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XXVIII. *Experimental Researches in Electricity.—Fifth Series.*

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§ 11. *On Electro-chemical Decomposition.* ¶ i. *New conditions of Electro-chemical Decomposition.* ¶ ii. *Influence of Water in Electro-chemical Decomposition.* ¶ iii. *Theory of Electro-chemical Decomposition.*

§ 11. *On Electro-chemical Decomposition.*

450. I HAVE in a recent series of these Researches (265.) proved (to my own satisfaction, at least,) the identity of electricities derived from different sources, and have especially dwelt upon the proofs of the sameness of those obtained by the use of the common electrical machine and of the voltaic battery.

451. The great distinction of the electricities obtained from these two sources is the very high tension to which the small quantity obtained by aid of the machine may be raised, and the enormous quantity (371. 376.) in which that of comparatively low tension, supplied by the voltaic battery, may be procured; but as their actions, whether magnetical, chemical, or of any other nature, are essentially the same (360.), it appeared evident that we might reason from the former as to the manner of action of the latter; and it was to me a probable consequence, that the use of electricity of such intensity as that afforded by the machine, would, when applied to effect and elucidate electro-chemical decomposition, show some new conditions of that action, evolve new views of the internal arrangements and changes of the substances under decomposition, and perhaps give efficient powers over matter as yet undecomposed.

452. For the purpose of rendering the bearings of the different parts of this series of researches more distinct, I shall divide it into several heads.

¶ i. *New conditions of Electro-chemical Decomposition.*

453. The tension of machine electricity causes it, however small in quantity, to pass through any length of water, solutions, or other substances classing with these as conductors, as fast as it can be produced, and therefore, in relation to quantity, as fast as it could have passed through much shorter portions of the same conducting substance. With the voltaic battery the case is very different, and the passing current of electricity supplied by it suffers serious diminution in any substance, by considerable extension of its length, but especially in such bodies as those mentioned above.

454. I endeavoured to apply this facility of transmitting the current of electricity through any length of a conductor, to an investigation of the transfer of the elements in a decomposing body, in contrary directions, towards the poles. The general form of apparatus used in these experiments has been already described (312. 316.); and also a particular experiment (319.), in which, when a piece of litmus paper and a piece of turmeric paper were combined and moistened in solution of sulphate of soda, the point of the wire from the machine (representing the positive pole) put upon the litmus paper, and the receiving point from the discharging train (292. 316.), representing the negative pole, upon the turmeric paper, a very few turns of the machine sufficed to show the evolution of acid at the former, and alkali at the latter, exactly in the manner effected by a volta-electric current.

455. The pieces of litmus and turmeric paper were now placed each upon a separate plate of glass, and connected by an insulated string four feet long, moistened in the same solution of sulphate of soda: the terminal decomposing wire points were placed upon the papers as before. On working the machine, the same evolution of acid and alkali appeared as in the former instance, and with equal readiness, notwithstanding that the places of their appearance were four feet apart from each other. Finally, a piece of string, seventy feet long, was used. It was insulated in the air by suspenders of silk, so that the electricity passed through its entire length: decomposition took place exactly as in former cases, alkali and acid appearing at the two extremities in their proper places.

456. Experiments were then made both with sulphate of soda and iodide of potassium, to ascertain if any diminution of decomposing effect was pro-

duced by such great extension of the moist conductor or body under decomposition; but whether the contact of the decomposing point connected with the discharging train was made with turmeric paper touching the prime conductor, or with other turmeric paper connected with it through the seventy feet of string, the spot of alkali for an equal number of turns of the machine had equal intensity of colour. The same results occurred at the other decomposing wire, whether the salt or the iodide were used; and it was fully proved that this great extension of the distance between the poles produced no effect whatever on the amount of decomposition, provided the same *quantity* of electricity were passed in both cases (377.).

457. The negative point of the discharging train, the turmeric paper, and the string were then removed; the positive point was left resting upon the litmus paper, and the latter touched by a piece of moistened string held in the hand. A few turns of the machine evolved acid at the positive point as freely as before.

458. The end of the moistened string, instead of being held in the hand, was suspended by glass in the air. On working the machine the electricity proceeded from the conductor through the wire point to the litmus paper, and thence away by the intervention of the string to the air, so that there was (as in the last experiment,) but one metallic pole; still acid was evolved there as freely as in any former case.

459. When any of these experiments were repeated with electricity from the negative conductor, corresponding effects were produced whether one or two decomposing wires were used. The results were always constant, being considered in relation to the *direction* of the electric current.

460. These experiments were varied so as to include the action of only one metallic pole, but that not the pole connected with the machine. Turmeric paper was moistened in solution of sulphate of soda, placed upon glass, and connected with the discharging train (292.) by a decomposing wire (312.); a piece of wet string was hung from it, the lower extremity of which was brought opposite a point connected with the positive prime conductor of the machine. The machine was then worked for a few turns, and alkali immediately appeared at the point of the discharging train which rested on the turmeric paper. Corresponding effects took place at the negative conductor of a machine.

461. These cases are abundantly sufficient to show that electro-chemical de-

composition does not depend upon the simultaneous action of two metallic poles, since a single pole might be used, decomposition ensue, and one or other of the elements liberated, pass to the pole, according as it was positive or negative. In considering the course taken by, and the final arrangement of, the other element, I had little doubt that I should find it had receded towards the other extremity, and that the air itself had acted as a pole, an expectation which was fully confirmed in the following manner.

462. A piece of turmeric paper, not more than 0·4 of an inch in length and 0·05 of an inch in width, was moistened with sulphate of soda and placed upon the edge of a glass plate opposite to, and about two inches from, a point connected with the discharging train (Plate XIX. fig. 1.); a piece of tinfoil, resting upon the same glass plate, was connected with the machine, and also with the turmeric paper, by a decomposing wire *a* (312). The machine was then worked, the positive electricity passing into the turmeric paper at the point *p*, and out at the extremity *n*. After forty or fifty turns of the machine, the extremity *n* was examined, and the two points or angles found deeply coloured by the presence of free alkali (fig. 2.).

463. A similar piece of litmus paper, dipped in solution of sulphate of soda *n*, fig. 3, was now supported upon the end of the discharging train *a*, and its extremity brought opposite a point *p*, connected with the conductor of the machine. After working the machine for a short time, acid was developed at both the corners towards the point, i. e. at both the corners receiving the electricities from the air. Every precaution was taken to prevent this acid from being formed by sparks or brushes passing through the air (322.); and these, with the accompanying general facts, are sufficient to show that the acid was really the result of electro-chemical decomposition (466.).

464. Then a long piece of turmeric paper, large at one end and pointed at the other, was moistened in the saline solution, and immediately connected with the conductor of the machine, so that its pointed extremity was opposite a point upon the discharging train. When the machine was worked, alkali was evolved at that point; and even when the discharging train was removed, and the electricity left to be diffused and carried off altogether by the air, still alkali was evolved where the electricity left the turmeric paper.

465. Arrangements were then made in which no metallic communication

with the decomposing matter was allowed, but both poles (if they might now be called by that name,) formed of air only. A piece of turmeric paper *a*, fig. 4, and a piece of litmus paper *b*, were dipped in solution of sulphate of soda, put together so as to form one moist pointed conductor, and supported on wax between two needle points, one *p* connected by a wire with the conductor of the machine, and the other, *n*, with the discharging train. The interval in each case between the points was about half an inch: the positive point *p* was opposite the litmus paper; the negative point *n* opposite the turmeric. The machine was then worked for a time, upon which evidence of decomposition quickly appeared, for the point of the litmus *b* became reddened from acid evolved there, and the point of the turmeric *a* red from a similar and simultaneous evolution of alkali.

466. Upon turning the paper conductor round, so that the litmus point should now give off the positive electricity, and the turmeric point receive it, and working the machine for a short time, both the red spots disappeared, and as on continuing the action of the machine no red spot was re-formed at the litmus extremity, it proved that in the first instance (463.) the effect was not due to the action of brushes or mere electric discharges causing the formation of nitric acid from the air (322.).

467. If the combined litmus and turmeric paper in this experiment be considered as constituting a conductor independent of the machine or the discharging train, and the final places of the elements evolved be considered in relation to this conductor, then it will be found that the acid collects at the *negative* or receiving end or pole of the arrangement, and the alkali at the *positive* or delivering extremity.

468. Similar litmus and turmeric paper points were now placed upon glass plates, and connected by a string six feet long, both string and paper being moistened in solution of sulphate of soda; a needle point connected with the machine was brought opposite the litmus paper point, and another needle point connected with the discharging train brought opposite the turmeric paper. On working the machine, acid appeared on the litmus, and alkali on the turmeric paper; but the latter was not so abundant as in former cases, for much of the electricity passed off from the string into the air, and diminished the quantity discharged at the turmeric point.

