms no perchloride of lead, but acts directly upon the platina, if that metal be used, it produces a solution of chloride of platina in the chloride of lead; in consequence of which a portion of platina can pass to the *cathode*, and will produce a vitiated result. I therefore sought for, and found in plumbago, another substance, which could be used safely as the positive electrode in such bodies as chlorides, iodides, &c. The chlorine or iodine does not act upon it, but is evolved in the free state; and the plumbago has no reaction, under the circumstances, upon the fused chloride or iodide in which it is plunged. Even if a few particles of plumbago should separate by the heat or the mechanical action of the evolved gas, they can do no harm in the chloride.

795. The mean of three experiments gave the number of 100·85 as the equivalent for lead. The chemical equivalent is 103·5. The deficiency in my experiments I attribute to the solution of part of the gas (716.) in the volta-electrometer; but the results leave no doubt on my mind that both the lead and the chlorine are, in this case, evolved in *definite quantities* by the action of a given quantity of electricity (814. &c.).

796. *Chloride of antimony.*—It was in endeavouring to obtain the electro-chemical equivalent of antimony from the chloride that I found reasons for the statement I have made respecting the presence of water in it in an earlier part of these Researches (690. 693. &c.).

797. I endeavoured to experiment upon the *oxide of lead* obtained by fusion and ignition of the nitrate in a platina crucible, but found great difficulty, from the high temperature required for perfect fusion, and the powerful fluxing qualities of the substance. Green glass tubes repeatedly failed. I at last fused the oxide in a small porcelain crucible, heated fully in a charcoal fire; and as it was essential that the evolution of the lead at the *cathode* should take place beneath the surface, the negative electrode was guarded by a green glass tube, fused around it in such a manner as to expose only the knob of platina at the lower end (fig. 15.), so that it could be plunged beneath the surface, and thus exclude contact of air or oxygen with the lead reduced there. A platina wire was employed for the positive electrode, that metal not being subject to any action from the oxygen evolved against it. The arrangement is given fig. 16.

798. In an experiment of this kind the equivalent for the lead came out 93·17, which is very much too small. This, I believe, was because of the small interval between the positive and negative electrodes in the oxide of lead, so that it was not unlikely that some of the froth and bubbles formed by the oxygen at the *anode* should occasionally even touch the lead reduced at the *cathode*, and re-oxidize it. When I endeavoured to correct this by having more litharge, the greater heat required to keep it all fluid caused a quicker action on the crucible, which was soon eaten through, and the experiment stopped.

799. In one experiment of this kind I used borate of lead (408. 673.). It evolves lead, under the influence of the electric current, at the *anode*, and oxygen at the *cathode*; and as the boracic acid is not either directly (408.) or incidentally decomposed during the operation, I expected a result dependent on the oxide of lead. The borate is not so violent a flux as the oxide, but it requires a higher temperature to make it quite liquid; and if not very hot, the bubbles of oxygen cling to the positive electrode, and retard the transfer of electricity. The number for lead came out 101·29, which is so near to 103·5 as to show that the action of the current had been definite.

800. *Oxide of bismuth.*—I found this substance required too high a temperature, and acted too powerfully as a flux, to allow of any experiment being made on it, without the application of more time and care than I could give at present.

801. The ordinary *protoxide of antimony*, which consists of one proportional of metal and one and a half of oxygen, was subjected to the action of the electric current in a green glass tube (789.), surrounded by a jacket of platina foil, and heated in a charcoal fire. The decomposition began and proceeded very well at first, apparently indicating, according to the general law (679. 697.), that this substance was one containing such elements and in such proportions as made it amenable to the power of the electric current. This effect I have already given reasons for supposing may be due to the presence of a true protoxide, consisting of single proportionals (696. 693.). The action soon diminished, and finally ceased, because of the formation of a higher oxide of the metal at the positive electrode. This compound, which was probably the peroxide, being infusible and insoluble in the protoxide, formed a crystalline crust around the positive electrode; and thus insulating it, prevented the transmission of the electricity. Whether if it had been fusible and still immiscible it would have decomposed, is doubtful, because of its departure from the required composition (697.). It was a very natural secondary product at the positive electrode (779.). On opening the tube it was found that a little antimony had been separated at the negative electrode; but the quantity was too small to allow of any quantitative result being obtained.

802. *Iodide of lead.*—This substance can be experimented with in tubes heated by a spirit-lamp (789.); but I obtained no good results from it, whether I used positive electrodes of platina or plumbago. In two experiments the numbers for the lead came out only 75·46 and 73·45, instead of 103·5. This I attribute to the formation of a periodide at the positive electrode, which dissolving in the mass of liquid iodide, came in contact with the lead evolved at the negative electrode, and dissolved part of it, becoming itself again protiodide. Such a periodide does exist; and it is very rarely that the iodide of lead formed by precipitation, and well washed, can be fused without evolving much iodine, from the presence of this percompound; nor does crystallization from its hot aqueous solution free it from this substance. Even when a little of the protiodide and iodine are merely rubbed together in a mortar, a portion of the periodide is formed. And though it is decomposed by being fused and heated

to dull redness for a few minutes, and the whole reduced to protiodide, yet that is not at all opposed to the possibility, that a little of that which is formed in great excess of iodine at the *anode*, should be carried by the rapid currents in the liquid into contact with the *cathode*.

803. This view of the results was strengthened by a third experiment, where the space between the electrodes was increased to one third of an inch; for now the interfering effects were much diminished, and the number of the lead came out 89·04; and it was fully confirmed by the results obtained in the cases of transfer to be immediately described (818.).

The experiments on iodide of lead, therefore, offer no exception to the *general law* under consideration, but, on the contrary, may, from general considerations, be admitted as included in it.

