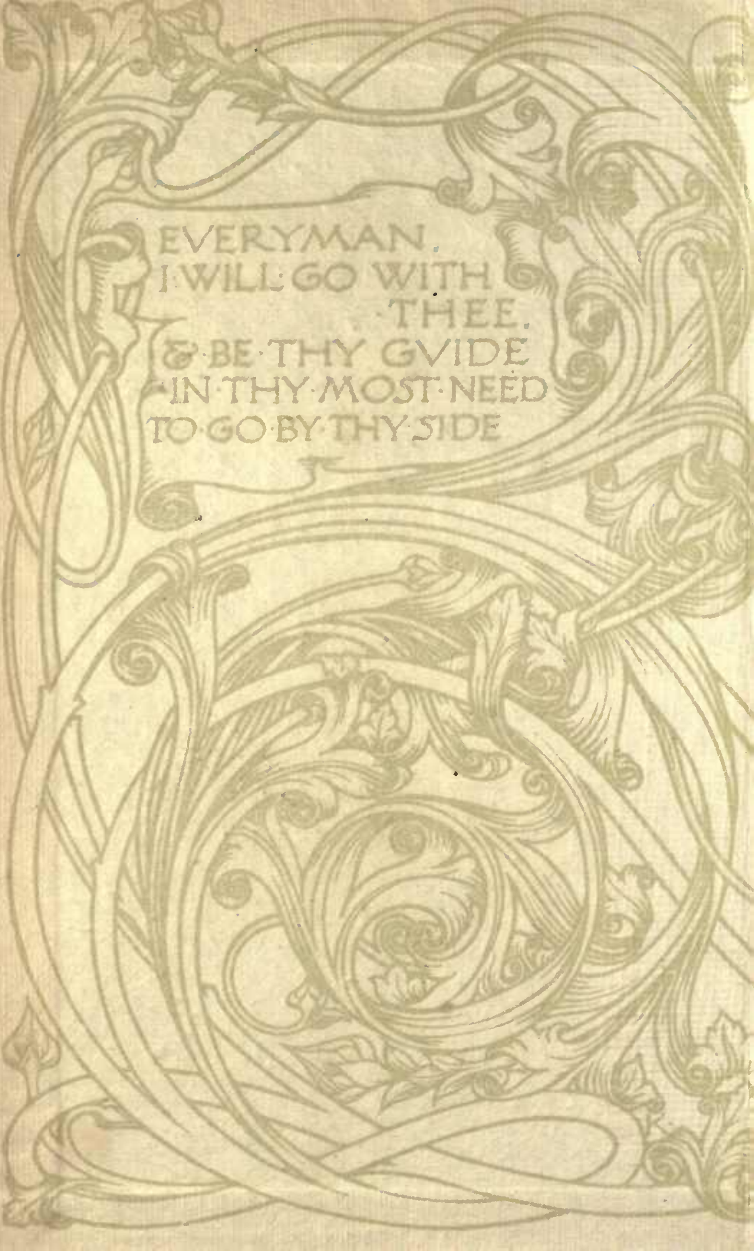

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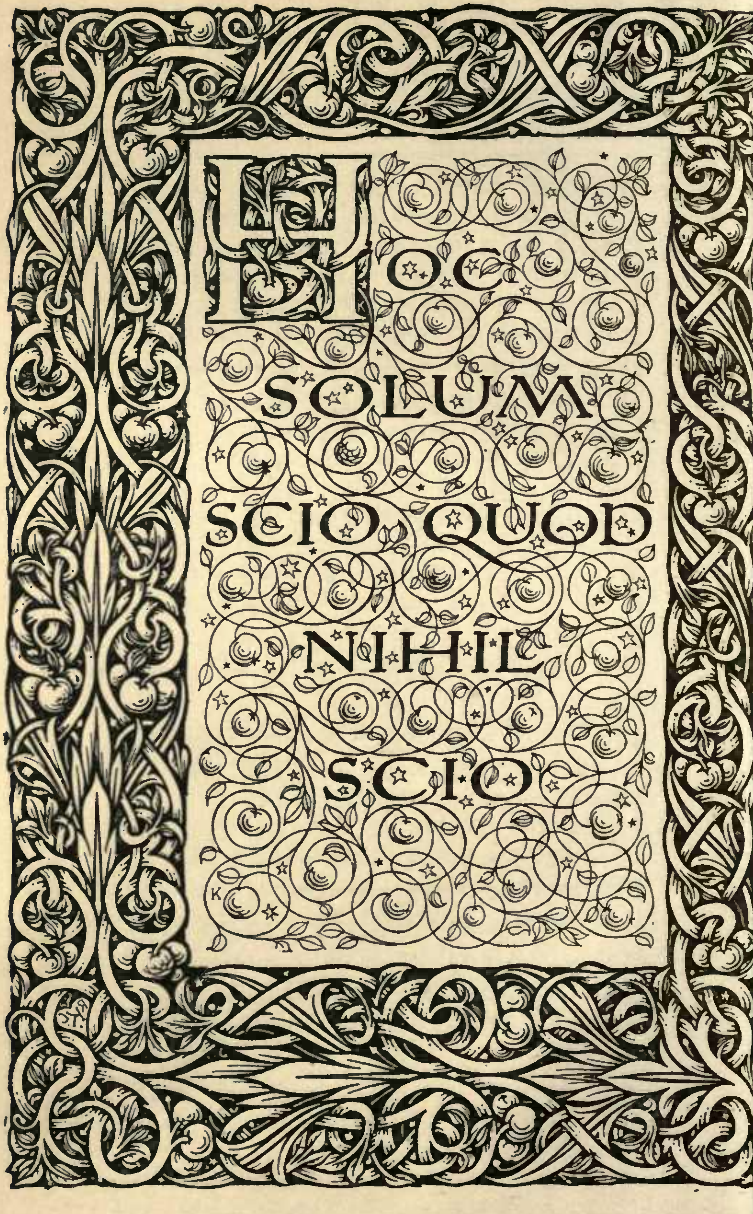

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EXPERIMENTAL RESEARCHES IN ELECTRICITY

by MICHAEL FARADAY D.C.L. F.R.S.

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INTRODUCTION[1]

By JOHN TYNDALL

When from an Alpine height the eye of the climber ranges over the mountains, he finds that for the most part they resolve themselves into distinct groups, each consisting of a dominant mass surrounded by peaks of lesser elevation. The power which lifted the mightier eminences, in nearly all cases lifted others to an almost equal height. And so it is with the discoveries of Faraday. As a general rule, the dominant result does not stand alone, but forms the culminating point of a vast and varied mass of inquiry. In this way, round about his great discovery of magneto-electric induction, other weighty labours group themselves. His investigations on the extra current; on the polar and other condition of diamagnetic bodies; on lines of magnetic force, their definite character and distribution; on the employment of the induced magneto-electric current as a measure and test of magnetic action; on the revulsive phenomena of the magnetic field, are all, notwithstanding the diversity of title, researches in the domain of magneto-electric induction.

Faraday's second group of researches and discoveries embrace the chemical phenomena of the current. The dominant result here is the great law of definite electro-chemical decomposition, around which are massed various researches on electro-chemical conduction and on electrolysis both with the machine and with the pile. To this group also belong his analysis of the contact theory, his inquiries as to the source of voltaic electricity, and his final development of the chemical theory of the pile.

His third great discovery is the magnetisation of light, which I should liken to the Weisshorn among mountains—high, beautiful, and alone.