469. Finally, a series of four small compound conductors, consisting of litmus and turmeric paper (fig. 5.) moistened in solution of sulphate of soda, were supported on glass rods, in a line at a little distance from each other, between the points *p* and *n* of the machine and discharging train, so that the electricity might pass in succession through them, entering in at the litmus points *b*, *b*, and passing out at the turmeric points *a*, *a*. On working the machine carefully, so as to avoid sparks and brushes (322.), I soon obtained evidence of decomposition in each of the moist conductors, for all the litmus points exhibited free acid, and the turmeric points equally showed free alkali.

470. On using solutions of iodide of potassium, acetate of lead, &c., similar effects were obtained; but as they were all consistent with the results above described, I refrain from describing the appearances minutely.

471. These cases of electro-chemical decomposition are in their nature exactly of the same kind as those effected under ordinary circumstances by the voltaic battery, notwithstanding the great differences as to the presence or absence, or at least as to the nature of the parts usually called poles; and also of the final situation of the elements eliminated at the boundary electrified surfaces (467.). They indicate at once an internal action of the parts suffering decomposition, and appear to show that the power which is effectual in separating the elements is exerted there, and not at the poles. But I shall defer the consideration of this point for a short time (493. 518.), that I may previously consider another supposed condition of electro-chemical decomposition *.

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* I find (since making and describing these results,) from a note to Sir HUMPHRY DAVY's paper in the Philosophical Transactions, 1807, p. 31, that that philosopher, in repeating WOLLASTON's experiment of the decomposition of water by common electricity (327. 330.), used an arrangement somewhat like some of those I have described. He immersed a guarded platina point connected with the machine in distilled water, and dissipated the electricity from the water into the air by moistened filaments of cotton. In this way he states that he obtained oxygen and hydrogen *separately* from each other. This experiment, had I known of it, ought to have been quoted in an earlier series of these Researches (342.); but it does not remove any of the objections I have made to the use of WOLLASTON's apparatus as a test of true chemical action (331.).

¶ ii. *Influence of Water in Electro-chemical Decomposition.*

472. It is the opinion of several philosophers, that the presence of water is essential in electro-chemical decomposition, and also for the evolution of electricity by the voltaic battery itself. As the decomposing cell is merely one of the cells of the battery, into which particular substances are introduced for the purpose of experiment, it is probable that what is an essential condition in the one case is more or less so in the other. The opinion, therefore, that water is necessary to decomposition, may have been founded on the statement made by Sir HUMPHRY DAVY, that "there are no fluids known, except such as contain water, which are capable of being made the medium of connexion between the metals or metal of the voltaic apparatus*:" and again, "when any substance rendered fluid by heat, consisting of *water*, oxygen, and inflammable or metallic matter, is exposed to those wires, similar phenomena (of decomposition) occur†."

473. This opinion has, I think, been shown by other philosophers not to be accurate, though I do not know where to refer for a contradiction of it. Sir HUMPHRY DAVY himself said in 1801‡, that dry nitre, caustic potash and soda are conductors of galvanism when rendered fluid by a high degree of heat; but he must have considered them, or the nitre at least, as not suffering decomposition, for the statements above were made by him eleven years subsequently. In 1826 he also pointed out, that bodies not containing water, as *fused litharge* and *chlorate of potassa,* were sufficient to form, with platina and zinc, powerful electromotive circles§; but he is here speaking of the *production* of electricity in the pile, and not of its effects when evolved; nor do his words at all imply that any correction of his former distinct statements relative to *decomposition* was required.

474. I may refer to the last series of these Experimental Researches (380. 402.) as setting the matter at rest, by proving that there are hundreds of bodies equally influential with water in this respect. That amongst binary compounds, oxides, chlorides, iodides, and even sulphurets (402.) were effective; and

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[*] Elements of Chemical Philosophy, p. 169, &c.

[†] Ibid. pp. 144, 145.

[‡] Journal of the Royal Institution, 1802, p. 53.

[§] Philosophical Transactions, 1826, p. 406.

that amongst more complicated compounds, cyanides and salts, of equal efficacy, occurred in great numbers (402.).

475. Water, therefore, is in this respect merely one of a very numerous class of substances, instead of being the *only one* and *essential*; and it is of that class one of the worst as to its capability of facilitating conduction and suffering decomposition. The reasons why it obtained for a time an exclusive character which it so little deserved are evident, and consist, in the general necessity of a fluid condition (394.); in its being the *only one* of this class of bodies existing in the fluid state at common temperatures; its abundant supply as the great natural solvent; and its constant use in that character in philosophical investigations, because of its having less interfering, injurious, or complicating action upon the bodies, either dissolved or evolved, than any other substance.

476. The analogy of the decomposing or experimental cell to the other cells of the voltaic battery, renders it nearly certain that any of those substances which are decomposable when fluid, as described in my last paper (402.), would, if they could be introduced between the metallic plates of the pile, be equally effectual with water, if not more so. Sir HUMPHRY DAVY found that litharge and chlorate of potassa were thus effectual*. I have constructed various voltaic arrangements, and found the above conclusion to hold good. When any of the following substances in a fused state were interposed between copper and platina, voltaic action more or less powerful was produced. Nitre; chlorate of potassa; carbonate of potassa; sulphate of soda; chloride of lead, of sodium, of bismuth, of calcium; iodide of lead; oxide of bismuth; oxide of lead: the electric current was in the same direction as if acids had acted upon the metals. When any of the same substances, or phosphate of soda, were made to act on platina and iron, still more powerful voltaic combinations of the same kind were produced. When either nitrate of silver or chloride of silver was the fluid substance interposed, there was voltaic action, but the electric current was in the reverse direction.

¶ iii. *Theory of Electro-chemical Decomposition.*

477. The extreme beauty and value of electro-chemical decompositions have given to that power which the voltaic pile possesses of causing their occur-

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* Philosophical Transactions, 1826, p. 406.

rence an interest surpassing that of any other of its properties; for the power is not only intimately connected with the continuance, if not the production, of the electrical phenomena, but has furnished us with the most beautiful demonstrations of the nature of many compound bodies; has in the hands of **Becquerel** been employed in compounding bodies; has given us several new substances, and sustains us with the hope that when thoroughly understood it will produce many more.

478. What may be considered as the general facts of electro-chemical decomposition are agreed to by nearly all who have written on the subject. They consist in the separation of the decomposable substance acted upon into its proximate or sometimes ultimate principles, whenever both poles of the pile are in contact with that substance in a proper condition; in the evolution of these principles at distant points, i. e. at the poles of the pile where they are either finally set free or enter into union with the substance of the poles; and in the constant determination of the evolved elements or principles to particular poles according to certain well ascertained laws.

479. But the views of men of science vary much as to the nature of the action by which these effects are produced; and as it is certain that we shall be better able to apply the power when we really understand the manner in which it operates, this difference of opinion is a strong inducement to further inquiry. I have been led to hope that the following investigations might be considered, not as an increase of that which is doubtful, but a real addition to this branch of knowledge.

480. It will be needful that I briefly state the views of electro-chemical decomposition already put forth, that their present contradictory and unsatisfactory state may be seen before I give that which seems to me more accurately to agree with facts; and I have ventured to discuss them freely, trusting that I should give no offence to their high-minded authors; for I felt convinced that if I were right, they would be pleased that their views should serve as stepping-stones for the advance of science, and that if I were wrong, they would excuse the zeal which misled me, since it was exerted for the service of that great cause whose prosperity and progress they have desired.

481. **Grotthuss**, in the year 1805, wrote expressly on the decomposition of

liquids by voltaic electricity[*]. He considers the pile as an electric magnet, i. e. as an *attractive* agent; the poles having *attractive* and *repelling* powers. The pole from whence resinous electricity issues attracts hydrogen and repels oxygen, whilst that from which vitreous electricity proceeds attracts oxygen and repels hydrogen; so that each of the elements of a particle of water, for instance, is subject to an attractive and a repulsive force, acting in contrary directions, the centres of action of which are reciprocally opposed. The action of each force in relation to a molecule of water situated in the course of the electric current is in the inverse ratio of the square of the distance at which it is exerted, thus giving (it is stated) for such a molecule a *constant force*[†]. He explains the appearance of the elements at a distance from each other by referring to a succession of decompositions and recompositions occurring amongst the intervening particles[‡], and he thinks it probable that those which are about to separate at the poles unite to the two electricities there, and in consequence become gases[§].