804. *Protiodide of tin.*—This substance, when fused (402.), conducts and is decomposed by the electric current, tin is evolved at the *anode*, and periodide of tin as a secondary result (779. 790.) at the *cathode*. The temperature required for its fusion is too high to allow of the production of any results fit for weighing.

805. *Iodide of potassium* was subjected to electrolytic action in a tube, fig. 13. (789.). The negative electrode was a globule of lead, and I hoped in this way to retain the potassium, and obtain results that could be weighed and compared with the volta-electrometer indication; but the difficulties dependent upon the high temperature required, the action upon the glass, the fusibility of the platina induced by the presence of the lead, and other circumstances, prevented me from obtaining such results. The iodide was decomposed with the evolution of iodine at the *anode*, and of potassium at the *cathode*, as in former cases.

806. In some of these experiments several substances were placed in succession, and decomposed simultaneously by the same electric current: thus, protochloride of tin, chloride of lead, and water, were thus acted on at once. It is needless to say that the results were comparable, the tin, lead, chlorine, oxygen, and hydrogen evolved being definite in quantity and electro-chemical equivalents to each other.

807. Let us turn to another kind of proof of the *definite chemical action of electricity*. If any circumstances could be supposed to exert an influence over the quantity of the matters evolved during electrolytic action, one would expect them to be present when electrodes of different substances, and possessing very different chemical affinities for the evolving bodies, were used. Platina has no power in dilute sulphuric acid of combining with the oxygen at the *anode*, though the latter be evolved in the nascent state against it. Copper, on the other hand, immediately unites to the oxygen, as the electric current sets it free from the hydrogen; and zinc is not only able to combine with it, but can, without any help from the electricity, abstract it directly from the water, at the same time setting torrents of hydrogen free. Yet in cases where these three substances were used as the positive electrodes in three similar portions of the same dilute sulphuric acid, specific gravity 1·336, precisely the same quantity of water

was decomposed by the electric current, and precisely the same quantity of hydrogen set free at the *cathodes* of the three solutions.

808. The experiment was made thus. Portions of the dilute sulphuric acid were put into three basins. Three volta-electrometer tubes, of the form figg. 5, 7. were filled with the same acid, and one inverted in each basin (707.). A zinc plate, connected with the positive end of a voltaic battery, was dipped into the first basin, forming the positive electrode there, the hydrogen, which was abundantly evolved from it by the direct action of the acid, being allowed to escape. A copper plate, which dipped into the acid of the second basin, was connected with the negative electrode of the *first* basin; and a platina plate, which dipped into the acid of the third basin, was connected with the negative electrode of the *second* basin. The negative electrode of the third basin was connected with a volta-electrometer (711.), and that with the negative end of the voltaic battery.

809. Immediately that the circuit was complete, the *electro-chemical action* commenced in all the vessels. The hydrogen still rose in, apparently, undiminished quantities from the positive zinc electrode in the first basin. No oxygen was evolved at the positive copper electrode in the second basin, but a sulphate of copper was formed there; whilst in the third basin the positive platina electrode evolved pure oxygen gas, and was itself unaffected. But in *all* the basins the hydrogen liberated at the *negative* platina electrodes was the *same in quantity*, and the same with the volume of hydrogen evolved in the volta-electrometer, showing that in all the vessels the current had decomposed an equal quantity of water. In this trying case, therefore, the *chemical action of electricity* proved to be *perfectly definite*.

810. A similar experiment was made with muriatic acid diluted with its bulk of water. The three positive electrodes were zinc, silver, and platina; the first being able to separate and combine with the chlorine *without* the aid of the current; the second combining with the chlorine only after the current had set it free; and the third rejecting almost the whole of it. The three negative electrodes were, as before, platina plates fixed within glass tubes. In this experiment, as in the former, the quantity of hydrogen evolved at the *cathodes* was the same for all, and the same as the hydrogen evolved in the volta-electrometer. I have already given my reasons for believing that in these experiments it is the muriatic acid which is directly decomposed by the electricity (764.); and the results prove that the quantities so decomposed are *perfectly definite* and proportionate to the quantity of electricity which has passed.

811. In this experiment the chloride of silver formed in the second basin retarded the passage of the current of electricity, by virtue of the law of conduction before described (394.), so that it had to be cleaned off four or five times during the course of the experiment; but this caused no difference between the results of that vessel and the others.

812. Charcoal was used as the positive electrode in both sulphuric and muriatic acids (808. 810.); but this change produced no variation of the results. A zinc positive

electrode, in sulphate of soda or solution of common salt, gave the same constancy of operation.

813. Experiments of a similar kind were then made with bodies altogether in a different state, i. e. with *fused* chlorides, iodides, &c. I have already described an experiment with fused chloride of silver, in which the electrodes were of metallic silver, the one rendered negative becoming increased and lengthened by the addition of metal, whilst the other was dissolved and eaten away by its abstraction. This experiment was repeated, two weighed pieces of silver wire being used as the electrodes, and a volta-electrometer included in the circuit. Great care was taken to withdraw the negative electrode so regularly and steadily that the crystals of reduced silver should not form a *metallic* communication beneath the surface of the fused chloride. On concluding the experiment the positive electrode was re-weighed, and its loss ascertained. The mixture of chloride of silver, and metal, withdrawn in successive portions at the negative electrode, was digested in solution of ammonia, to remove the chloride, and the metallic silver remaining also weighed : it was the reduction at the *cathode*, and exactly equalled the solution at the *anode* ; and each portion was as nearly as possible the equivalent to the water decomposed in the volta-electrometer.