The dominant result of his fourth group of researches is the discovery of diamagnetism, announced in his memoir as the

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[1] These pages form the "Summary" and the concluding passages of *Faraday the Discoverer*: 1869.

magnetic condition of all matter, round which are grouped his inquiries on the magnetism of flame and gases; on magnecrystallic action, and on atmospheric magnetism, in its relations to the annual and diurnal variation of the needle, the full significance of which is still to be shown,

These are Faraday's most massive discoveries, and upon them his fame must mainly rest. But even without them, sufficient would remain to secure for him a high and lasting scientific reputation. We should still have his researches on the liquefaction of gases; on frictional electricity; on the electricity of the gymnotus; on the source of power in the hydro-electric machine, the two last investigations being untouched in the foregoing memoir; on electro-magnetic rotations; on regelation; all his more purely chemical researches, including his discovery of benzol. Besides these he published a multitude of minor papers, most of which, in some way or other, illustrate his genius. I have made no allusion to his power and sweetness as a lecturer. Taking him for all and all, I think it will be conceded that Michael Faraday was the greatest experimental philosopher the world has ever seen; and I will add the opinion, that the progress of future research will tend, not to dim or to diminish, but to enhance and glorify the labours of this mighty investigator.

Thus far I have confined myself to topics mainly interesting to the man of science, endeavouring, however, to treat them in a manner unrepellent to the general reader who might wish to obtain a notion of Faraday as a worker. On others will fall the duty of presenting to the world a picture of the man. But I know you will permit me to add to the foregoing analysis a few personal reminiscences and remarks, tending to connect Faraday with a wider world than that of science—namely, with the general human heart.

One word in reference to his married life may find a place here. As in the former case, Faraday shall be his own spokesman. The following paragraph, though written in the third person, is from his hand:—"On June 12, 1821, he married, an event which more than any other contributed to his earthly happiness and healthful state of mind. The union has continued for twenty-eight years and has in no wise changed, except in the depth and strength of its character."

Faraday's immediate forefathers lived in a little place called Clapham Wood Hall, in Yorkshire. Here dwelt Robert Faraday and Elizabeth his wife, who had ten children, one of them, James Faraday, born in 1761, being father to the philosopher. A family tradition exists that the Faradays came originally from Ireland. Faraday himself has more than once expressed to me his belief that his blood was in part Celtic, but how much of it was so, or when the infusion took place, he was unable to say. He could imitate the Irish brogue, and his wonderful vivacity may have been in part due to his extraction. But there were other qualities which we should hardly think of deriving from Ireland. The most prominent of these was his sense of order, which ran like a luminous beam through all the transactions of his life. The most entangled and complicated matters fell into harmony in his hands. His mode of keeping accounts excited the admiration of the managing board of this institution. And his science was similarly ordered. In his experimental researches, he numbered every paragraph, and welded their various parts together by incessant reference. His private notes of the experimental researches, which are happily preserved, are similarly numbered: their last paragraph bears the figure 16,041. His working qualities, moreover, showed the tenacity of the Teuton. His nature was impulsive, but there was a force behind the impulse which did not permit it to retreat. If in his warm moments he formed a resolution, in his cool ones he made that resolution good. Thus his fire was that of a solid combustible, not that of a gas, which blazes suddenly, and dies as suddenly away.

And here I must claim your tolerance for the limits by which I am confined. No materials for a life of Faraday are in my hands, and what I have now to say has arisen almost wholly out of our close personal relationship.

Letters of his, covering a period of sixteen years, are before me, each one of which contains some characteristic utterance; —strong, yet delicate in counsel, joyful in encouragement, and warm in affection. References which would be pleasant to such of them as still live are made to Humboldt, Biot, Dumas, Chevreul, Magnus, and Arago. Accident brought these names prominently forward; but many others would be required to complete his list of continental friends. He prized the love and sympathy of men—prized it almost more than the renown which his science brought him. Nearly a dozen years ago it fell to my lot to write a review of his *Experimental Researches* for the *Philosophical Magazine*. After he had read it, he took me by the hand, and said, "Tyndall, the sweetest reward of my work is the sympathy and good will which it has caused to flow in upon me from all quarters of the world." Among his letters I find little sparks of kindness, precious to no one but myself, but more precious to me than all. He would peep into the laboratory when he thought me weary, and take me upstairs with him to rest. And if I happened to be absent he would leave a little note for me, couched in this or some other similar form:—"Dear Tyndall,—I was looking for you, because we were at tea—we have not yet done—will you come up?" I frequently shared his early dinner; almost always, in fact, while my lectures were going on. There was no trace of asceticism in his nature. He preferred the meat and wine of life to its locusts and wild honey. Never once during an intimacy of fifteen years did he mention religion to me, save when I drew him on to the subject. He then spoke to me without hesitation or reluctance; not with any apparent desire to "improve the occasion," but to give me such information as I sought. He believed the human heart to be swayed by a power to which science or logic opened no approach, and right or wrong, this faith, held in perfect tolerance of the faiths of others, strengthened and beautified his life.

From the letters just referred to, I will select three for publication here. I choose the first, because it contains a passage revealing the feelings with which Faraday regarded his vocation, and also because it contains an allusion which will give pleasure to a friend.

(Royal Institution.)
"Ventnor, Isle of Wight, June 28, 1854.

"MY DEAR TYNDALL,—You see by the top of this letter how much habit prevails over me; I have just read yours from thence, and yet I think myself there. However, I have left its science in very good keeping, and I am glad to learn that you are at experiment once more. But how is the health? Not well, I fear. I wish you would get yourself strong first and work afterwards. As for the fruits, I am sure they will be good, for though I sometimes despond as regards myself, I do not as regards you. You are young, I am old. . . . *But then our subjects are so glorious, that to work at them rejoices and encourages the feeblest; delights and enchants the strongest.*

"I have not yet seen anything from Magnus. Thoughts of him always delight me. We shall look at his black sulphur together. I heard from Schonbein the other day. He tells me that Liebig is full of ozone, *i.e.* of allotropic oxygen.

"Good-bye for the present.—Ever, my dear Tyndall, yours truly, M. FARADAY."

The contemplation of nature, and his own relation to her, produced in Faraday a kind of spiritual exaltation which makes itself manifest here. His religious feeling and his philosophy could not be kept apart; there was an habitual overflow of the one into the other.

Whether he or another was its exponent, he appeared to take equal delight in science. A good experiment would make him almost dance with delight. In November 1850, he wrote to me thus:—"I hope some day to take up the point respecting the magnetism of associated particles. In the meantime I rejoice at every addition to the facts and reasoning connected with the subject. When science is a republic, then it gains: and though I am no republican in other matters, I am in that." All his letters illustrate this catholicity of feeling. Ten years ago, when going down to Brighton, he carried with him a little paper I had just completed, and afterwards wrote to me. His letter is a mere sample of the sympathy which he always showed to me and my work.

"Brighton, December 9, 1857.

"MY DEAR TYNDALL,—I cannot resist the pleasure of saying how very much I have enjoyed your paper. Every part has given me delight. It goes on from point to point beautifully. You will find many pencil marks, for I made them as I read. I let them stand, for though many of them receive their answer as the story proceeds, yet they show how the wording impresses a mind fresh to the subject, and perhaps here and there you may like to alter it slightly, if you wish the full idea, *i.e.* not an inaccurate one, to be suggested at first; and yet after all I believe it is not your exposition, but the natural jumping to a conclusion that affects or has affected my pencil.

"We return on Friday, when I will return you the paper.—Ever truly yours, M. FARADAY."

The third letter will come in its proper place towards the end.

While once conversing with Faraday on science, in its relations to commerce and litigation, he said to me that at a certain period of his career he was forced definitely to ask himself, and finally to decide, whether he should make wealth or science the pursuit of his life. He could not serve both masters, and he was therefore compelled to choose between them. After the discovery of magneto-electricity his fame was so noised abroad that the commercial world would hardly have considered any remuneration too high for the aid of abilities like his. Even before he became so famous, he had done a little "professional business." This was the phrase he applied to his purely commercial work. His friend, Richard Phillips, for example, had induced him to undertake a number of analyses, which produced, in the year 1830, an addition to his income of more than a thousand pounds; and in 1831, a still greater addition. He had only to will it to raise in 1832 his professional business income to £5000 a year. Indeed, this is a wholly insufficient estimate of what he might, with ease, have realised annually during the last thirty years of his life.