482. Sir HUMPHRY DAVY's celebrated Bakerian Lecture on some chemical agencies of electricity was read in November 1806, and is almost entirely occupied in the consideration of *electro-chemical decompositions*. The facts are of the utmost value, and, with the general points established, are universally known. The mode of action by which the effects take place is stated very generally, so generally, indeed, that probably a dozen precise schemes of electro-chemical action might be drawn up, differing essentially from each other, yet all agreeing with the statement there given.

483. When Sir HUMPHRY DAVY uses more particular expressions, he seems to refer the decomposing effects to the attractions of the poles. This is the case in the "general expression of facts" given at pp. 28 and 29 of the Philosophical Transactions for 1807, also at p. 30. Again, at p. 160 of the Elements of Chemical Philosophy, he speaks of the great attracting powers of the surfaces of the poles. He mentions the probability of a succession of decompositions and recompositions throughout the fluid,—agreeing in that respect with GROTTHUSS[||];

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[*] Annales de Chimie, 1806, tom. lviii. p. 64.

[†] Ibid. pp. 66, 67, also tom. lxiii. p. 20.

[‡] Ibid. tom. lviii. p. 68, tom. lxiii. p. 20.

[§] Ibid. tom. lxiii. p. 34.

[||] Philosophical Transactions, 1807, pp. 29, 30.

and supposes that the attractive and repellent agencies may be communicated from the metallic surfaces throughout the whole of the menstruum*, being communicated from *one particle to another particle of the same kind*†, and diminishing in strength from the place of the poles to the middle point, which is necessarily neutral‡. In reference to this diminution of power at increased distances from the poles, he states that in a circuit of ten inches of water, solution of sulphate of potassa placed four inches from the positive pole, did not decompose; whereas when only two inches from that pole, it did render up its elements§.

484. When in 1826 Sir HUMPHRY DAVY wrote again on this subject, he stated that he found nothing to alter in the fundamental theory laid down in the original communication ||, and uses the terms attraction and repulsion apparently in the same sense as before ¶.

485. Messrs. RIFFAULT and CHOMPRÉ experimented on this subject in 1807. They came to the conclusion that the voltaic current caused decompositions throughout its whole course in the humid conductor, not merely as preliminary to the recompositions spoken of by GROTTHUSS and DAVY, but producing final separation of the elements in the *course* of the current, and elsewhere than at the poles. They considered the *negative* current as collecting and carrying the acids, &c., to the *positive* pole, and the *positive* current as doing the same duty with the bases, and collecting them at the *negative* pole. They likewise consider the currents as *more powerful* the nearer they are to their respective poles, and state that the positive current is *superior* in power to the negative current**.

486. M. BIOT is very cautious in expressing an opinion as to the cause of the separation of the elements of a compound body††. But as far as the effects can be understood, he refers them to the opposite electrical states of the portions of the decomposing substance in the neighbourhood of the two poles. The fluid is most positive at the positive pole; that state gradually diminishes to the middle distance, where the fluid is neutral or not electrical; but from thence to the negative pole it becomes more and more negative‡‡. When a particle of salt

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* Philosophical Transactions, 1807, p. 39.

† Ibid. p. 29.

‡ Ibid. p. 42.

§ Ibid. p. 42.

|| Ibid. 1826, p. 383.

¶ Ibid. pp. 389, 407, 415.

** Annales de Chimie, 1807, tom. lxiii. p. 83, &c.

†† Précis Elémentaire de Physique, 3^{me} edition, 1824, tom. i. p. 641.

‡‡ Ibid. p. 637.

is decomposed at the negative pole, the acid particle is considered as acquiring a negative electrical state from the pole stronger than that of the surrounding *undecomposed* particles, and is therefore repelled from amongst them, and from out of that portion of the liquid towards the positive pole, towards which also it is drawn by the attraction of the pole itself and the particles of positive *undecomposed* fluid around it [*].

487. M. BIOT does not appear to admit the successive decompositions and recompositions spoken of by GROTTHUSS, DAVY, &c. &c.; but seems to consider the substance whilst in transit as combined with, or rather attached to, the electricity for the time [†], and though it communicates this electricity to the surrounding undecomposed matter with which it is in contact, yet it retains during the transit a little superiority with respect to that kind which it first received from the pole, and is, by virtue of that difference, carried forward through the fluid to the opposite pole [‡].

488. This theory implies that decomposition takes place at both poles upon distinct portions of fluid, and not at all in the intervening parts. The latter serve merely as imperfect conductors, which, assuming an electric state, urge particles electrified more highly at the poles through them in opposite directions, by virtue of a series of ordinary electrical attractions and repulsions [§].

489. M. A. DE LA RIVE investigated this subject particularly, and published a paper on it in 1825 [||]. He thinks those who have referred the phenomena to the attractive powers of the poles, express the fact generally, rather than give any explication of it. He considers the results as due to an actual combination of the elements, or rather of half of them, with the electricities passing from the poles in consequence of a kind of play of affinities between the matter and electricity [¶]. The current from the positive pole combining with the hydrogen, or the bases it finds there, leaves the oxygen and acids at liberty, but carries the substances it is united with across to the negative pole, where, because of the peculiar character of the metal as a conductor [**], it is separated from them, entering the metal, and leaving the hydrogen or bases upon its surface. In the same manner the electricity from the negative pole sets the

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[*] Précis Elémentaire de Physique, 3^{me} edition, 1824, tom. i. pp. 641, 642.

[†] Ibid. p. 636.

[‡] Ibid. p. 642.

[§] Ibid. pp. 638, 642.

[||] Annales de Chimie, tom. xxviii. p. 190.

[¶] Ibid. pp. 200, 202.

[**] Ibid. p. 202.

hydrogen and bases which it finds there, free, but combines with the oxygen and acids, carries them across to the positive pole, and there deposits them *. In this respect M. DE LA RIVE's hypothesis accords in part with that of MM. RIFFAULT and CHOMPRÉ (485.).

490. M. DE LA RIVE considers the portions of matter which are decomposed to be those contiguous to *both* poles †. He does not admit with others the successive decompositions and recompositions in the whole course of the electricity through the humid conductor ‡, but thinks the middle parts are in themselves unaltered, or at least serve only to conduct the two contrary currents of electricity and matter which set off from the opposite poles §. The decomposition, therefore, of a particle of water, or a particle of salt, may take place at either pole, and when once effected, it is final for the time, no recombination taking place, except the momentary union of the transferred particle with the electricity be so considered.

491. The latest communication that I am aware of on the subject is by M. HACHETTE: its date is October 1832 ||. It is incidental to the description of the decomposition of water by the magneto-electric currents (346.). One of the results of the experiment is, that "it is not necessary, as has been supposed, that for the chemical decomposition of water, the action of the two electricities, positive and negative, should be simultaneous."

492. It is more than probable that many other views of electro-chemical decomposition may have been published, and perhaps amongst them some which, differing from those above, might, even in my own opinion, were I acquainted with them, obviate the necessity for the publication of my views. If such be the case, I have to regret my ignorance of them, and apologize to the authors.

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493. That electro-chemical decomposition does not depend upon any direct attraction and repulsion of the poles (meaning thereby the metallic terminations either of the voltaic battery, or ordinary electrical machine arrangements (312.),) upon the elements in contact with or near to them, appeared very evident from the experiments made in air (462, 465, &c.), when the substances evolved did not collect about any poles, but, in obedience to the direction

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* Annales de Chimie, tom. xxviii. p. 201.

† Ibid. pp. 197, 198.

‡ Ibid. pp. 192, 199.

§ Ibid. p. 200.

|| Ibid. tom. li. p. 73.

of the current, were evolved, and I would say ejected, at the extremities of the decomposing substance. But notwithstanding the extreme dissimilarity in the character of air and metals, and the almost total difference existing between them as to their mode of conducting electricity, and becoming charged with it, it might perhaps still be contended, although quite hypothetically, that the bounding portions of air were now the surfaces or places of attraction, as the metals had been supposed to be before. In illustration of this and other points, I endeavoured to devise an arrangement by which I could decompose a body against a surface of water, as well as against air or metal, and succeeded in doing so unexceptionably in the following manner. As the experiment for very natural reasons requires many precautions, to be successful, and will be referred to hereafter in illustration of the views I shall venture to give, I must describe it minutely.