814. The infusible condition of the silver at the temperature used, and the length and ramifying character of its crystals, render the above experiment difficult to perform, and uncertain in its results. I therefore wrought with a chloride of lead, using a green glass tube, formed as in fig. 17. A weighed platina wire was fused into the bottom of a small tube, as before described (789.). The tube was then bent to an angle, at about half an inch distance from the closed end; and the part between the angle and the extremity being softened, was forced upward, as in the figure, so as to form a bridge, or rather separation, producing two little depressions or basins *a, b*, within the tube. This arrangement was suspended by a platina wire, as before, so that the heat of a spirit-lamp could be applied to it, such inclination being given to it as would allow all air to escape during the fusion of the chloride of lead. A positive electrode was then provided, by binding up the end of a platina wire into a knob, and fusing about twenty grains of metallic lead on to it, in a small closed tube of glass, which was afterwards broken away. Being so furnished, the wire with its knob was weighed, and the weight recorded.

815. Chloride of lead was now introduced into the tube, and carefully fused. The leaded electrode was also introduced; after which the metal, at its extremity, soon melted. In this state of things the tube was filled up to *c* with melted chloride of lead ; the end of the electrode to be rendered negative was in the basin *b*, and the electrode of melted lead was retained in the basin *a*, and, by connexion with the proper conducting wire of a voltaic battery, was rendered positive. A volta-electrometer was included in the circuit.

816. Immediately upon the completion of the communication with the voltaic battery, the current passed, and decomposition proceeded. No chlorine was evolved at

the positive electrode; but as the fused chloride was transparent, a button of alloy could be observed gradually forming and increasing in size at *b*, whilst the lead at *a* could also be seen gradually to diminish. After a time, the experiment was stopped; the tube allowed to cool, and broken open; the wires, with their buttons, cleaned and weighed; and their change in weight compared with the indication of the *volta-electrometer*.

817. In this experiment the positive electrode had lost just as much lead as the negative one had gained (795.), and the loss or gain was very nearly the equivalent of the water decomposed in the volta-electrometer, giving for lead the number 101·5. It is therefore evident, in this instance, that causing a *strong affinity*, or *no affinity*, for the substance evolved at the *anode*, to be active during the experiment (807.), produces no variation in the definite action of the electric current.

818. A similar experiment was then made with iodide of lead, and in this manner all confusion from the formation of a periodide avoided (803.). No iodine was evolved during the whole action, and finally the loss of lead at the *anode* was the same as the gain at the *cathode*, the equivalent number, by comparison with the result in the volta-electrometer, being 103·5.

819. Then protochloride of tin was subjected to the electric current in the same manner, using, of course, a tin positive electrode. No bichloride of tin was now formed (779. 790.). On examining the two electrodes, the positive had lost precisely as much as the negative had gained; and by comparison with the volta-electrometer, the number for tin came out 59.

820. It is quite necessary in these and similar experiments to examine the interior of the bulbs of alloy at the ends of the conducting wires; for occasionally, and especially with those which have been positive, they are cavernous, and contain portions of the chloride or iodide used, which must be removed before the final weight is ascertained. This is more usually the case with lead than tin.

821. All these facts combine into, I think, an irresistible mass of evidence, proving the truth of the important proposition which I at first laid down, namely, *that the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes* (377. 783.). They prove, too, that this is not merely true with one substance, as water, but generally with all electrolytic bodies; and, further, that the results obtained with any *one substance* do not merely agree amongst themselves, but also with those obtained from *other substances*, the whole combining together into *one series of definite electro-chemical actions* (505.). I do not mean to say that no exceptions will appear: perhaps some may arise, especially amongst substances existing only by weak affinity; but I do not expect that any will seriously disturb the result announced. If, in the well considered, well examined, and, I may surely say, well ascertained doctrines of the definite nature of ordinary chemical affinity, such exceptions occur, as they do in abundance, yet, without being allowed to disturb our minds as to the general conclusion, they ought also to be allowed if they should

present themselves at this, the opening of a new view of electro-chemical action; not being held up as obstructions to those who may be engaged in rendering that view more and more perfect, but laid aside for a while, in hopes that their perfect and consistent explanation will finally appear.

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822. The doctrine of *definite electro-chemical action* just laid down, and, I believe, established, leads to some new views of the relations and classifications of bodies associated with or subject to this action.   Some of these I shall proceed to consider.

823. In the first place, compound bodies may be separated into two great classes, namely, those which are decomposable by the electric current, and those which are not. Of the latter, some are conductors, others non-conductors, of voltaic electricity*. The former do not depend for their decomposability, upon the nature of their elements only; for, of the same two elements, bodies may be formed, of which one shall belong to one class and another to the other class; but probably on the proportions also (697.).   It is further remarkable, that with very few, if any, exceptions (414. 691.), these decomposable bodies are exactly those governed by the remarkable law of conduction I have before described (394.); for that law does not extend to the many compound fusible substances that are excluded from this class.   I propose to call bodies of this, the decomposable class, *Electrolytes* (664.).

824. Then, again, the substances into which these divide, under the influence of the electric current, form an exceedingly important general class.   They are combining bodies; are directly associated with the fundamental parts of the doctrine of chemical affinity; and have each a definite proportion, in which they are always evolved during electrolytic action.   I have proposed to call these bodies generally *ions*, or particularly *anions* and *cations*, according as they appear at the *anode* or *cathode* (665.); and the numbers representing the proportions in which they are evolved *electro-chemical equivalents*.   Thus hydrogen, oxygen, chlorine, iodine, lead, tin, are *ions*; the three former are *anions*, the two metals are *cations*, and 1, 8, 36, 125, 104, 58, are their *electro-chemical equivalents* nearly.

825. A summary of certain points already ascertained respecting *electrolytes*, *ions*, and *electro-chemical equivalents*, may be given in the following general form of propositions, without, I hope, including any serious error.