While restudying the experimental researches with reference to the present memoir, the conversation with Faraday here alluded to came to my recollection, and I sought to ascertain the period when the question, "wealth or science," had presented itself with such emphasis to his mind. I fixed upon the year 1831 or 1832, for it seemed beyond the range of human power to pursue science as he had done during the subsequent years, and to pursue commercial work at the same time. To test this conclusion I asked permission to see his accounts, and on my own responsibility, I will state the result. In 1832, his professional business-income, instead of rising to £5000, or more, fell from £1090 4*s*. to £155 9*s*. From this it fell with slight oscillations to £92 in 1837, and to zero in 1838. Between 1839 and 1845, it never, except in one instance, exceeded £22; being for the most part much under this. The exceptional year referred to was that in which he and Sir Charles Lyell were engaged by Government to write a report on the Haswell Colliery explosion, and then his business income rose to £112. From the end of 1845 to the day of his death, Faraday's annual professional business income was exactly zero. Taking the duration of his life into account, this son of a blacksmith, and apprentice to a bookbinder, had to decide between a fortune of £150,000 on the one side, and his undowered science on the other.

He chose the latter, and died a poor man. But his was the glory of holding aloft among the nations the scientific name of England for a period of forty years.

The outward and visible signs of fame were also of less account to him than to most men. He had been loaded with scientific honours from all parts of the world. Without, I imagine, a dissentient voice, he was regarded as the prince of the physical investigators of the present age. The highest scientific position in this country he had, however, never filled. When the late excellent and lamented Lord Wrottesley resigned the presidency of the Royal Society, a deputation from the council, consisting of his lordship, Mr. Grove, and Mr. Gassiot, waited upon Faraday, to urge him to accept the president's chair. All that argument or friendly persuasion could do was done to induce him to yield to the wishes of the council, which was also the unanimous wish of scientific men. A knowledge of the quickness of his own nature had induced in Faraday the habit of requiring an interval of reflection, before he decided upon any question of importance. In the present instance he followed his usual habit, and begged for a little time.

On the following morning, I went up to his room, and said on entering that I had come to him with some anxiety of mind. He demanded its cause, and I responded "lest you should have decided against the wishes of the deputation that waited on you yesterday." "You would not urge me to undertake this responsibility," he said. "I not only urge you," was my reply, "but I consider it your bounden duty to accept it." He spoke of the labour that it would involve; urged that it was not in his nature to take things easy; and that if he became president, he would surely have to stir many new questions, and agitate for some changes. I said that in such cases he would find himself supported by the youth and strength of the royal society. This, however, did not seem to satisfy him. Mrs. Faraday came into the room, and he appealed to her. Her decision was adverse, and I deprecated her decision. "Tyndall," he said at length, "I must remain plain Michael Faraday to the last; and let me now tell you, that if I accepted the honour which the royal society desires to confer upon me, I would not answer for the integrity of my intellect for a single year." I urged him no more, and Lord Wrottesley had a most worthy successor in Sir Benjamin Brodie.

After the death of the Duke of Northumberland, our board of managers wished to see Mr. Faraday finish his career as President of the institution which he had entered on weekly wages more than half a century before. But he would have nothing to do with the presidency. He wished for rest, and the reverent affection of his friends was to him infinitely more precious than all the honours of official life.

. . . .

In the year 1835, Sir Robert Peel wished to offer Faraday a pension, but that great statesman quitted office before he was able to realise his wish. The minister who founded these pensions intended them, I believe, to be marks of honour which even proud men might accept without compromise of independence. When, however, the intimation first reached Faraday, in an unofficial way, he wrote a letter announcing his determination to decline the pension; and stating that he was quite competent to earn his livelihood himself. That letter still exists, but it was never sent, Faraday's repugnance having been overruled by his friends. When Lord Melbourne came into office, he desired to see Faraday; and probably in utter ignorance of the man—for, unhappily for them and us, ministers of state in England are only too often ignorant of great Englishmen—his Lordship said something that must have deeply displeased his visitor. The whole circumstances were once communicated to me, but I have forgotten the details. The term "humbug," I think, was incautiously employed by his lordship, and other expressions were used of a similar kind. Faraday quitted the minister with his own resolves, and that evening he left his card and a short and decisive note at the residence of Lord Melbourne, stating that he had manifestly mistaken his lordship's intention of honouring science in his person, and declining to have anything whatever to do with the proposed pension. The good-humoured nobleman at first considered the matter a capital joke; but he was afterwards led to look at it more seriously. An excellent lady, who was a friend both to Faraday and the minister, tried to arrange matters between them; but she found Faraday very difficult to move from the position he had assumed. After many fruitless efforts, she at length begged of him to state what he would require of Lord Melbourne to induce him to change his mind. He replied, "I should require from his lordship what I have no right or reason to expect that he would grant—a written apology for the words he permitted himself to use to me." The required apology came, frank and full, creditable, I thought, alike to the prime minister and the philosopher.

Considering the enormous strain imposed on Faraday's intellect, the boy-like buoyancy even of his later years was astonishing. He was often prostrate, but he had immense resiliency, which he brought into action by getting away from London whenever his health failed. I have already indicated the thoughts which filled his mind during the evening of his life. He brooded on magnetic media and lines of force; and the great object of the last investigation he ever undertook was the decision of the question whether magnetic force requires *time* for its propagation. How he proposed to attack this subject we may never know. But he has left some beautiful apparatus behind; delicate wheels and pinions, and associated mirrors, which were to have been employed in the investigation. The mere conception of such an inquiry is an illustration of his strength and hopefulness, and it is impossible to say to what results it might have led him. But the work was too heavy for his tired brain. It was long before he could bring himself to relinquish it, and during this struggle he often suffered from fatigue of mind. It was at this period, and before he resigned himself to the repose which marked the last two years of his life, that he wrote to me the following letter—one of many priceless letters now before me—which reveals, more than anything another pen could express, the state of his mind at the time. I was sometimes censured in his presence for my doings in the Alps, but his constant reply was, "Let him alone, he knows how to take care of himself." In this letter, anxiety on this score reveals itself, for the first time.

"Hampton Court, August 1, 1864.

"MY DEAR TYNDALL,—I do not know whether my letter will catch you, but I will risk it, though feeling very unfit to communicate with a man whose life is as vivid and active as yours; but the receipt of your kind letter makes me to know that though I forget, I am not forgotten, and though I am not able to remember at the end of a line what was said at the beginning of it, the imperfect marks will convey to you some sense of what I long to say. We had heard of your illness through Miss Moore, and I was therefore very glad to learn that you are now quite well; do not run too many risks or make your happiness depend too much upon dangers, or the hunting of them. Sometimes the very thinking of you, and what you may be about, wearies *me* with fears, and then the cogitations pause and change, but without giving me rest. I know that much of this depends upon my own worn-out nature, and I do not know why I write it, save that when I write to you I cannot help thinking it, and the thoughts stand in the way of other matter.

. . . .

"See what a strange desultory epistle I am writing to you, and yet I feel so weary that I long to leave my desk and go to the couch.

"My dear wife and Jane desire their kindest remembrances: I hear them in the next room: . . . I forget—but not you, my dear Tyndall, for I am ever yours,

"M. FARADAY."

This weariness subsided when he relinquished his work, and I have a cheerful letter from him, written in the autumn of 1865. But towards the close of that year he had an attack of illness, from which he never completely rallied. He continued to attend the Friday evening meetings, but the advance of infirmity was apparent to us all. Complete rest became finally essential to him, and he ceased to appear among us. There was no pain in his decline to trouble the memory of those who loved him. Slowly and peacefully he sank towards his final rest, and when it came, his death was a falling asleep. In the fulness of his honours and of his age he quitted us; the good fight fought, the work of duty—shall I not say of glory—done. The "Jane" referred to in the foregoing letter is Faraday's niece, Miss Jane Barnard, who, with an affection raised almost to religious devotion, watched him and tended him to the end.