494. A glass basin (fig. 6.), four inches in diameter and four inches deep, had a division of mica *a*, fixed across the upper part so as to descend one inch and a half below the edge, and be perfectly water-tight at the sides: a plate of platina *b*, three inches wide, was put into the basin on one side of the division *a*, and retained there by a glass block below, so that any gas produced by it in a future stage of the experiment should not ascend beyond the mica, and cause currents in the liquid on that side. A strong solution of sulphate of magnesia was carefully poured without splashing into the basin, until it rose a little above the lower edge of the mica division *a*, great care being taken that the glass or mica on the unoccupied or *c* side of the division in the figure, should not be moistened by agitation of the solution above the level to which it rose. A thin piece of clean cork, well wetted in distilled water, was then carefully and lightly placed on the solution at the *c* side, and distilled water poured gently on to it until a stratum the eighth of an inch in thickness appeared over the sulphate of magnesia; all was then left for a few minutes, that any solution adhering to the cork might sink away from it, or be removed by the water on which it now floated; and then more distilled water was added in a similar manner, until it reached nearly to the top of the glass. In this way solution of the sulphate occupied the lower part of the glass, and also the upper on the right hand side of the mica; but on the left hand side of the division a stratum of water from *c* to *d*, one inch and a half in depth, reposed upon it,

the two presenting, when looked through horizontally, a very definite plane of contact. A second platina pole *e*, was arranged so as to be just under the surface of the water, in a position nearly horizontal, a little inclination being given to it, that gas evolved during decomposition might escape: the part immersed was three inches and a half long by one inch wide, and about seven eighths of an inch of water intervened between it and the solution of sulphate of magnesia.

495. The latter pole *e* was now connected with the negative end of a voltaic battery, of forty pairs of plates four inches square, whilst the former pole *b* was connected with the positive end. There was action and gas evolved at both poles; but from the intervention of the pure water, the decomposition was very feeble compared to what the battery would have effected in a uniform solution. After a little while (less than a minute,) magnesia also appeared at the negative side: *it did not make its appearance at the negative pole*, but in the water, at the plane where the solution and the water met; and on looking at it horizontally, it could be there perceived lying in the water upon the solution, not rising more than the fourth of an inch above the latter, whilst the water between it and the negative pole was perfectly clear. On continuing the action, the bubbles of hydrogen rising upwards from the negative pole impressed a circulatory movement on the stratum of water, upwards in the middle, and downwards at the side, which gradually gave an ascending form to the cloud of magnesia in the part just under the pole, having an appearance as if it were there attracted to it; but this was altogether an effect of the currents, and did not occur until long after the phenomena required were satisfactorily ascertained.

496. After a little while the voltaic communication was broken, and the platina poles removed with as little agitation as possible from the water and solution, for the purpose of examining the liquid adhering to them. The pole *e*, when touched by turmeric paper, gave no traces of alkali, nor could anything but pure water be found upon it. The pole *b*, though drawn through a much greater depth and quantity of fluid, was found so acid as to give abundant evidence to litmus paper, the tongue, and other tests. Hence there had been no interference of alkaline salts in any way, undergoing first decomposition, and then causing the separation of the magnesia at a distance from the pole by mere chemical agencies.

This experiment was repeated again and again, and always successfully.

497. As, therefore, the substances evolved in cases of electro-chemical decomposition may be made to appear against air (465. 469.),—which, according to common language, is not a conductor, nor is decomposed; or against water (495.), which is a conductor, and can be decomposed,—as well as against the metal poles, which are excellent conductors, but undecomposable, there appears but little reason to consider the phenomena generally, as due to the *attraction* or attractive powers of the latter, when used in the ordinary way, since similar attractions can hardly be imagined in the former instances.

498. It may be said that the surfaces of air or of water in these cases become the poles, and exert attractive powers; but what proof is there of that, except the fact that the matters evolved collect there, which is the point to be explained, and cannot be justly quoted as its own explanation? Or it may be said, that any section of the humid conductor, as that in the present case, where the solution and the water meet, may be considered as representing the pole. But such does not appear to me to be the view of those who have written on the subject, certainly not of some of them, and is inconsistent with the supposed laws which they have assumed, as governing the diminution of power at increased distances from the poles.

499. GROTTHUSS, for instance, describes the poles as centres of attractive and repulsive forces (481), these forces varying inversely as the squares of the distances, and says, therefore, that a particle placed anywhere between the poles will be acted upon by a constant force. But the compound force, resulting from such a combination as he supposes, would be anything but a constant force; it would evidently be a force greatest at the poles, and diminishing to the middle distance. GROTTHUSS is right, however, *in the fact*, according to my experiments (502. 505.), that the particles are acted upon by equal force everywhere in the circuit, when the conditions of the experiment are the simplest possible; but the fact is against his theory, and is also, I think, against all theories that place the decomposing effect in the attractive power of the poles.

500. Sir HUMPHRY DAVY, who also speaks of the *diminution* of power with increase of distance from the poles * (483.), supposes, that when both poles are acting on substances to decompose them, still the power of decomposition

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* Philosophical Transactions, 1807, p. 42.

diminishes to the middle distance. In this statement of fact he is opposed to Grotthuss, and quotes an experiment in which sulphate of potassa, placed at different distances from the poles in a humid conductor of constant length, decomposed when near the pole, but not when at a distance. Such a consequence would necessarily result theoretically from considering the poles as centres of attraction and repulsion; but I have not found the statement borne out by other experiments (505.); and in the one quoted by him the effect was doubtless due to some of the many interfering causes of variation which attend such investigations.

501. A glass vessel had a platina plate fixed perpendicularly across it, so as to divide it into two cells: a head of mica was fixed over it, so as to collect the gas it might evolve during experiments; then each cell, and the space beneath the mica, was filled with dilute sulphuric acid. Two poles were provided, consisting each of a platina wire terminated by a plate of the same metal; each was fixed into a tube passing through its upper end by an air-tight joint, that it might be moveable, and yet that the gas evolved at it might be collected. The tubes were filled with the acid, and one immersed in each cell. Each platina pole was equal in surface to one side of the dividing plate in the middle glass vessel, and the whole might be considered as an arrangement between the poles of the battery of a humid decomposable conductor divided in the middle by the interposed platina diaphragm. It was easy, when required, to draw one of the poles further up the tube, and then the platina diaphragm was no longer in the middle of the humid conductor. But whether it were thus arranged at the middle, or towards one side, it always evolved a quantity of oxygen and hydrogen equal to that evolved by both the extreme plates*.

502. If the wires of a galvanometer be terminated by plates, and these be immersed in dilute acid, contained in a regularly formed rectangular glass trough, connected at each end with a voltaic battery by poles equal to the section of the fluid, a part of the electricity will pass through the instrument and cause a certain deflection. And if the plates are always retained at the same distance from each other and from the sides of the trough, are always parallel to each

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* There are certain precautions, in this and such experiments, which can only be understood and guarded against by a knowledge of the phenomena to be described in the first part of the Sixth Series of these Researches.

other, and uniformly placed relative to the fluid, then, whether the galvanometer plates are immersed near the middle of the decomposing solution, or near one end, still the instrument will indicate the same deflection, and consequently the same electric influence.

503. It is very evident that when the width of the decomposing conductor varies, as is always the case when mere wires or plates, as poles, are dipped into or are surrounded by solution, no constant expression can be given as to the action upon a single particle placed in the course of the current, nor any conclusion of use relative to the supposed attractive or repulsive force of the poles be drawn. The force will vary as the distance from the pole varies; as the particle is directly between the poles, or more or less on one side; and even as it is nearer to or further from the sides of the containing vessels, or as the shape of the vessel itself varies; and, in fact, by making variations in the form of the arrangement, the force upon any single particle may be made to increase, or diminish, or remain constant, whilst the distance between the particle and the pole shall remain the same; or the force may be made to increase, or diminish, or remain constant, either as the distance increases or as it diminishes.

504. From numerous experiments, I am led to believe the following general expression to be correct; but I purpose examining it much further, and would therefore wish not to be considered at present as pledged to its accuracy. The sum of chemical decomposition is constant for any section taken across a decomposing conductor, uniform in its nature, at whatever distance the poles may be from each other or from the section; or however that section may intersect the currents, whether directly across them, or so oblique as to reach almost from pole to pole, or whether it be plane, or curved, or irregular in the utmost degree; provided the current of electricity be retained constant in quantity (377.), and that the section include all portions of the current through the decomposing conductor.

505. I have reason to believe that the statement might be made still more general, and expressed thus: That for a constant quantity of electricity, whatever the decomposing conductor may be, whether water, saline solutions, acids, fused bodies, &c., the amount of electro-chemical action is also a constant quantity, i. e. would always be equivalent to a standard chemical effect founded

upon ordinary chemical affinity. I have this investigation in hand, with several others, and shall be prepared to give it in the next series but one of these Researches.