826. i. A single *ion*, i. e. one not in combination with another, will have no tendency to pass to either of the electrodes, and will be perfectly indifferent to the passing current, unless it be itself a compound of more elementary *ions*, and so subject to actual decomposition.   Upon this fact is founded much of the proof adduced in favour of the new theory of electro-chemical decomposition, which I put forth in a former series of these Researches (518. &c.).

827. ii. If one *ion* be combined in right proportions (697.) with another strongly

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* I mean here by voltaic electricity, merely electricity from a most abundant source, but having very small intensity.

opposed to it in its ordinary chemical relations, i. e. if an *anion* be combined with a *cation*, then both will travel, the one to the *anode*, the other to the *cathode*, of the decomposing body (530. 542. 547.).

828. iii. If, therefore, an *ion* pass towards one of the electrodes, another *ion* must also be passing simultaneously to the other electrode, although, from secondary action, it may not make its appearance (743.).

829. iv. A body decomposable directly by the electric current, i. e. an *electrolyte*, must consist of two *ions*, and must also render them up during the act of decomposition.

830. v. There is but one *electrolyte* composed of the same two elementary *ions*; at least such appears to be the fact (697.), dependent upon a law, that *only single electro-chemical equivalents of elementary ions can go to the electrodes, and not multiples*.

831. vi. A body not decomposable when alone, as boracic acid, is not directly decomposable by the electric current when in combination (780.). It may act as an *ion*, going wholly to the *anode* or *cathode*, but does not yield up its elements, except occasionally by a secondary action. Perhaps it is superfluous for me to point out that this proposition has *no relation* to such cases as that of water, which, by the presence of other bodies, is rendered a better conductor of electricity, and *therefore* is more freely decomposed.

832. vii. The nature of the substance of which the electrode is formed, provided it be a conductor, causes no difference in the electro-decomposition, either in kind or degree (807. 813.); but it seriously influences, by secondary action (744.), the state in which the *ions* finally appear. Advantage may be taken of this principle in combining and collecting such *ions* as, if evolved in their free state, would be unmanageable *.

833. viii. A substance which, being used as the electrode, can combine altogether with the *ion* evolved against it, is also, I believe, an *ion*, and combines, in such cases, in the quantity represented by its *electro-chemical equivalent*. All the experiments I have made agree with this view; and it seems to me, at present, to result as a necessary consequence. Whether, in the secondary actions that take place, where the *ion* acts, not upon the matter of the electrode, but on that which is around it in the liquid (744.), the same consequence follows, will require more extended investigation to determine.

834. ix. Compound *ions* are not necessarily composed of electro-chemical equivalents of simple *ions*. For instance, sulphuric acid, boracic acid, phosphoric acid, are *ions*, but not *electrolytes*, i. e. not composed of electro-chemical equivalents of simple *ions*.

* It will often happen that the electrodes used may be of such a nature as, with the fluid in which they are immersed, to produce an electric current, either according with or opposing that of the voltaic arrangement used, and in this way, or by direct chemical action, may sadly disturb the results. Still, in the midst of all these confusing effects, the electric current, which actually passes in any direction through the decomposing body, will produce its own definite electrolytic action.

835. x. Electro-chemical equivalents are always consistent; i. e. the same number which represents the equivalent of a substance A when it is separating from a substance B, will also represent A when separating from a third substance C. Thus, 8 is the electro-chemical equivalent of oxygen, whether separating from hydrogen, or tin, or lead; and 103·5 is the electro-chemical equivalent of lead, whether separating from oxygen, or chlorine, or iodine.

836. xi. Electro-chemical equivalents coincide, and are the same, with ordinary chemical equivalents.

837. By means of experiment and the preceding propositions, a knowledge of *ions* and their electro-chemical equivalents may be obtained in various ways.

838. In the first place, they may be determined directly, as has been done with hydrogen, oxygen, lead, and tin, in the numerous experiments already quoted.

839. In the next place, from propositions ii. and iii., may be deduced the knowledge of many other *ions*, and also their equivalents. When chloride of lead was decomposed, platina being used for both electrodes (395.), there could remain no more doubt that chlorine was passing to the *anode*, although it combined with the platina there, than when the positive electrode, being of plumbago (794.), allowed its evolution in the free state; neither could there, in either case, remain any doubt, that for every 103·5 parts of lead evolved at the *cathode*, 36 parts of chlorine were evolved at the *anode*, for the remaining chloride of lead was unchanged. So also when in a metallic solution one volume of oxygen, or a secondary compound containing that proportion, appeared at the *anode*, no doubt could arise that hydrogen, equivalent to two volumes, had been determined to the *cathode*, although, by a secondary action, it had been employed in reducing oxides of lead, copper, or other metals, to the metallic state. In this manner, then, we learn from the experiments already described in these Researches, that chlorine, iodine, bromine, fluorine, calcium, potassium, strontium, magnesium, manganese, &c., are *ions*, and that their *electro-chemical equivalents* are the same as their *ordinary chemical equivalents*.

840. Propositions iv. and v. extend our means of gaining information. For if a body of known chemical composition is found to be decomposable, and the nature of the substance evolved as a primary or even a secondary result (743. 777.) at one of the electrodes, be ascertained, the electro-chemical equivalent of that body may be deduced from the known constant composition of the substance evolved. Thus, when fused protiodide of tin is decomposed by the voltaic current (804.), the conclusion may be drawn, that both the iodine and tin are *ions*, and that the proportions in which they combine in the fused compound express their electro-chemical equivalents. Again, with respect to the fused iodide of potassium (805.), it is an electrolyte; and the chemical equivalents will also be the electro-chemical equivalents.

841. If proposition viii. sustain extensive experimental investigation, then it will not only help to confirm the results obtained by the use of the other propositions, but will give abundant original information of its own.