I saw Mr. Faraday for the first time on my return from Marburg in 1850. I came to the Royal Institution, and sent up my card, with a copy of the paper which Knoblauch and myself had just completed. He came down and conversed with me for half-an-hour. I could not fail to remark the wonderful play of intellect and kindly feeling exhibited by his countenance. When he was in good health the question of his age would never occur to you. In the light and laughter of his eyes you never thought of his grey hairs. He was then on the point of publishing one of his papers on magne-crystallic action, and he had time to refer in a flattering note to the memoir I placed in his hands. I returned to Germany, worked there for nearly another year, and in June 1851 came back finally from Berlin to England. Then, for the first time, and on my way to the meeting of the British Association, at Ipswich, I met a man who has since made his mark upon the intellect of his time; who has long been, and who by the strong law of natural affinity must continue to be, a brother to me. We were both without definite outlook at the time, needing proper work, and only anxious to have it to perform. The chairs of natural history and of physics being advertised as vacant in the university of Toronto, we applied for them, he for the one, I for the other; but, possibly guided by a prophetic instinct, the university authorities declined having anything to do with either of us. If I remember aright, we were equally unlucky elsewhere.

One of Faraday's earliest letters to me had reference to this Toronto business, which he thought it unwise in me to neglect. But Toronto had its own notions, and in 1853, at the instance of Dr. Bence Jones, and on the recommendation of Faraday himself, a chair of physics at the royal institution was offered to me. I was tempted at the same time to go elsewhere, but a strong attraction drew me to his side. Let me say that it was mainly his and other friendships, precious to me beyond all expression, that caused me to value my position here more highly than any other that could be offered to me in this land. Nor is it for its honour, though surely that is great, but for the strong personal ties that bind me to it, that I now chiefly prize this place. You might not credit me were I to tell you how lightly I value the honour of being Faraday's successor compared with the honour of being Faraday's friend. His friendship was energy and inspiration; his "mantle" is a burden almost too heavy to be borne.

Sometimes during the last year of his life, by the permission or invitation of Mrs. Faraday, I went up to his rooms to see him. The deep radiance, which in his time of strength flashed with such extraordinary power from his countenance, had subsided to a calm and kindly light, by which my latest memory of him is warmed and illuminated. I knelt one day beside him on the carpet and placed my hand upon his knee; he stroked it affectionately, smiled, and murmured, in a low soft voice, the last words that I remember as having been spoken to me by Michael Faraday.

It was my wish and aspiration to play the part of Schiller to this Goethe: and he was at times so strong and joyful—his body so active, and his intellect so clear—as to suggest to me the thought that he, like Goethe, would see the younger man laid low. Destiny ruled otherwise, and now he is but a memory to us all. Surely no memory could be more beautiful. He was equally rich in mind and heart. The fairest traits of a character sketched by Paul, found in him perfect illustration. For he was "blameless, vigilant, sober, of good behaviour, apt to teach, not given to filthy lucre." He had not a trace of worldly ambition; he declared his duty to his sovereign by going to the levee once a year, but beyond this he never sought contact with the great. The life of his spirit and of his intellect was so full that the things which men most strive after were absolutely indifferent to him. "Give me health and a day," says the brave Emerson, "and I will make the pomp of emperors ridiculous." In an eminent degree Faraday could say the same. What to him was the splendour of a palace compared with a thunderstorm upon Brighton downs?—what among all the appliances of royalty to compare with the setting sun? I refer to a thunderstorm and a sunset, because these things excited a kind of ecstasy in his mind, and to a mind open to such ecstasy the pomps and pleasures of the world are usually of small account. Nature, not education, rendered Faraday strong and refined. A favourite experiment of his own was representative of himself. He loved to show that water in crystallising excluded all foreign ingredients, however intimately they might be mixed with it. Out of acids, alkalis, or saline solutions, the crystal came sweet and pure. By some such natural process in the formation of this man, beauty and nobleness coalesced, to the exclusion of everything vulgar and low. He did not learn his gentleness in the world, for he withdrew himself from its culture; and still this land of England contained no truer gentleman than he. Not half his greatness was incorporate in his science, for science could not reveal the bravery and delicacy of his heart.

But it is time that I should end these weak words, and lay my poor garland on the grave of this

JUST AND FAITHFUL KNIGHT OF GOD.

The following is a list of the works of Michael Faraday:—

Some Observations on the Means of Obtaining Knowledge, 1817; History of the Progress of Electro-Magnetism, 1821; Chemical Manipulation, 1827; edition On the Alleged Decline of Science in England, 1831; On the Practical Prevention of Dry Rot in Timber, 1833; Experimental Researches in Electricity, 3 vols., 1839-55; Observations on Mental Education, 1855; Experimental Researches in Chemistry and Physics (reprinted from Philosophical Transactions, The Journal of the Royal Institution, etc.), 1859; The Various Forces of Matter (six lectures edited by Sir Wm. Crookes), 1860; The Chemical History of a Candle (six lectures edited by Sir Wm. Crookes), 1861; Some Thoughts on the Conservation of Force, 1865; The Liquefaction of Gases (papers given, 1823-45), 1896.

LIFE.—Prof. J. Tyndall, Faraday as a Discoverer, 1868; J. B. A. Dumas, Eloge historique de M. Faraday, 1868; Dr. Bence Jones, The Life and Letters of Faraday, 2 vols., 1870; Dr. J. H. Gladstone, 1872; W. Jerrold, Michael Faraday, Man of Science, 1893; Silvanus P. Thompson, Michael Faraday: His Life and Work, 1898; The Letters of Faraday and Schoenbein, 1836-62, edited by G. W. A. Kahlbaum and F. V. Darbishire, 1899.

NOTE.—The present select edition of the Experimental Researches in Electricity consists of Series III.-VIII. and XVI., XVII. of the original issue in three volumes (1839-55), with the plates and figures distributed for the reader's convenience in the text, and the sections and paragraphs consecutively renumbered.

CONTENTS

EXPERIMENTAL RESEARCHES IN ELECTRICITY

I[1]

§ 1. IDENTITY OF ELECTRICITIES DERIVED FROM DIFFERENT SOURCES. § 2. RELATION BY MEASURE OF COMMON AND VOLTAIC ELECTRICITY

§ 1. *Identity of Electricities derived from different sources*

1. THE progress of the electrical researches which I have had the honour to present to the Royal Society, brought me to a point at which it was essential for the further prosecution of my inquiries that no doubt should remain of the identity or distinction of electricities excited by different means. It is perfectly true that Cavendish,[2] Wollaston,[3] Colladon[4] and others, have in succession removed some of the greatest objections to the acknowledgment of the identity of common, animal and voltaic electricity, and I believe that most philosophers consider these electricities as really the same. But on the other hand it is also true, that the accuracy of Wollaston's experiments has been denied;[5] and also that one of them, which really is no proper proof of chemical decomposition by common electricity (45, 63), has been that selected by several experimenters as the test of chemical action (72, 82). It is a fact, too, that many philosophers are still drawing distinctions between the electricities from different sources; or at least doubting whether their identity is proved. Sir Humphry Davy, for instance, in his paper on the Torpedo,[6] thought it

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[1] Third Series, original edition, vol. i. p. 76.

[2] *Phil. Trans.* 1776, p. 196.

[3] *Ibid.* 1801, p. 434.

[4] *Annales de Chimie*, 1826, p. 62, etc.

[5] *Phil. Trans.* 1832, p. 282, note.