506. Many other arguments might be adduced against the hypotheses of the attraction of the poles being the cause of electro-chemical decomposition; but I would rather pass on to the view I have thought more consistent with facts, with this single remark; that if decomposition by the voltaic battery depended upon the attraction of the poles, or the parts about them, being stronger than the mutual attraction of the particles separated, it would follow that the weakest electrical attraction was stronger than, if not the strongest yet, very strong chemical attraction, namely, such as exists between oxygen and hydrogen, potassium and oxygen, chlorine and sodium, acid and alkali, &c., a consequence which, although perhaps not impossible, seems in the present state of the subject very unlikely.

507. The view which M. de la Rive has taken (489.), and also MM. Riffault and Chompré (485), of the manner in which electro-chemical decomposition is effected, is very different to that already considered, and is not affected by either arguments or facts against the latter. Considering it as stated by the former philosopher, it appears to me to be incompetent to account for the experiments of decomposition against surfaces of air (462. 469.) and water (495.), which I have described; for if the physical differences between metals and humid conductors, which M. de la Rive supposes to account for the transmission of the compound of matter and electricity in the latter, and the transmission of the electricity only with the rejection of the matter in the former, be allowed for a moment, still the relation of air to metal is, electrically considered, so small, that instead of the former replacing the latter (462.), an effect the very reverse might have been expected. Or if even that were allowed, the experiment with water (495.), at once sets the matter at rest, the decomposing pole being now of a substance which is admitted as competent to transmit the compound of electricity and matter.

508. With regard to the views of MM. Riffault and Chompré (485.), the occurrence of deposition in the course of the current is so contrary to the well known effects obtained in the forms of experiment adopted up to this time, that it must be proved before the hypothesis depending on it need be considered.

509. The consideration of the various theories of electro-chemical decomposition, whilst it has made me diffident, has also given me confidence to add another to the number; for it is because the one I have to propose appears, after the most attentive consideration, to explain and agree with the immense collection of facts belonging to this branch of science, and to remain uncontradicted by, or unopposed to, any of them, that I have been encouraged to give it.

510. Electro-chemical decomposition is well known to depend essentially upon the *current* of electricity. I have shown that in certain cases (375.) the decomposition is proportionate to the quantity of electricity passing, whatever may be its intensity or its source, and that the same is probably true for all cases (377.), even when the utmost generality is taken on the one hand, and great precision of expression on the other.

511. In speaking of the current, I find myself obliged to be still more particular than on a former occasion (283.), in consequence of the variety of views taken by philosophers, all agreeing in the effect of the current itself. Some philosophers, with FRANKLIN, assume but one electric fluid; and such must agree together in the general uniformity and character of the electric current. Others assume two electric fluids; and here singular differences have arisen.

512. MM. RIFFAULT and CHOMPRÉ, for instance, consider the positive and negative currents each as causing decomposition, and state that the positive current is *more powerful* than the negative current*, the nitrate of soda being, under similar circumstances, decomposed by the former, but not by the latter.

513. M. HACHETTE states† that "it is not necessary, as has been believed, that the action of the two electricities, positive and negative, should be simultaneous for the decomposition of water." The passage implying, if I have caught the meaning aright, that one electricity can be obtained, and can be applied in effecting decompositions, independent of the other.

514. The view of M. DE LA RIVE to a certain extent agrees with that of M. HACHETTE, for he considers that the two electricities decompose separate portions of water (490.)‡. In one passage he speaks of the two electricities as two influences, wishing perhaps to avoid offering a decided opinion upon the independent existence of electric fluids; but as these influences are consi-

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* Annales de Chimie, 1807, tom. lxiii. p. 84.

† Ibid. 1832, tom. li. p. 73.

‡ Ibid. 1825, tom. xxviii. pp. 197, 201.

dered as combining with the elements set free as by a species of chemical affinity, and for the time entirely masking their character, great vagueness of idea is thus introduced, inasmuch as such species of combination can only be conceived to take place between things having independent existence. The two elementary electric currents, moving in opposite directions, from pole to pole, constitute the ordinary *voltaic current*.

515. M. Grotthuss is inclined to believe that the elements of water, when about to separate at the poles, combine with the electricities, and so become gases. M. de la Rive's view is the exact reverse of this: whilst passing through the fluid, they are, according to him, compounds with the electricities; when evolved at the poles, they are de-electrified.

516. I have sought amongst the various experiments quoted in support of these views, or connected with electro-chemical decompositions or electric currents, for any which might be considered as sustaining the theory of two electricities rather than that of one, but have not been able to perceive a single fact which could be brought forward for such a purpose: or, admitting the hypothesis of two electricities, much less have I been able to perceive the slightest grounds for believing that one electricity in a current can be more powerful than the other, or that it can be present without the other, or that one can be varied, or in the slightest degree affected, without a corresponding variation in the other. If, upon the supposition of two electricities, a current of one can be obtained without the other, or the current of one be exalted or diminished more than the other, we might surely expect some variation either of the chemical or magnetical effects, or of both; but no such variations have been observed. If a current be so directed that it may act chemically in one part of its course, and magnetically in another, the two actions are always found to take place together. A current has not, to my knowledge, been produced which could act chemically and not magnetically, nor any which can act on the magnet, and not *at the same time* chemically*.

517. *Judging from facts only*, there is not as yet the slightest reason for considering the influence which is present in what we call the electric current,—whether in metals or fused bodies or humid conductors, or even in air, flame,

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* Thermo-electric currents are of course no exception, because when they fail to act chemically they also fail to be currents.

and rarefied elastic media,—as a compound or complicated influence. It has never been resolved into simpler or elementary influences, and may perhaps best be conceived of as *an axis of power having contrary forces, exactly equal in amount, in contrary directions.*

518. Passing to the consideration of electro-chemical decomposition, it appears to me that the effect is produced by an *internal corpuscular action,* exerted according to the direction of the electric current, and that it is due to a force either *superadded to,* or *giving direction to the ordinary chemical affinity* of the bodies present. The decomposing body may be considered as a mass of acting particles, all those which are included in the course of the electric current contributing to the final effect; and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralized by the influence of the electric current in one direction, parallel to the course of the latter, and strengthened or added to in the opposite direction, that the combining particles have a tendency to pass in opposite courses.

519. In this view the effect is considered as *essentially dependent* upon the *mutual chemical affinity* of the particles of opposite kinds. Particles *a a,* fig. 7, could not be transferred or travel from one pole N towards the other P, unless they found particles of the opposite kind *b b,* ready to pass in the contrary direction: for it is by virtue of their increased affinity for those particles, combined with their diminished affinity for such as are behind them in their course, that they are urged forward: and when any one particle *a,* fig. 8, arrives at the pole, it is excluded or set free, because the particle *b* of the opposite kind, with which it was the moment before in combination, has, under the superinducing influence of the current, a greater attraction for the particle a', which is before it in its course, than for the particle *a,* towards which its affinity has been weakened.

520. As far as regards any single compound particle, the case may be considered as analogous to one of ordinary decomposition, for in fig. 8, *a* may be conceived to be expelled from the compound *a b* by the superior attraction of a' for *b,* that superior attraction belonging to it in consequence of the relative position of a' *b* and *a* to the direction of the axis of electric power (517.) superinduced by the current. But as all the compound particles in the course of the current, except those actually in contact with the poles, act conjointly, and consist of elementary particles, which, whilst they are in one direction

expelling, are in the other being expelled, the case becomes more complicated, but not more difficult of comprehension.

521. It is not here assumed that the acting particles must be in a right line between the poles. The lines of action which may be supposed to represent the electric currents passing through a decomposing liquid, have in many experiments very irregular forms; and even in the simplest case of two wires or points immersed as poles in a drop, or larger single portion of fluid, these lines must diverge rapidly from the poles; and the direction in which the chemical affinity between particles is most powerfully modified (519. 520.) will vary with the direction of these lines, according constantly with them. But even in reference to these lines or currents, it is not supposed that the particles which mutually affect each other must of necessity be parallel to them, but only that they shall accord generally with their direction. Two particles, placed in a line perpendicular to the electric current passing in any particular place, are not supposed to have their ordinary chemical relations towards each other affected; but as the line joining them is inclined one way to the current, their mutual affinity is increased; as it is inclined in the other direction, it is diminished; and the effect is a maximum, when that line is parallel to the current.

522. That the actions, of whatever kind they may be, take place frequently in oblique directions is evident from the circumstance of those particles being included which in numerous cases are not in a line between the poles. Thus, when wires are used as poles in a glass of solution, the decompositions and recompositions occur to the right or left of the direct line between the poles, and indeed in every part to which the currents extend, as is proved by many experiments, and must therefore often occur between particles obliquely placed as respects the current itself; and when a metallic vessel containing the solution is made one pole, whilst a mere point or wire is used for the other, the decompositions and recompositions must frequently be still more oblique to the course of the currents.