842. In many instances, the *secondary results* obtained by the action of the evolving *ion* on the substances present in the surrounding liquid or solution, will give the electro-chemical equivalent. Thus, in the solution of acetate of lead, and, as far as I have gone, in other proto-salts subjected to the reducing action of the nascent hydrogen at the *cathode*, the metal precipitated has been in the same quantity as if it had been a primary product, (provided no free hydrogen escaped there,) and therefore gave as accurately the number representing its electro-chemical equivalent.

843. Upon this principle it is that secondary results may occasionally be used as measurers of the volta-electric current (706. 740.) ; but there are not many metallic solutions that answer this purpose well : for unless the metal is easily precipitated, hydrogen will be evolved at the *cathode* and vitiate the result. If a soluble peroxide is formed at the *anode*, or if the precipitated metal crystallize across the solution and touch the positive electrode, similar vitiated results are obtained. I expect to find in some vegetable salts, as the acetates of mercury and zinc, solutions favourable for this use.

844. After the first experimental investigations to establish the definite chemical action of electricity, I have not hesitated to apply the more strict results of chemical analysis to correct the numbers obtained as electrolytical results. This, it is evident, may be done in a great number of cases, without using too much liberty towards the due severity of scientific research. The series of numbers representing electro-chemical equivalents must, like those expressing the ordinary equivalents of chemically acting bodies, remain subject to the continual correction of experiment and sound reasoning.

845. I give the following brief Table of *ions* and their electro-chemical equivalents, rather as a specimen of a first attempt than as anything that can supply the want which must very quickly be felt, of a full and complete tabular account of this class of bodies. Looking forward to such a table as of extreme utility (if well constructed) in developing the intimate relation of ordinary chemical affinity to electrical actions, and identifying the two, not to the imagination merely, but to the conviction of the senses and a sound judgement, I may be allowed to express a hope, that the endeavour will always be to make it a table of *real*, and not *hypothetical*, electro-chemical equivalents ; for we shall else overrun the facts, and lose all sight and consciousness of the knowledge lying directly in our path.

846. The equivalent numbers do not profess to be exact, and are taken almost entirely from the chemical results of other philosophers in whom I could repose more confidence, as to these points, than in myself.

847. TABLE OF IONS.

Anions.

Oxygen 8	Cyanogen 26	Phosphoric acid.... 35·7	Citric acid 58
Chlorine.......... 35·5	Sulphuric acid 40	Carbonic acid 22	Oxalic acid 36
Iodine 126	Selenic acid 64	Boracic acid 24	Sulphur (?) 16
Bromine.......... 78·3	Nitric acid........ 54	Acetic acid........ 51	Selenium (?) ......
Fluorine.......... 18·7	Chloric acid ...... 75·5	Tartaric acid 66	Sulpho-cyanogen ..

Cations.

Hydrogen	1	Tin	57·9	Mercury	200	Strontia	51·8
Potassium	39·2	Lead	103·5	Silver	108	Lime	28·5
Sodium	23·3	Iron	28	Platina	98·6?	Magnesia	20·7
Lithium	10	Copper	31·6	Gold	(?)	Alumina	(?)
Barium	68·7	Cadmium	55·8			Protoxides generally.	
Strontium	43·8	Cerium	46	Ammonia	17	Quinia	171·6
Calcium	20·5	Cobalt	29·5	Potassa	47·2	Cinchona	160
Magnesium	12·7	Nickel	29·5	Soda	31·3	Morphia	290
Manganese	27·7	Antimony	64·6?	Lithia	18	Vegeto-alkalies generally.	
Zinc	32·5	Bismuth	71	Baryta	76·7		

848. This Table might be further arranged into groups of such substances as either act with, or replace, each other. Thus, for instance, acids and bases act in relation to each other; but they do not act in association with oxygen, hydrogen, or elementary substances. There is indeed little or no doubt that, when the electrical relations of the particles of matter come to be closely examined, this division must be made. The simple substances, with cyanogen, sulpho-cyanogen, and one or two other compound bodies, will probably form the first group; and the acids and bases, with such analogous compounds as may prove to be *ions*, the second group. Whether these will include all *ions*, or whether a third class of more complicated results will be required, must be decided by future experiments.

849. It is *probable* that all our present elementary bodies are *ions*, but that is not as yet certain. There are some, such as carbon, phosphorus, nitrogen, silicon, boron, alumium, the right of which to the title of *ion* it is desirable to decide as soon as possible. There are also many compound bodies, and amongst them alumina and silica, which it is desirable to class immediately by unexceptionable experiments. It is also *possible*, that all combinable bodies, compound as well as simple, may enter into the class of *ions*; but at present it does not seem to me probable. Still the experimental evidence I have is so small in proportion to what must gradually accumulate around, and bear upon, this point, that I am afraid to give a strong opinion upon it.

850. I think I cannot deceive myself in considering the doctrine of definite electro-chemical action as of the utmost importance. It touches by its facts more directly and closely than any former fact, or set of facts, have done, upon the beautiful idea, that ordinary chemical affinity is a mere consequence of the electrical attractions of the particles of different kinds of matter; and it will probably lead us to the means by which we may enlighten that which is at present so obscure, and either fully demonstrate the truth of the idea, or develope that which ought to replace it.

851. A very valuable use of electro-chemical equivalents will be to decide, in cases of doubt, what is the true chemical equivalent, or definite proportional, or atomic number of a body; for I have such conviction that the power which governs electro-decomposition and ordinary chemical attractions is the same; and such confidence in the overruling influence of those natural laws which render the former definite, as to

feel no hesitation in believing that the latter must submit to them also. Such being the case, I can have no doubt that, assuming hydrogen as 1, and dismissing small fractions for the simplicity of expression, the equivalent number or atomic weight of oxygen is 8, of chlorine 36, of bromine 78·4, of lead 103·5, of tin 59, &c., notwithstanding that a very high authority doubles several of these numbers.