[6] *Phil. Trans.* 1829, p. 17. "Common electricity is excited upon non-conductors, and is readily carried off by conductors and imperfect conductors. Voltaic electricity is excited upon combinations of perfect and imperfect conductors, and is only transmitted by perfect conductors or imperfect conductors of the best kind. Magnetism, if it be a form of electricity, belongs only to perfect conductors; and, in its modifications, to a peculiar class of them." (Dr. Ritchie has shown this is not the case, *Phil. Trans.* 1832, p. 294.) "Animal electricity resides only in the imperfect conductors forming the organs of living animals, etc."

probable that animal electricity would be found of a peculiar kind; and referring to it, to common electricity, voltaic electricity and magnetism, has said, "Distinctions might be established in pursuing the various modifications or properties of electricity in these different forms, etc." Indeed I need only refer to the last volume of the *Philosophical Transactions* to show that the question is by no means considered as settled.[1]

2. Notwithstanding, therefore, the general impression of the identity of electricities, it is evident that the proofs have not been sufficiently clear and distinct to obtain the assent of all those who were competent to consider the subject; and the question seemed to me very much in the condition of that which Sir H. Davy solved so beautifully,—namely, whether voltaic electricity in all cases merely eliminated, or did not in some actually produce, the acid and alkali found after its action upon water. The same necessity that urged him to decide the doubtful point, which interfered with the extension of his views, and destroyed the strictness of his reasoning, has obliged me to ascertain the identity or difference of common and voltaic electricity. I have satisfied myself that they are identical, and I hope the experiments which I have to offer, and the proofs flowing from them, will be found worthy the attention of the Royal Society.

3. The various phenomena exhibited by electricity may, for the purposes of comparison, be arranged under two heads; namely, those connected with electricity of tension, and those belonging to electricity in motion. This distinction is taken at

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[1] *Phil. Trans.* 1832, p. 259. Dr. Davy, in making experiments on the torpedo, obtains effects the same as those produced by common and voltaic electricity, and says that in its magnetic and chemical power it does not seem to be essentially peculiar,—p. 274; but he then says, p. 275, there are other points of difference: and after referring to them, adds, "How are these differences to be explained? Do they admit of explanation similar to that advanced by Mr. Cavendish in his theory of the torpedo; or may we suppose, according to the analogy of the solar ray, that the electrical power, whether excited by the common machine, or by the voltaic battery, or by the torpedo, is not a simple power, but a combination of powers, which may occur variously associated, and produce all the varieties of electricity with which we are acquainted?"

At p. 279 of the same volume of *Transactions* is Dr. Ritchie's paper, from which the following are extracts: "Common electricity is diffused over the surface of the metal;—voltaic electricity exists within the metal. Free electricity is conducted over the surface of the thinnest gold leaf as effectually as over a mass of metal having the same surface;—voltaic electricity requires thickness of metal for its conduction," p. 280: and again, "The supposed analogy between common and voltaic electricity, which was so eagerly traced after the invention of the pile, completely fails in this case, which was thought to afford the most striking resemblance," p. 291.

present not as philosophical, but merely as convenient. The effect of electricity of tension, at rest, is either attraction or repulsion at sensible distances. The effects of electricity in motion or electrical currents may be considered as 1st, Evolution of heat; 2nd, Magnetism; 3rd, Chemical decomposition; 4th, Physiological phenomena; 5th, Spark. It will be my object to compare electricities from different sources, and especially common and voltaic electricities, by their power of producing these effects.

I. *Voltaic Electricity*

4. *Tension.*—When a voltaic battery of 100 pairs of plates has its extremities examined by the ordinary electrometer, it is well known that they are found positive and negative, the gold leaves at the same extremity repelling each other, the gold leaves at different extremities attracting each other, even when half an inch or more of air intervenes.

5. That ordinary electricity is discharged by points with facility through air; that it is readily transmitted through highly rarefied air; and also through heated air, as for instance a flame; is due to its high tension. I sought, therefore, for similar effects in the discharge of voltaic electricity, using as a test of the passage of the electricity either the galvanometer or chemical action produced by the arrangement hereafter to be described (48, 52).

6. The voltaic battery I had at my disposal consisted of 140 pairs of plates four inches square, with double coppers. It was insulated throughout, and diverged a gold leaf electrometer about one-third of an inch. On endeavouring to discharge this battery by delicate points very nicely arranged and approximated, either in the air or in an exhausted receiver, I could obtain no indications of a current, either by magnetic or chemical action. In this, however, was found no point of discordance between voltaic and common electricity; for when a Leyden battery (27) was charged so as to deflect the gold leaf electrometer to the same degree, the points were found equally unable to discharge it with such effect as to produce either magnetic or chemical action. This was not because common electricity could not produce both these effects (43, 46), but because when of such low intensity the quantity required to make the effects visible (being enormously great (107, 111)) could not be transmitted in any reasonable time. In conjunction with the other

proofs of identity hereafter to be given, these effects of points also prove identity instead of difference between voltaic and common electricity

7. As heated air discharges common electricity with far greater facility than points, I hoped that voltaic electricity might in this way also be discharged. An apparatus was therefore constructed (fig. 1), in which A B is an insulated glass rod upon which two copper wires, C, D, are fixed firmly; to these wires are soldered two pieces of fine platina wire, the ends of which are brought very close to each other at *e*, but without touching; the copper wire C was connected with the positive pole of a voltaic battery, and the wire D with a decomposing apparatus (48, 52), from which the communication was completed to the negative pole of the battery. In these experiments only two troughs, or twenty pairs of plates, were used.

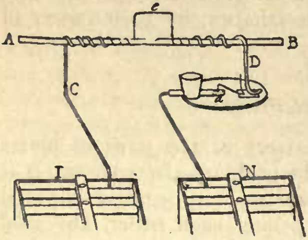

Fig. 1.

8. Whilst in the state described, no decomposition took place at the point *a*, but when the side of a spirit-lamp flame was applied to the two platina extremities at *e*, so as to make them bright red-hot, decomposition occurred; iodine soon appeared at the point *a*, and the transference of electricity through the heated air was established. On raising the temperature of the points *e* by a blowpipe, the discharge was rendered still more free, and decomposition took place instantly. On removing the source of heat, the current immediately ceased. On putting the ends of the wires very close by the side of and parallel to each other, but not touching, the effects were perhaps more readily obtained than before. On using a larger voltaic battery (6), they were also more freely obtained.

9. On removing the decomposing apparatus and interposing a galvanometer instead, heating the points *e* as the needle would swing one way, and removing the heat during the time of its return (38), feeble deflections were soon obtained: thus also proving the current through heated air; but the instrument used was not so sensible under the circumstances as chemical action.

10. These effects, not hitherto known or expected under this form, are only cases of the discharge which takes place through

air between the charcoal terminations of the poles of a powerful battery, when they are gradually separated after contact. Then the passage is through heated air exactly as with common electricity, and Sir H. Davy has recorded that with the original battery of the Royal Institution this discharge passed through a space of at least four inches.[1] In the exhausted receiver the electricity would *strike* through nearly half an inch of space, and the combined effects of rarefaction and heat was such upon the inclosed air as to enable it to conduct the electricity through a space of six or seven inches.

11. The instantaneous charge of a Leyden battery by the poles of a voltaic apparatus is another proof of the tension, and also the quantity, of electricity evolved by the latter. Sir H. Davy says,[2] "When the two conductors from the ends of the combination were connected with a Leyden battery, one with the internal, the other with the external coating, the battery instantly became charged; and on removing the wires and making the proper connections, either a shock or a *spark* could be perceived: and the least possible time of contact was sufficient to renew the charge to its full intensity."

12. *In motion :* i. *Evolution of heat.*—The evolution of heat in wires and fluids by the voltaic current is matter of general notoriety.

13. ii. *Magnetism.*—No fact is better known to philosophers than the power of the voltaic current to deflect the magnetic needle, and to make magnets according to *certain laws ;* and no effect can be more distinctive of an electrical current.

14. iii. *Chemical decomposition.*—The chemical powers of the voltaic current, and their subjection to *certain laws*, are also perfectly well known.