523. The theory which I have ventured to put forth (almost) requires an admission, that in a compound body capable of electro-chemical decomposition the elementary particles have a mutual relation to, and influence upon each other, extending beyond those with which they are immediately combined. Thus in water, a particle of hydrogen in combination with oxygen is considered

as not altogether indifferent to other particles of oxygen, although they are combined with other particles of hydrogen; but to have an affinity or attraction towards them, which, though it does not at all approach in force, under ordinary circumstances, to that by which it is combined with its own particle, can under the electric influence, exerted in a definite direction, be made even to surpass it. This general relation of particles already in combination to other particles with which they are not combined, is sufficiently distinct in numerous results of a purely chemical character, especially in those where partial decompositions only take place, and in Berthollet's experiments on the effects of quantity upon affinity; and it probably has a direct relation to, and connexion with, attraction of aggregation, both in solids and fluids. It is a remarkable circumstance, that in gases and vapours, where the attraction of aggregation ceases, there likewise the decomposing powers of electricity apparently cease, and there also the chemical action of quantity is no longer evident. It seems not unlikely, that the inability to suffer decomposition in these cases may be dependent upon the absence of that mutual attractive relation of the particles which is the cause of aggregation.

524. I hope I have now distinctly stated, although in general terms, the view I entertain of the cause of electro-chemical decomposition, as far as that cause can at present be traced and understood. I conceive the effects to arise from forces which are *internal*, relative to the matter under decomposition—and not *external*, as they might be considered, if directly dependent upon the poles. I suppose that the effects are due to a modification, by the electric current, of the chemical affinity of the particles through or by which that current is passing, giving them the power of acting more forcibly in one direction than in another, and consequently making them travel by a series of successive decompositions and recompositions in opposite directions, and finally causing their expulsion or exclusion at the boundaries of the decomposing body, in the direction of the current, and *that* in larger or smaller quantities, according as the current is more or less powerful (377.). I think, therefore, it would be more philosophical, and more directly expressive of the facts, to speak of a decomposing body, in relation to the current passing through it, rather than to the poles, as they are usually called, in contact with it; and say that whilst under decomposition, oxygen, chlorine, iodine, acids, &c., are rendered at the

negative extremity, and combustibles, metals, alkalies, bases, &c., at the positive extremity of the decomposing substance (467.). I do not believe that a substance can be transferred in the electric current beyond the point where it ceases to find particles with which it can combine; and I may refer to the experiments made in air (465.), and in water (495.), already quoted, for facts illustrating these views in the first instance; to which I will now add others.

525. In order to show the dependence of the decomposition and transfer of elements upon the chemical affinity of the substances present, experiments were made upon sulphuric acid in the following manner. Dilute sulphuric acid was prepared: its specific gravity was 1021·2. A solution of sulphate of soda was also prepared, of such strength that a measure of it contained exactly as much sulphuric acid as an equal measure of the diluted acid just referred to. A solution of pure soda, and another of pure ammonia, were likewise prepared, of such strengths that a measure of either should be exactly neutralized by a measure of the prepared sulphuric acid.

526. Four glass cups were then arranged, as in fig. 9; seventeen measures of the free sulphuric acid (525.) were put into each of the vessels *a* and *b*, and seventeen measures of the solution of sulphate of soda into each of the vessels A and B. Asbestus, which had been well washed in acid, acted upon by the voltaic pile, well washed in water, and dried by pressure, was used to connect *a* with *b* and A with B, the portions being as equal as they could be made in quantity, and cut as short as was consistent with their performing the part of effectual communications. *b* and A were connected by two platina plates or poles soldered to the extremities of one wire, and the cups *a* and B were by similar platina plates connected with a voltaic battery of forty pairs of plates four inches square, that in *a* being connected with the negative, and that in B with the positive pole. The battery, which was not powerfully charged, was retained in communication above half an hour. In this manner it was certain that the same electric current had passed through *a b* and A B, and that in each instance the same quantity and strength of acid had been submitted to its action, but in one case merely dissolved in water, and in the other dissolved and also combined with an alkali.

527. On breaking the connexion with the battery, the portions of asbestus were lifted out, and the drops hanging at the ends allowed to fall each into its

respective vessel. The acids in *a* and *b* were then first compared, for which purpose two evaporating dishes were balanced, and the acid from *a* put into one, and that from *b* into the other; but as one was a little heavier than the other, a small drop was transferred from the heavier to the lighter, and the two rendered equal in weight. Being neutralized by addition of the soda solution (525.), that from *a*, or the negative vessel, required 15 parts of the soda solution, and that from *b*, or the positive vessel, required 16·3 parts. That the sum of these is not 34 parts is principally due to the acid removed with the asbestus; but, taking the mean of 15·65 parts, it would appear that a twenty-fourth part of the acid originally in the vessel *a* had passed, through the influence of the electric current, from *a* into *b*.

528. In comparing the difference of acid in A and B, the necessary equality of weight was considered as of no consequence, because the solution was at first neutral, and would not, therefore, affect the test liquids, and all the evolved acid would be in B, and the free alkali in A. The solution in A required 3·2 measures of the prepared acid (525.) to neutralize it, and the solution in B required also 3·2 measures of the soda solution (525.) to neutralize it. As the asbestus must have removed a little acid and alkali from the glasses, these quantities are by so much too small; and therefore it would appear that about a tenth of the acid originally in the vessel A had been transferred into B during the continuance of the electric action.

529. In another similar experiment, whilst a thirty-fifth part of the acid passed from *a* to *b* in the free acid vessels, between a tenth and an eleventh passed from A to B in the combined acid vessels. Other experiments of the same kind gave similar results.

530. The variation of electro-chemical decomposition, the transfer of elements and their accumulation at the poles, according as the substance submitted to action consists of particles opposed more or less in their chemical affinity, together with the consequent influence of the latter circumstances, are sufficiently obvious in these cases, where sulphuric acid is acted upon in the *same quantity* by the *same* electric current, but in one case opposed to the comparatively weak affinity of water for it, and in the other to the stronger one of soda. In the latter case the quantity transferred is from two and a half to three times what it is in the former; and it appears therefore very evident that

the transfer is greatly dependent upon the mutual action of the particles of the decomposing bodies.

531. In some of the experiments the acid from the vessels *a* and *b* was neutralized by ammonia, then evaporated to dryness, heated to redness, and the residue examined for sulphates. In these cases more sulphate was always obtained from *a* than from *b*; showing that it had been impossible to exclude saline bases (derived from the asbestus, the glass, or perhaps impurities originally in the acid,) and that they had helped in transferring the acid into *b*. But the quantity was small, and the acid was principally transferred by relation to the water present.

532. I endeavoured to arrange certain experiments by which saline solutions should be decomposed against surfaces of water; and at first worked with the electric machine upon a piece of bibulous paper, or asbestus moistened in the solution, and in contact at its two extremities with pointed pieces of paper moistened in pure water, which served to carry the electric current to and from the solution in the middle piece. But I found numerous interfering difficulties. Thus, the water and solutions in the pieces of paper could not be prevented from mingling at the point where they touched. Again, sufficient acid could be derived from the paper connected with the discharging train, or it may be even from the air itself, under the influence of electric action, to neutralize the alkali developed at the positive extremity of the decomposing solution, and so not merely prevent its appearance, but actually transfer it on to the metal termination: and, in fact, when the paper points were not allowed to touch there, and the machine was worked until alkali was evolved at the delivering or positive end of the turmeric paper, containing the sulphate of soda solution, it was merely necessary to place the opposite receiving point of the paper connected with the discharging train, which had been moistened by distilled water, upon the browned turmeric point and press them together, when the alkaline effect immediately disappeared.

533. The experiment with sulphate of magnesia already described (495.) is a case in point, however, and shows most clearly that the sulphuric acid and magnesia contributed to each other's transfer and final evolution, exactly as the same acid and soda affected each other in the results just given (527, &c.); and that so soon as the magnesia advanced beyond the reach of the acid, and

found no other substance with which it could combine, it appeared in its proper character, and was no longer able to continue its progress towards the negative pole.

534. The theory I have ventured to put forth appears to me to explain all the prominent features of electro-chemical decomposition in a satisfactory manner.

535. In the first place it explains why, in all ordinary cases, the evolved substances appear only at the poles; for the poles are the limiting surfaces of the decomposing substance, and except at them, every particle finds other particles having a contrary tendency with which it can combine.