§ 13. *On the absolute quantity of Electricity associated with the particles or atoms of Matter.*

852. The theory of definite electrolytical or electro-chemical action appears to me to touch immediately upon the *absolute quantity* of electricity or electric power belonging to different bodies. It is impossible, perhaps, to speak on this point without committing oneself beyond what present facts will sustain; and yet it is equally impossible, and perhaps would be impolitic, not to reason upon the subject. Although we know nothing of what an atom is, yet we cannot resist forming some idea of a small particle, which represents it to the mind; and though we are in equal, if not greater, ignorance of electricity, so as to be unable to say whether it is a particular matter or matters, or mere motion of ordinary matter, or some third kind of power or agent, yet there is an immensity of facts which justify us in believing that the atoms of matter are in some way endowed or associated with electrical powers, to which they owe their most striking qualities, and amongst them their mutual chemical affinity. As soon as we perceive, through the teaching of DALTON, that chemical powers are, however varied the circumstances in which they are exerted, definite for each body, we learn to estimate the relative degree of force which resides in such bodies: and when upon that knowledge comes the fact, that the electricity, which we appear to be capable of loosening from its habitation for a while, and conveying from place to place, *whilst it retains its chemical force*, can be measured out, and, being so measured, is found to be *as definite in its action* as any of *those portions* which, remaining associated with the particles of matter, give them their *chemical relation*; we seem to have found the link which connects the proportion of that we have evolved to the proportion of that belonging to the particles in their natural state.

853. Now it is wonderful to observe how small a quantity of a compound body is decomposed by a certain portion of electricity. Let us, for instance, consider this and a few other points in relation to water. *One grain* of water acidulated to facilitate conduction, will require an electric current to be continued for three minutes and three quarters of time to effect its decomposition, which current must be powerful enough to retain a platina wire $\frac{1}{104}$ of an inch in thickness*, red hot, in the air during the whole time; and if interrupted anywhere by charcoal points, will produce a very

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* I have not stated the length of wire used, because I find by experiment, as would be expected in theory, that it is indifferent. The same quantity of electricity which, passed in a given time, can heat an inch of platina wire of a certain diameter red hot, can also heat a hundred, a thousand, or any length of the same wire to the same degree, provided the cooling circumstances are the same for every part in both cases. This I have proved by the volta-electrometer. I found that whether half an inch or eight inches were retained at one constant

brilliant and constant star of light. If attention be paid to the instantaneous discharge of electricity of tension, as illustrated in the beautiful experiments of Mr. WHEATSTONE*, and to what I have said elsewhere on the relation of common and voltaic electricity (371. 375.), it will not be too much to say, that this necessary quantity of electricity is equal to a very powerful flash of lightning. Yet we have it under perfect command; can evolve, direct, and employ it at pleasure; and when it has performed its full work of electrolyzation, it has only separated the elements of a single grain of water.

854. On the other hand, the relation between the conduction of the electricity and the decomposition of the water is so close, that one cannot take place without the other. If the water is altered only in that small degree which consists in its having the solid instead of the fluid state, the conduction is stopped, and the decomposition is stopped with it. Whether the conduction be considered as depending upon the decomposition, or not (413. 703.), still the relation of the two functions is equally intimate and inseparable.

855. Considering this close and twofold relation, namely, that without decomposition transmission of electricity does not occur; and, that for a given definite quantity of electricity passed, an equally definite and constant quantity of water or other matter is decomposed; considering also that the agent, which is electricity, is simply employed in overcoming electrical powers in the body subjected to its action; it seems a probable, and almost a natural consequence, that the quantity which passes is the *equivalent* of, and therefore equal to, that of the particles separated; i. e. that if the electrical power which holds the elements of a grain of water in combination, or which makes a grain of oxygen and hydrogen in the right proportions unite into water when they are made to combine, could be thrown into the condition of *a current*, it would exactly equal the current required for the separation of that grain of water into its elements again.

856. This view of the subject gives an almost overwhelming idea of the extraordinary quantity or degree of electric power which naturally belongs to the particles of matter; but it is not inconsistent in the slightest degree with the facts which can be brought to bear on this point. To illustrate this I must say a few words on the voltaic pile †.

temperature of dull redness, equal quantities of water were decomposed in equal times in both cases. When the half-inch was used, only the centre portion of wire was ignited. A fine wire may even be used as a rough but ready regulator of a voltaic current; for if it be made part of the circuit, and the larger wires communicating with it be shifted nearer to or further apart, so as to keep the portion of wire in the circuit sensibly at the same temperature, the current passing through it will be nearly uniform.

* Literary Gazette, 1833, March 1 and 8. Philosophical Magazine, 1833, p. 204. L'Institute, 1833, p. 261.

† By the term voltaic pile, I mean such apparatus or arrangement of metals as up to this time have been called so, and which contain water, brine, acids, or other aqueous solutions or decomposable substances (476.), between their plates. Other kinds of electric apparatus may be hereafter invented, and I hope to construct some not belonging to the class of instruments discovered by VOLTA.

857. Intending hereafter to apply the results given in this and the preceding series of Researches to a close investigation of the source of electricity in the voltaic instrument, I have refrained from forming any decided opinion on the subject; and without at all meaning to dismiss metallic contact, or the contact of dissimilar substances, being conductors, but not metallic, as if they had nothing to do with the origin of the current, I still am fully of opinion with Davy, that it is at least continued by chemical action, and that the supply constituting the current is almost entirely from that source.