15. iv. *Physiological effects.*—The power of the voltaic current, when strong, to shock and convulse the whole animal system, and when weak to affect the tongue and the eyes, is very characteristic.

16. v. *Spark.*—The brilliant star of light produced by the discharge of a voltaic battery is known to all as the most beautiful light that man can produce by art.

17. That these effects may be almost infinitely varied, some being exalted whilst others are diminished, is universally acknowledged; and yet without any doubt of the identity of character of the voltaic currents thus made to differ in their

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[1] *Elements of Chemical Philosophy.*

[2] *Ibid.* p. 154.

effect. The beautiful explication of these variations afforded by Cavendish's theory of quantity and intensity requires no support at present, as it is not supposed to be doubted.

18. In consequence of the comparisons that will hereafter arise between wires carrying voltaic and ordinary electricities, and also because of certain views of the condition of a wire or any other conducting substance connecting the poles of a voltaic apparatus, it will be necessary to give some definite expression of what is called the voltaic current, in contradistinction to any supposed peculiar state of arrangement, not progressive, which the wire or the electricity within it may be supposed to assume. If two voltaic troughs P N, P′ N′, fig. 2, be symmetrically arranged and insulated, and the ends N P′ connected by a wire, over which a magnetic needle is suspended, the wire will exert no effect over the needle; but immediately that the ends P N′ are connected by another wire, the needle will be deflected, and will remain so as long as the circuit is complete. Now if the troughs merely act by causing a peculiar arrangement in the wire either of its particles or its electricity, that arrangement constituting its electrical and magnetic state, then the wire N P′ should be in a similar state of arrangement *before* P and N′ were connected, to what it is afterwards, and should have deflected the needle, although less powerfully, perhaps to one-half the extent which would result when the communication is complete throughout. But if the magnetic effects depend upon a current, then it is evident why they could not be produced in *any* degree before the circuit was complete; because prior to that no current could exist.

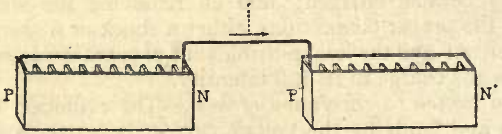

Fig. 2.

19. By *current*, I mean anything progressive, whether it be a fluid of electricity, or two fluids moving in opposite directions, or merely vibrations, or, speaking still more generally, progressive forces. By *arrangement*, I understand a local adjustment of particles, or fluids, or forces, not progressive. Many other reasons might be urged in support of the view of a *current*

rather than an *arrangement*, but I am anxious to avoid stating unnecessarily what will occur to others at the moment.

II. *Ordinary Electricity*

20. By ordinary electricity I understand that which can be obtained from the common machine, or from the atmosphere, or by pressure, or cleavage of crystals, or by a multitude of other operations; its distinctive character being that of great intensity, and the exertion of attractive and repulsive powers, not merely at sensible but at considerable distances.

21. *Tension.*—The attractions and repulsions at sensible distances, caused by ordinary electricity, are well known to be so powerful in certain cases, as to surpass, almost infinitely, the similar phenomena produced by electricity, otherwise excited. But still those attractions and repulsions are exactly of the same nature as those already referred to under the head *Tension, Voltaic electricity* (4); and the difference in degree between them is not greater than often occurs between cases of ordinary electricity only. I think it will be unnecessary to enter minutely into the proofs of the identity of this character in the two instances. They are abundant; are generally admitted as good; and lie upon the surface of the subject: and whenever in other parts of the comparison I am about to draw, a similar case occurs, I shall content myself with a mere announcement of the similarity, enlarging only upon those parts where the great question of distinction or identity still exists.

22. The discharge of common electricity through heated air is a well-known fact. The parallel case of voltaic electricity has already been described (8, etc.).

23. *In motion:* i. *Evolution of heat.*—The heating power of common electricity, when passed through wires or other substances, is perfectly well known. The accordance between it and voltaic electricity is in this respect complete. Mr. Harris has constructed and described[1] a very beautiful and sensible instrument on this principle, in which the heat produced in a wire by the discharge of a small portion of common electricity is readily shown, and to which I shall have occasion to refer for experimental proof in a future part of this paper (80).

24. ii. *Magnetism.*—Voltaic electricity has most extraordinary

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[1] *Philosophical Transactions*, 1827, p. 18. *Edinburgh Transactions*, 1831. *Harris on a New Electrometer*, etc., etc.

and exalted magnetic powers. If common electricity be identical with it, it ought to have the same powers. In rendering needles or bars magnetic, it is found to agree with voltaic electricity, and the *direction* of the magnetism, in both cases, is the same; but in deflecting the magnetic needle, common electricity has been found deficient, so that sometimes its power has been denied altogether, and at other times distinctions have been hypothetically assumed for the purpose of avoiding the difficulty.[1]

25. M. Colladon, of Geneva, considered that the difference might be due to the use of insufficient quantities of common electricity in all the experiments before made on this head; and in a memoir read to the Académie des Sciences in 1826,[2] describes experiments, in which, by the use of a battery, points, and a delicate galvanometer, he succeeded in obtaining deflections, and thus establishing identity in that respect. MM. Arago, Ampère, and Savary, are mentioned in the paper as having witnessed a successful repetition of the experiments. But as no other one has come forward in confirmation, MM. Arago, Ampère, and Savary, not having themselves published (that I am aware of) their admission of the results, and as some have not been able to obtain them, M. Colladon's conclusions have been occasionally doubted or denied; and an important point with me was to establish their accuracy, or remove them entirely from the body of received experimental research. I am happy to say that my results fully confirm those by M. Colladon, and I should have had no occasion to describe them, but that they are essential as proofs of the accuracy of the final and general conclusions I am enabled to draw respecting the magnetic and chemical action of electricity (96, 102, 103, 113, etc.).

26. The plate electrical machine I have used is fifty inches in diameter; it has two sets of rubbers; its prime conductor consists of two brass cylinders connected by a third, the whole length being twelve feet, and the surface in contact with air about 1422 square inches. When in good excitation, one revolution of the plate will give ten or twelve sparks from the conductors, each an inch in length. Sparks or flashes from ten to fourteen inches in length may easily be drawn from the conductors. Each turn of the machine, when worked moderately, occupies about four-fifths of a second.

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[1] Demonferrand's *Manuel d'Electricité dynamique*, p. 121.

[2] *Annales de Chimie*, xxxiii. p. 62.

27. The electric battery consisted of fifteen equal jars. They are coated eight inches upwards from the bottom, and are twenty-three inches in circumference, so that each contains 184 square inches of glass, coated on both sides; this is independent of the bottoms, which are of thicker glass, and contain each about fifty square inches.

28. A good *discharging train* was arranged by connecting metallically a sufficiently thick wire with the metallic gas pipes of the house, with the metallic gas pipes belonging to the public gas works of London, and also with the metallic water pipes of London. It was so effectual in its office as to carry off instantaneously electricity of the feeblest tension, even that of a single voltaic trough, and was essential to many of the experiments.

29. The galvanometer was one or the other of those formerly described,[1] but the glass jar covering it and supporting the needle was coated inside and outside with tinfoil, and the upper part (left uncoated, that the motions of the needle might be examined) was covered with a frame of wirework, having numerous sharp points projecting from it. When this frame and the two coatings were connected with the discharging train (28), an insulated point or ball, connected with the machine when most active, might be brought within an inch of any part of the galvanometer, yet without affecting the needle within by ordinary electrical attraction or repulsion.