536. Then it explains why, in numerous cases, the elements or evolved substances are not *retained* by the poles; and this is no small difficulty in those theories which refer the decomposing effect directly to the attractive power of the poles. If a piece of platina have sufficient power given to it by any means to attract a particle of hydrogen from the particle of oxygen with which it was the instant before combined, there seems no sufficient reason, nor any fact, except those to be explained, which show why it should not, according to analogy with all ordinary attractive forces, as those of gravitation, the magnet, cohesion, chemical affinity, &c., *retain* that particle which it had just before taken from a distance and from previous combination. Yet it does not do so, but allows it to escape freely. Nor does this depend upon its assuming the gaseous state, for acids and alkalies, &c., are left equally at liberty to diffuse themselves through the fluid surrounding the pole, and show no particular tendency to combine with or cleave to the latter. And though there are plenty of cases where combination with the pole does take place, they do not at all explain the instances of non-combination, and do not therefore in their particular action reveal the general principle of decomposition.

537. But in the theory that I have just given, the effect appears to be a natural consequence of the action: the evolved substances are expelled from the decomposing mass (518. 519.), not *drawn out by an attraction* which ceases to act on one particle without any assignable reason, while it continues to act on another of the same kind: and whether the poles be metal, water, or air, still the substances are evolved, and sometimes are set free, or sometimes unite to the matter of the poles, according to the chemical nature of the latter, i. e. the chemical relation of their particles to those which are leaving the substance under operation.

538. The theory accounts for the transfer of elements in a manner which seems to me at present to leave nothing unexplained; and it was, indeed, the phenomena of transfer in the numerous cases of decomposition of bodies rendered fluid by heat (380. 402.), which, in conjunction with the experiments in air, led to its construction. Such cases as the former where binary compounds of easy decomposability are acted upon, are perhaps the best to illustrate the theory.

539. Chloride of lead, for instance, fused in a bent tube (400.), and decomposed by platina wires, evolves lead, passing to what is usually called the negative pole, and chlorine, which being evolved at the positive pole, is in part set free, and in part combines with the platina. The chloride formed, being soluble in the chloride of lead, is subject to decomposition, and the platina itself is gradually transferred across the decomposing matter, and found with the lead at the negative pole.

540. Iodide of lead evolves abundance of lead at the negative pole, and abundance of iodine at the positive pole.

541. Chloride of silver furnishes a beautiful instance, especially when decomposed by silver wire poles. Upon fusing a portion of it on a piece of glass, and bringing the poles into contact with it, there is abundance of silver evolved at the negative pole, and an equal abundance absorbed at the positive pole, for no chlorine is set free; and by careful management, the negative wire may be withdrawn from the fused globule as the silver is reduced there, the latter serving as the continuation of the pole, until a wire or thread of revived silver, five or six inches in length, is produced; at the same time the silver at the positive pole is as rapidly dissolved by the chlorine, which seizes upon it, so that the wire has to be continually advanced as it is melted away. The whole experiment includes the action of only two elements, silver and chlorine, and illustrates in a beautiful manner their progress in opposite directions, parallel to the electric current, which is for the time giving a uniform general direction to their mutual affinities (524.).

542. According to my theory, an element or a substance not decomposable under the circumstances of the experiment, (as, for instance, a dilute acid or alkali,) should not be transferred, or pass from pole to pole, unless it be in chemical relation to some other element or substance tending to pass in the opposite direction, for the effect is considered as essentially due to the mutual

relation of such particles. But the theories attributing the determination of the elements to the attractions and repulsions of the poles require no such condition, i. e. there is no reason apparent why the attraction of the positive pole, and the repulsion of the negative pole, upon a particle of free acid, placed in water between them, should not (with equal currents of electricity) be as strong as if that particle were previously combined with alkali; but, on the contrary, as they have not a powerful chemical affinity to overcome, there is every reason to suppose they would be stronger, and would sooner bring the acid to rest at the positive pole*. Yet such is not the case, as has been shown by the experiments on free and combined acid (526. 528.).

543. Neither does M. DE LA RIVE's theory, as I understand it, require that the particles should be in combination: it does not even admit, where there are two sets of particles capable of combining with and passing by each other, that they do combine, but supposes that they travel as separate compounds of matter and electricity. Yet in fact, the free substance *cannot* travel, the combined one *can*.

544. It is very difficult to find cases amongst solutions or fluids which shall illustrate this point, because of the difficulty of finding two fluids which shall conduct, shall not mingle, and in which an element evolved from one shall not find a combinable element in the other. Solutions of acids or alkalies will not answer, because they exist by virtue of an attraction; and increasing the solubility of a body in one direction, and diminishing it in the opposite, is just as good a reason for transfer, as modifying the affinity between the acid and alkali themselves. Nevertheless the case of sulphate of magnesia is in point (494. 495.), and shows that one element or principle only has no power of transference or of passing towards either pole.

545. Many of the metals, however, in their solid state, offer very fair instances of the kind required. Thus, if a plate of platina be used as the positive pole in a solution of sulphuric acid, oxygen will pass towards it, and so will acid; but these are not substances having such chemical relation to the platina as, even under the favourable condition superinduced by the current (518. 524.), to combine with it; the platina therefore remains where it was first placed, and has

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* Even Sir HUMPHRY DAVY considered the attraction of the pole as being communicated from one particle to another of the *same* kind (483.).

no tendency to pass towards the negative pole. But if a plate of iron, zinc or copper, be substituted for the platina, then the oxygen and acid can combine with these, and the metal immediately begins to travel as an oxide, to the opposite pole, and is finally deposited there. Or if, retaining the platina pole, a fused chloride, as of lead, zinc, silver, &c., be substituted for the sulphuric acid, then, as the platina finds an element it can combine with, it enters into union, acts as other elements do in cases of voltaic decomposition, is rapidly transferred across the melted matter, and expelled at the negative pole.

546. I can see but little reason in the theories referring the electro-chemical decomposition to the attractions and repulsions of the poles, and I can perceive none in M. DE LA RIVE's theory, why the metal of the positive pole should not be transferred across the intervening conductor, and deposited at the negative pole, even when it cannot act chemically upon the element of the fluid surrounding it. It cannot be referred to the attraction of cohesion preventing such an effect; for if the pole be made of the lightest spongy platina, the effect is the same. Or if gold precipitated by sulphate of iron be diffused through the solution, still accumulation of it at the negative pole will not take place; and yet in it the attraction of cohesion is almost perfectly overcome, the particles are so small as to remain for hours in suspension, and are perfectly free to move by the slightest impulse towards either pole; and *if in relation* by chemical affinity to any substance present, are powerfully determined to the negative pole *.

547. In support of these arguments, it may be observed, that as yet no determination of a substance to a pole, or tendency of obedience to the electric current, has been observed (that I am aware of,) in cases of mere mixture; i. e. a substance diffused through a fluid, but having no sensible chemical affinity with it, or with substances that may be evolved from it during the action,

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* In making this experiment, care must be taken that no substance be present that can act chemically on the gold. Although I used the metal very carefully washed, and diffused through dilute sulphuric acid, yet in the first instance I obtained gold at the negative pole, and the effect was repeated when the platina poles were changed. But on examining the clear liquor in the cell, after subsidence of the metallic gold, I found a little of that metal in solution, and a little chlorine was also present. I therefore well washed the gold which had thus been subjected to voltaic action, diffused it through other pure dilute sulphuric acid, and then found that on subjecting it to the action of the poles, not the slightest tendency to the negative pole could be perceived.

does not in any case seem to be affected by the electric current. Pulverised charcoal was diffused through dilute sulphuric acid, and subjected with the solution to the action of a voltaic battery, terminated by platina poles; but not the slightest tendency of the charcoal to the negative pole could be observed. Sublimed sulphur was diffused through similar acid, and submitted to the same action, a silver plate being used as the negative pole; but the sulphur had no tendency to pass to that pole, the silver was not tarnished, nor did any sulphuretted hydrogen appear. The case of magnesia and water (495. 533.), with those of comminuted metals in certain solutions (546.), are also of this kind; and, in fact, substances which have the instant before been powerfully determined towards the pole, as magnesia from sulphate of magnesia, become entirely indifferent to it the moment they assume their independent state, and pass away, diffusing themselves in the surrounding fluid.

548. There are, it is true, many instances of insoluble bodies being acted upon, as glass, sulphate of baryta, marble, slate, basalt, &c., but they form no exception; for the substances they give up are in direct and strong relation as to chemical affinity with those which they find in the surrounding solution, so that these decompositions enter into the class of ordinary effects.