858. Those bodies which, being interposed between the metals of the voltaic pile, render it active, *are all of them electrolytes* (476.); and it cannot but press upon the attention of every one engaged in considering this subject, that in those bodies (so essential to the pile) decomposition and the transmission of a current are so intimately connected, that one cannot happen without the other. This I have shown abundantly in water, and numerous other cases (402. 476.). If, then, a voltaic trough have its extremities connected by a decomposing body, as water, we shall have a continuous current through the apparatus; and whilst it remains in this state may look at the part where the acid is acting upon the plates, and that where the current is acting upon the water, as the reciprocals of each other. In both parts we have the two conditions *inseparable in such bodies as these,* namely, the passing of a current, and decomposition; and this is as true of the cells in the battery as of the water cell; for no voltaic battery has as yet been constructed in which the chemical action is only that of combination: decomposition is always included, and is, I believe, an essential chemical part.

859. But the difference in the two parts of the connected battery, that is, the decomposing or experimental cell, and the acting cells, is simply this. In the former we urge the current through, but it, apparently of necessity, is accompanied by decomposition: in the latter we cause decompositions by ordinary chemical actions, (which are, however, themselves electrical,) and, as a consequence, have the electrical current; and as the decomposition dependent upon the current is definite in the former case, so is the current associated with the decomposition also definite in the latter (862. &c.).

860. Let us apply this in support of what I have surmised respecting the enormous electric power of each particle or atom of matter (856.). I showed in a former series of these Researches on the relation by measure of common and voltaic electricity, that two wires, one of platina and one of zinc, each one eighteenth of an inch in diameter, placed five sixteenths of an inch apart, and immersed to the depth of five eighths of an inch in acid, consisting of one drop of oil of vitriol and four ounces of distilled water at a temperature of about 60° Fahr., and connected at the other extremities by a copper wire eighteen feet long, and one eighteenth of an inch in thickness, yielded as much electricity in little more than three seconds of time as a Leyden battery charged by thirty turns of a very large and powerful plate electric machine

in full action (371.). This quantity, though sufficient if passed at once through the head of a rat or a cat to have killed it, as by a flash of lightning, was evolved by the mutual action of so small a portion of the zinc wire and water in contact with it, that the loss of weight sustained by either would be inappreciable by our most delicate instruments; and as to the water which could be decomposed by that current, it must have been insensible in quantity, for no trace of hydrogen appeared upon the surface of the platina during those three seconds.

861. What an enormous quantity of electricity, therefore, is required for the decomposition of a single grain of water! We have already seen that it must be in quantity sufficient to sustain a platina wire $\frac{1}{104}$ of an inch in thickness, red hot, in contact with the air for three minutes and three quarters (853.), a quantity which is almost infinitely greater than that which could be evolved by the little standard voltaic arrangement to which I have just referred (860. 371.). I have endeavoured to make a comparison by the loss of weight of such a wire in a given time in such an acid, according to a principle and experiment to be almost immediately described (862.); but the proportion is so high, that I am almost afraid to mention it. It would appear that 800,000 such charges of the Leyden battery as I have referred to above, would be necessary to supply electricity sufficient to decompose a single grain of water; or, if I am right, to equal the quantity of electricity which is naturally associated with the elements of that grain of water, endowing them with their mutual chemical affinity.

862. In further proof of this high electric condition of the particles of matter, and the *identity as to quantity, of that belonging to them with that necessary for their separation,* I will describe an experiment of great simplicity but extreme beauty, when viewed in relation to the evolution of an electric current and its decomposing powers.

863. A dilute sulphuric acid, made by adding about one part by measure of oil of vitriol to thirty parts of water, will act energetically upon a piece of plate zinc in its ordinary and simple state; but, as Mr. STURGEON has shown*, not at all, or scarcely so, if the surface of the metal has in the first instance been amalgamated; yet the amalgamated zinc will act powerfully with platina as an electromotor, hydrogen being evolved on the surface of the latter metal, as the zinc is oxidized and dissolved. The amalgamation is best effected by sprinkling a few drops of mercury upon the surface of the zinc, the latter being moistened with the dilute acid, and rubbing with the fingers so as to extend the liquid metal over the whole of the surface. Any mercury in excess forming liquid drops upon the zinc, should be wiped off†.

864. Two plates of zinc thus amalgamated were dried and accurately weighed; one, which we will call A, weighed 163·1 grains; the other, to be called B, weighed 148·3

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* Recent Experimental Researches, &c., 1830, p. 74, &c.

† The experiment may be made with pure zinc, which, as chemists well know, is but slightly acted upon by dilute sulphuric acid in comparison with ordinary zinc, which during the action is subject to an infinity of voltaic actions. See DE LA RIVE on this subject, Bibliothèque Universelle, 1830, p. 391.

grains. They were about five inches long, and 0·4 of an inch wide. An earthenware pneumatic trough was filled with dilute sulphuric acid, of the strength just described (863.), and a gas jar, also filled with the acid, inverted in it*. A plate of platina of nearly the same length, but about three times as wide as the zinc plates, was put up into this jar. The zinc plate A was also introduced into the jar, and brought in contact with the platina, and at the same moment the plate B was put into the acid of the trough, but out of contact with other metallic matter.

865. Strong action immediately occurred in the jar upon the contact of the zinc and platina plates. Hydrogen gas rose from the platina, and was collected in the jar, but no hydrogen or other gas rose from *either* zinc plate. In about ten or twelve minutes, sufficient hydrogen having been collected, the experiment was stopped; during its progress a few small bubbles had appeared upon plate B, but none upon plate A. The plates were washed in distilled water, dried, and reweighed. Plate B weighed 148·3 grains, as before, having lost nothing by the direct chemical action of the acid. Plate A weighed 154·65 grains, 8·45 grains of it having been oxidized and dissolved during the experiment.