30. In connection with these precautions, it may be necessary to state that the needle of the galvanometer is very liable to have its magnetic power deranged, diminished, or even inverted by the passage of a shock through the instrument. If

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[1] The galvanometer was roughly made, yet sufficiently delicate in its indications. The wire was of copper covered with silk, and made sixteen or eighteen convolutions. Two sewing-needles were magnetised and fixed on to a stem of dried grass parallel to each other, but in opposite directions, and about half an inch apart; this system was suspended by a fibre of unspun silk, so that the lower needle should be between the convolutions of the multiplier, and the upper above them. The latter was by much the most powerful magnet, and gave terrestrial direction to the whole; fig. 3 represents the direction of the wire and of the needles when the instrument was placed in the magnetic meridian: the ends of the wires are marked A and B. The letters S and N designate the south and north ends of the needle when affected merely by terrestrial magnetism; the end N is therefore the marked pole. The whole instrument was protected by a glass jar, and stood about eight feet from, and about sixteen or seventeen degrees on one side of, the large magnet (which was composed of about 450 bar magnets, fifteen inches long, one inch wide, and half an inch thick, arranged in a box so as to present at one of its extremities two external poles).

the needle be at all oblique, in the wrong direction, to the coils of the galvanometer when the shock passes, effects of this kind are sure to happen.

31. It was to the retarding power of bad conductors, with the intention of diminishing its *intensity* without altering its *quantity*, that I first looked with the hope of being able to make common electricity assume more of the characters and power of voltaic electricity, than it is usally supposed to have.

32. The coating and armour of the galvanometer were first connected with the discharging train (28); the end B (fig. 3) of the galvanometer wire was connected with the outside coating of the battery, and then both these with the discharging train; the end A of the galvanometer wire was connected with a discharging rod by a wet thread four feet long; and finally, when the battery (27) had been positively charged by about forty turns of the machine, it was discharged by the rod and the thread through the galvanometer. The needle immediately moved.

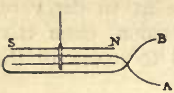

Fig. 3.

33. During the time that the needle completed its vibration in the first direction and returned, the machine was worked, and the battery recharged; and when the needle in vibrating resumed its first direction, the discharge was again made through the galvanometer. By repeating this action a few times, the vibrations soon extended to above 40° on each side of the line of rest.

34. This effect could be obtained at pleasure. Nor was it varied, apparently, either in direction or degree, by using a short thick string, or even four short thick strings in place of the long fine thread. With a more delicate galvanometer, an excellent swing of the needle could be obtained by one discharge of the battery.

35. On reversing the galvanometer communications so as to pass the discharge through from B to A, the needle was equally well deflected, but in the opposite direction.

36. The deflections were in the same direction as if a voltaic current had been passed through the galvanometer, *i.e.* the positively charged surface of the electric battery coincided with the positive end of the voltaic apparatus (4), and the negative surface of the former with the negative end of the latter.

37. The battery was then thrown out of use, and the communications so arranged that the current could be passed from the prime conductor, by the discharging rod held against it,

through the wet string, through the galvanometer coil, and into the discharging train, by which it was finally dispersed. This current could be stopped at any moment, by removing the discharging rod, and either stopping the machine or connecting the prime conductor by another rod with the discharging train; and could be as instantly renewed. The needle was so adjusted, that whilst vibrating in moderate and small arcs, it required time equal to twenty-five beats of a watch to pass in one direction through the arc, and of course an equal time to pass in the other direction.

38. Thus arranged, and the needle being stationary, the current, direct from the machine, was sent through the galvanometer for twenty-five beats, then interrupted for other twenty-five beats, renewed for twenty-five beats more, again interrupted for an equal time, and so on continually. The needle soon began to vibrate visibly, and after several alternations of this kind, the vibration increased to 40° or more.

39. On changing the direction of the current through the galvanometer, the direction of the deflection of the needle was also changed. In all cases the motion of the needle was in direction the same as that caused either by the use of the electric battery or a voltaic trough (36).

40. I now rejected the wet string, and substituted a copper wire, so that the electricity of the machine passed at once into wires communicating directly with the discharging train, the galvanometer coil being one of the wires used for the discharge. The effects were exactly those obtained above (38).

41. Instead of passing the electricity through the system, by bringing the discharging rod at the end of it into contact with the conductor, four points were fixed on to the rod; when the current was to pass, they were held about twelve inches from the conductor, and when it was not to pass, they were turned away. Then operating as before (38), except with this variation, the needle was soon powerfully deflected, and in perfect consistency with the former results. Points afforded the means by which Colladon, in all cases, made his discharges.

42. Finally, I passed the electricity first through an exhausted receiver, so as to make it there resemble the aurora borealis, and then through the galvanometer to the earth; and it was found still effective in deflecting the needle, and apparently with the same force as before.

43. From all these experiments, it appears that a current of common electricity, whether transmitted through water or

metal, or rarefied air, or by means of points in common air, is still able to deflect the needle; the only requisite being, apparently, to allow time for its action: that it is, in fact, just as magnetic in every respect as a voltaic current, and that in this character therefore no distinction exists.

44. Imperfect conductors, as water, brine, acids, etc., etc., will be found far more convenient for exhibiting these effects than other modes of discharge, as by points or balls; for the former convert at once the charge of a powerful battery into a feeble spark discharge, or rather continuous current, and involve little or no risk of deranging the magnetism of the needles (30).

45. iii. *Chemical decomposition.*—The chemical action of voltaic electricity is characteristic of that agent, but not more characteristic than are the *laws* under which the bodies evolved by decomposition arrange themselves at the poles. Dr. Wollaston showed[1] that common electricity resembled it in these effects, and "that they are both essentially the same;" but he mingled with his proofs an experiment having a resemblance, and nothing more, to a case of voltaic decomposition, which however he himself partly distinguished; and this has been more frequently referred to by some, on the one hand, to prove the occurrence of electro-chemical decomposition, like that of the pile, and by others to throw doubt upon the whole paper, than the more numerous and decisive experiments which he has detailed.

46. I take the liberty of describing briefly my results, and of thus adding my testimony to that of Dr. Wollaston on the identity of voltaic and common electricity as to chemical action, not only that I may facilitate the repetition of the experiments, but also lead to some new consequences respecting electro-chemical decomposition (112, 113).

47. I first repeated Wollaston's fourth experiment,[2] in which the ends of coated silver wires are immersed in a drop of sulphate of copper. By passing the electricity of the machine through such an arrangement, that end in the drop which received the electricity became coated with metallic copper. One hundred turns of the machine produced an evident effect; two hundred turns a very sensible one. The decomposing action was however very feeble. Very little copper was precipitated, and no sensible trace of silver from the other pole appeared in the solution.

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[1] *Philosophical Transactions*, 1801, pp. 427, 434.

[2] *Ibid.* 1801, p. 429.

48. A much more convenient and effectual arrangement for chemical decompositions by common electricity is the following. Upon a glass plate, fig. 4, placed over, but raised above a piece of white paper, so that shadows may not interfere, put two pieces of tinfoil *a*, *b*; connect one of these by an insulated wire *c*, or wire and string (37), with the machine, and the other *g*, with the discharging train (28) or the negative conductor; provide two pieces of fine platina wire, bent as in fig. 5, so that the part *d*, *f* shall be nearly upright, whilst the whole is resting on the three bearing points *p*, *c*, *f*; place these as in fig. 4; the points *p*, *n* then become the decomposing poles. In this way surfaces of contact, as minute as possible, can be obtained at pleasure, and the connection can be broken or renewed in a moment, and the substances acted upon examined with the utmost facility.

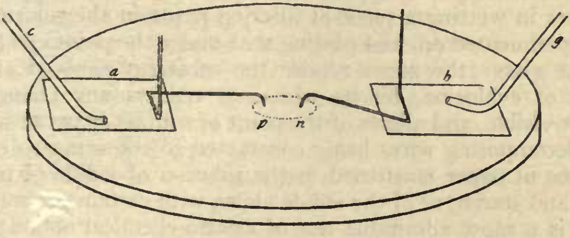

Fig. 4.

49. A coarse line was made on the glass with solution of sulphate of copper, and the terminations *p* and *n* put into it; the foil *a* was connected with the positive conductor of the machine by wire and wet string, so that no sparks passed: twenty turns of the machine caused the precipitation of so much copper on the end *n*, that it looked like copper wire; no apparent change took place at *p*.