549. It may be expressed as a general consequence, that the more directly bodies are opposed to each other in chemical affinity, the more *ready* is their separation from each other in cases of electro-chemical decomposition, i. e. provided other circumstances, as insolubility, deficient conducting power, proportions, &c., do not interfere. This is well known to be the case with water and saline solutions; and I have found it to be equally true with *dry* chlorides, iodides, salts, &c., rendered subject to electro-chemical decomposition by fusion (402.). So that in applying the voltaic battery for the purpose of decomposing bodies not yet resolved into forms of matter simpler than their own, it must be remembered, that success may depend not upon the weakness, or failure upon the strength, of the affinity by which the elements sought for are held together, but contrariwise; and then modes of application may be devised by which, in *association* with ordinary chemical powers, and the assistance of fusion (394. 417.), we may be able to penetrate much further than at present into the constitution of our chemical elements.

550. Some of the most beautiful and surprising cases of electro-chemical

decomposition and transfer which Sir HUMPHRY DAVY described in his celebrated paper*, were those in which acids were passed through alkalies, and alkalies or earths through acids†; and the way in which substances having the most powerful attractions for each other were thus prevented from combining, or, as it is said, had their natural affinity destroyed or suspended throughout the whole of the circuit, excited the utmost astonishment. But if I be right in the view I have taken of the effects, it will appear, that that which made the *wonder*, is in fact the *essential condition* of transfer and decomposition, and that the more alkali there is in the course of an acid, the more will the transfer of that acid be facilitated from pole to pole; and perhaps a better illustration of the difference between the theory I have ventured, and those previously existing, cannot be offered than the views they respectively give of such facts as these.

551. The instances in which sulphuric acid could not be passed through baryta, or baryta through sulphuric acid‡, because of the precipitation of sulphate of baryta, enter within the pale of the law already described (380. 412.), by which liquidity is so generally required. In assuming the solid state of sulphate of baryta, they became virtually non-conductors to electricity of so low a tension as that of the voltaic battery, and the power of the latter over them was almost infinitely diminished.

552. The theory I have advanced accords in a most satisfactory manner with the fact of an element or substance finding its place of rest, or rather of evolution, sometimes at one pole and sometimes at the other. Sulphur illustrates this effect very well. When sulphuric acid is decomposed by the pile, sulphur is evolved at the negative pole; but when sulphuret of silver is decomposed in a similar way (436.), then the sulphur appears at the positive pole; and if a hot platina pole be used so as to vaporize the sulphur evolved in the latter case, then the relation of that pole to the sulphur is exactly the same as the relation of the same pole to oxygen upon its immersion in water. In both cases the element evolved is liberated at the pole, but not retained by it; but by virtue of its elastic, uncombinable, and immiscible condition passes away into the surrounding medium. The sulphur is evidently determined in these opposite directions by its opposite chemical relations to oxygen and silver; and it is to such relations generally that I have referred all electro-chemical phenomena.

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* Philosophical Transactions, 1807, p. 1.

† Ibid. p. 24, &c.

‡ Ibid. p. 25, &c.

Where they do not exist, no electro-chemical action can take place. Where they are strongest, it is most powerful; where they are reversed, the direction of transfer of the substance is reversed with them.

553. *Water* may be considered as one of those substances which can be made to pass to *either* pole. When the poles are immersed in dilute sulphuric acid (527.), acid passes towards the positive pole, and water towards the negative pole; but when they are immersed in dilute alkali, the alkali passes towards the negative pole, and water towards the positive pole.

554. Nitrogen is another substance which is considered as determinable to either pole; but in consequence of the numerous compounds which it forms, some of which pass to one pole and some to the other, I have not always found it easy to determine the true circumstances of its appearance. A pure strong solution of ammonia is so bad a conductor of electricity that it is scarcely more decomposable than pure water; but if sulphate of ammonia be dissolved in it, then decomposition takes place very well, nitrogen almost pure, and in some cases quite, is evolved at the positive pole, and hydrogen at the negative pole.

555. On the other hand, if a strong solution of nitrate of ammonia be decomposed, oxygen appears at the positive pole, and hydrogen, with sometimes nitrogen, at the negative pole. If fused nitrate of ammonia be employed, hydrogen appears at the negative pole, mingled with a little nitrogen. Strong nitric acid yields plenty of oxygen at the positive pole, but no gas (only nitrous acid,) at the negative pole. Weak nitric acid yields the oxygen and hydrogen of the water present, the acid apparently remaining unchanged. Strong nitric acid, with nitrate of ammonia dissolved in it, yields a gas at the negative pole, of which the greater part is hydrogen, but apparently a little nitrogen is present. I believe, that in some of these cases a little nitrogen appeared at the negative pole. I suspect, however, that in all these, and in all former cases, the appearance of the nitrogen at the positive or negative pole is entirely a secondary effect, and not an immediate consequence of the decomposing power of the electric current.

556. A few observations on what are called the *poles* of the voltaic battery now seem necessary. The poles are merely the surfaces or doors by which the electricity enters into or passes out of the decomposing substance. They limit the extent of that substance in the course of the electric current, being its

termination in that direction: hence the elements evolved pass so far and no further.

557. Metals make admirable poles, in consequence of their high conducting power, their immiscibility with the substances generally acted upon, their solid form, and the opportunity afforded of selecting some upon which ordinary substances exert no chemical action.

558. Water makes a pole of difficult application, except in a few cases (494.), because of its small conducting power, its miscibility with most of the substances acted upon, and its general relation to them in respect to chemical affinity. It consists of elements, which in their electrical and chemical relations are directly and powerfully opposed, yet combining to produce a body more neutral in its character than any other. So that there are but few substances which do not come into relation, by chemical affinity, with water or one of its elements; and therefore either the water or its elements are transferred and assist in transferring the infinite variety of bodies which, in association with it, can be placed in the course of the electric current. Hence the reason why it so rarely happens that the evolved substances rest at the first surface of the water, and why it therefore does not exhibit the ordinary action of a pole.

559. Air, however, and some gases are free from the latter objection, and may be used as poles in many cases (461, &c.); but, in consequence of the extremely low degree of conducting power belonging to them, they cannot be employed with the voltaic apparatus. This limits their use; for the voltaic apparatus is the only one as yet discovered which supplies sufficient quantity of electricity (371. 376.) to effect electro-chemical decomposition with facility.

560. Where the poles are liable to the chemical action of the substances evolved, either simply in consequence of their natural relation to them, or of that relation aided by the influence of the current (518.), then they suffer corrosion, and the parts dissolved are subject to transference, in the same manner as particles of the original decomposing body. An immense series of phenomena of this kind might be quoted in support of the view I have taken of the cause of electro-chemical decomposition, and transfer and evolution of the elements. Thus platina, as the positive and negative poles in a solution of sulphate of soda, has no affinity or attraction for the oxygen, hydrogen, acid, or alkali evolved, and refuses to combine with or retain them. Zinc can com-

bine with the oxygen and acid; at the positive pole it does combine, and immediately begins to travel as oxide towards the negative pole. Charcoal, which cannot combine with the metals, if made the negative pole in a metallic solution, refuses to unite to the bodies which are ejected from the solution upon its surface; but if made the positive pole in a dilute solution of sulphuric acid, it is capable of combining with the oxygen evolved there, and consequently unites with it, producing both carbonic acid and carbonic oxide in abundance.

561. A great advantage is frequently supplied, by the opportunity afforded amongst the metals of selecting a substance for the pole which shall or shall not be acted upon by the elements to be evolved. The consequent use of platina is notorious. In the decomposition of sulphuret of silver and other sulphurets, a positive silver pole is superior to a platina one, because in the former case the sulphur evolved there is combined with the silver, and the decomposition of the original sulphuret rendered evident; whereas in the latter case it is dissipated, and the assurance of its separation at the pole not easily obtained.

562. The effects which take place when a succession of conducting decomposable and undecomposable substances are placed in the electric circuit, as, for instance, of wires and solutions, or of air and solutions (465. 469.), are explained in the simplest possible manner by the view I have given. In consequence of the reaction of the constituents of each portion of decomposable matter, affected as they are by the supervention of the electric current (524.), portions of the proximate or ultimate elements proceed in the direction of the current as far as they find matter of a contrary kind capable of effecting their transfer, and being equally affected by them; and where they cease to find such matter, they are evolved in their free state, i. e. upon the surfaces of metal or air bounding the extent of decomposable matter in the direction of the currents.

563. Having thus given my theory of the mode in which electro-chemical decomposition is effected, I will refrain for the present from entering upon the numerous general considerations which it suggests, wishing first to submit it to the test of publication and discussion.

Royal Institution,
June 1833.