866. The hydrogen gas was next transferred to a water-trough and measured; it amounted to 12·5 cubic inches, the temperature being 52°, and the barometer 29·2 inches. This quantity, corrected for temperature, pressure, and moisture, becomes 12·15453 cubic inches of dry hydrogen at mean temperature and pressure; which, increased by one half for the oxygen that must have gone to the *anode*, i. e. to the zinc, gives 18·232 cubic inches as the quantity of oxygen and hydrogen evolved from the water decomposed by the electric current. According to the estimate of the weight of the mixed gas before adopted (791.), this volume is equal to 2·3535544 grains, which therefore is the weight of water decomposed; and this quantity is to 8·45, the quantity of zinc oxidized, as 9 is to 32·31. Now taking 9 as the equivalent number of water, the number 32·5 is given as the equivalent number of zinc; a coincidence sufficiently near to show, what indeed could not but happen, that for an equivalent of zinc oxidized an equivalent of water must be decomposed†.

867. But let us observe *how* the water is decomposed. It is electrolyzed, i. e. is decomposed voltaically, and not in the ordinary manner (as to appearance) of chemical decompositions; for the oxygen appears at the *anode* and the hydrogen at the *cathode* of the decomposing body, and these were in many parts of the experiment above an inch asunder. Again, the ordinary chemical affinity was not enough under the circumstances to effect the decomposition of the water, as was abundantly proved by the inaction on plate B; the voltaic current was essential. And to prevent any idea that the chemical affinity was almost sufficient to decompose the water, and that a smaller current of electricity might, under the circumstances, cause the hydrogen to

* The acid was left during a night with a small piece of unamalgamated zinc in it, for the purpose of evolving such air as might be inclined to separate, and bringing the whole into a constant state.

† The experiment was repeated several times with the same results.

pass to the *cathode*, I need only refer to the results which I have given (807. 813.) to show that the chemical action at the electrodes has not the slightest influence over the *quantities* of water or other substances decomposed between them, but that they are entirely dependent upon the quantity of electricity which passes.

868. What, then, follows as a necessary consequence of the whole experiment? Why, this: that the chemical action upon 32·31 parts, or one equivalent of zinc, in this simple voltaic circle, was able to evolve such quantity of electricity in the form of a current as, passing through water, should decompose 9 parts, or one equivalent of that substance: and, considering the definite relations of electricity as developed in the preceding parts of the present paper, the results prove that the quantity of electricity which, being naturally associated with the particles of matter, gives them their combining power, is able, when thrown into a current, to separate those particles from their state of combination; or, in other words, that *the electricity which decomposes, and that which is evolved by the decomposition of, a certain quantity of matter, are alike.*

869. The harmony which this theory of the definite evolution and the equivalent definite action of electricity introduces into the associated theories of definite proportions and electro-chemical affinity, is very great. According to it, the equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity, or have naturally equal electric powers; it being the ELECTRICITY which *determines* the equivalent number, *because* it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalents to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them. But I must confess I am jealous of the term *atom*; for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration.

870. I cannot refrain from recalling here the beautiful idea put forth, I believe, by BERZELIUS (703.) in his development of his views of the electro-chemical theory of affinity, that the heat and light evolved during cases of powerful combination are the consequence of the electric discharge which is at the moment taking place. The idea is in perfect accordance with the view I have taken of the *quantity* of electricity associated with the particles of matter.

871. In this exposition of the law of the definite action of electricity, and its corresponding definite proportion in the particles of bodies, I do not pretend to have brought, as yet, every case of chemical or electro-chemical action under its dominion. There are numerous considerations of a theoretical nature, especially respecting the compound particles of matter and the resulting electrical forces which they ought to possess, which I hope will gradually receive their development; and there are numerous experimental cases, as, for instance, those of compounds formed by weak affinities, the simultaneous decomposition of water and salts, &c., which still require

investigation. But whatever the results on these and numerous other points may be, I do not believe that the facts which I have advanced, or even the general laws deduced from them, will suffer any serious change; and they are of sufficient importance to justify their publication, even though much may remain imperfect or undone. Indeed, it is the great beauty of our science, CHEMISTRY, that advancement in it, whether in a degree great or small, instead of exhausting the subjects of research, opens the doors to further and more abundant knowledge, overflowing with beauty and utility to those who will be at the easy personal pains of undertaking its experimental investigation.

872. The definite production of electricity (868.) in association with its definite action proves, I think, that the current of electricity in the voltaic pile is sustained by chemical decomposition, or rather by chemical action, and not by contact only. But here, as elsewhere (857.), I beg to reserve my opinion as to the real action of contact, not having yet been able to make up my mind as to its being either an exciting cause of the current, or merely necessary to allow of the conduction of electricity, otherwise generated, from one metal to the other.

873. But admitting that chemical action is the source of electricity, what an infinitely small fraction of that which is active do we obtain and employ in our voltaic batteries ! Zinc and platina wires, one eighteenth of an inch in diameter and about half an inch long, dipped into dilute sulphuric acid, so weak that it is not sensibly sour to the tongue, or scarcely to our most delicate test papers, will evolve more electricity in one twentieth of a minute (860.) than any man would willingly allow to pass through his body at once. The chemical action of a grain of water upon four grains of zinc can evolve electricity equal in quantity to that of a powerful thunder-storm (868. 861.). Nor is it merely true that the quantity is active; it can be directed and made to perform its full equivalent duty (867. &c.). Is there not, then, great reason to hope and believe that, by a closer *experimental* investigation of the principles which govern the development and action of this subtile agent, we shall be able to increase the power of our batteries, or invent new instruments which shall a thousandfold surpass in energy those which we at present possess ?

874. Here for a while I must leave the consideration of the *definite chemical action of electricity*. But before I dismiss this series of experimental Researches, I would call to mind that, in a former series, I showed the current of electricity was also *definite in its magnetic action* (366. 367. 376. 377.); and, though this result was not pursued to any extent, I have no doubt that the success which has attended the development of the chemical effects is not more than would accompany an investigation of the magnetic phenomena.

Royal Institution,
December 31st, 1833.