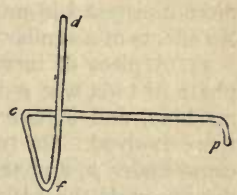

Fig. 5

50. A mixture of equal parts of muriatic acid and water was rendered deep blue by sulphate of indigo, and a large drop put on the glass, fig. 4, so that *p* and *n* were immersed at opposite sides: a single turn of the machine showed bleaching effects round *p*, from evolved chlorine. After twenty revolutions no effect of the kind was visible at *n*, but so much chlorine

had been set free at *p*, that when the drop was stirred the whole became colourless.

51. A drop of solution of iodide of potassium mingled with starch was put into the same position at *p* and *n*; on turning the machine, iodine was evolved at *p*, but not at *n*.

52. A still further improvement in this form of apparatus consists in wetting a piece of filtering paper in the solution to be experimented on, and placing that under the points *p* and *n*, on the glass: the paper retains the substance evolved at the point of evolution, by its whiteness renders any change of colour visible, and allows of the point of contact between it and the decomposing wires being contracted to the utmost degree. A piece of paper moistened in the solution of iodide of potassium and starch, or of the iodide alone, with certain precautions (58), is a most admirable test of electro-chemical action; and when thus placed and acted upon by the electric current, will show iodine evolved at *p* by only half a turn of the machine. With these adjustments and the use of iodide of potassium on paper, chemical action is sometimes a more delicate test of electrical currents than the galvanometer (9). Such cases occur when the bodies traversed by the current are bad conductors, or when the quantity of electricity evolved or transmitted in a given time is very small.

53. A piece of litmus paper moistened in solution of common salt or sulphate of soda was quickly reddened at *p*. A similar piece moistened in muriatic acid was very soon bleached at *p*. No effects of a similar kind took place at *n*.

54. A piece of turmeric paper moistened in solution of sulphate of soda was reddened at *n* by two or three turns of the machine, and in twenty or thirty turns plenty of alkali was there evolved. On turning the paper round, so that the spot came under *p*, and then working the machine, the alkali soon disappeared, the place became yellow, and a brown alkaline spot appeared in the new part under *n*.

55. On combining a piece of litmus with a piece of turmeric paper, wetting both with solution of sulphate of soda, and putting the paper on the glass, so that *p* was on the litmus and *n* on the turmeric, 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.

56. All these decompositions took place equally well, whether the electricity passed from the machine to the foil *a*, through water, or through wire only; by *contact* with the conductor,

or by *sparks* there; provided the sparks were not so large as to cause the electricity to pass in sparks from *p* to *n*, or towards *n*; and I have seen no reason to believe that in cases of true electro-chemical decomposition by the machine, the electricity passed in sparks from the conductor, or at any part of the current, is able to do more, because of its tension, than that which is made to pass merely as a regular current.

57. Finally, the experiment was extended into the following form, supplying in this case the fullest analogy between common and voltaic electricity. Three compound pieces of litmus and turmeric paper (55) were moistened in solution of sulphate of soda, and arranged on a plate of glass with platina wires, as in fig. 6. The wire *m* was connected with the prime conductor of the machine, the wire *t* with the discharging train, and the wires *r* and *s* entered into the course of the electrical current by means of the pieces of moistened paper; they were so bent as to rest each on three points, *n*, *r*, *p*; *n*, *s*, *p*, the points *r* and *s* being supported by the glass, and the others by the papers: the three terminations *p*, *p*, *p* rested on the litmus, and the other three *n*, *n*, *n* on the turmeric paper. On working the machine for a short time only, acid was evolved at *all* the poles or terminations *p*, *p*, *p*, by which the electricity entered the solution, and alkali at the other poles *n*, *n*, *n*, by which the electricity left the solution.

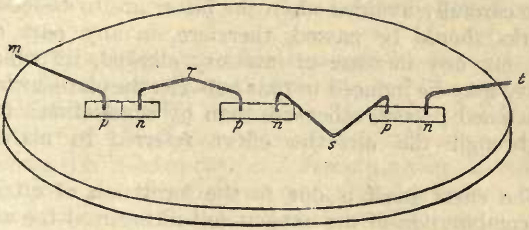

Fig. 6.

58. In all experiments of electro-chemical decomposition by the common machine and moistened papers (52), it is necessary to be aware of and to avoid the following important source of error. If a spark passes over moistened litmus and turmeric paper, the litmus paper (provided it be delicate and not too alkaline) is reddened by it; and if several sparks are passed, it becomes powerfully reddened. If the electricity pass a little

way from the wire over the surface of the moistened paper, before it finds mass and moisture enough to conduct it, then the reddening extends as far as the ramifications. If similar ramifications occur at the termination *n*, on the turmeric paper, they *prevent* the occurrence of the red spot due to the alkali, which would otherwise collect there: sparks or ramifications from the points *n* will also redden litmus paper. If paper moistened by a solution of iodide of potassium (which is an admirably delicate test of electro-chemical action) be exposed to the sparks or ramifications, or even a feeble stream of electricity through the air from either the point *p* or *n*, iodine will be immediately evolved.

59. These effects must not be confounded with those due to the true electro-chemical powers of common electricity, and must be carefully avoided when the latter are to be observed. No sparks should be passed, therefore, in any part of the current, nor any increase of intensity allowed, by which the electricity may be induced to pass between the platina wires and the moistened papers, otherwise than by conduction; for if it burst through the air, the effect referred to above (58) ensues.

60. The effect itself is due to the formation of nitric acid by the combination of the oxygen and nitrogen of the air, and is, in fact, only a delicate repetition of Cavendish's beautiful experiment. The acid so formed, though small in quantity, is in a high state of concentration as to water, and produces the consequent effects of reddening the litmus paper; or preventing the exhibition of alkali on the turmeric paper; or, by acting on the iodide of potassium, evolving iodine.

61. By moistening a very small slip of litmus paper in solution of caustic potassa, and then passing the electric spark over its length in the air, I gradually neutralised the alkali, and ultimately rendered the paper red; on drying it, I found that nitrate of potassa had resulted from the operation, and that the paper had become touch paper.

62. Either litmus paper or white paper, moistened in a strong solution of iodide of potassium, offers therefore a very simple, beautiful, and ready means of illustrating Cavendish's experiment of the formation of nitric acid from the atmosphere.

63. I have already had occasion to refer to an experiment (1, 45) made by Dr. Wollaston, which is insisted upon too much, both by those who oppose and those who agree with the accuracy of his views respecting the identity of voltaic and

ordinary electricity. By covering fine wires with glass or other insulating substances, and then removing only so much matter as to expose the point, or a section of the wires, and by passing electricity through two such wires, the guarded points of which were immersed in water, Wollaston found that the water could be decomposed even by the current from the machine, without sparks, and that two streams of gas arose from the points, exactly resembling, in appearance, those produced by voltaic electricity, and, like the latter, giving a mixture of oxygen and hydrogen gases. But Dr. Wollaston himself points out that the effect is different from that of the voltaic pile, inasmuch as both oxygen and hydrogen are evolved from *each* pole; he calls it " a very close *imitation* of the galvanic phenomena," but adds that " in fact the resemblance is not complete," and does not trust to it to establish the principles correctly laid down in his paper.

64. This experiment is neither more nor less than a repetition, in a refined manner, of that made by Dr. Pearson in 1797,[1] and previously by MM. Paets Van Troostwyk and Deiman in 1789 or earlier. That the experiment should never be quoted as proving true electro-chemical decomposition, is sufficiently evident from the circumstance, that the *law* which regulates the transference and final place of the evolved bodies (14, 45) has no influence here. The water is decomposed at both poles independently of each other, and the oxygen and hydrogen evolved at the wires are the elements of the water existing the instant before in those places. That the poles, or rather points, have no mutual decomposing dependence, may be shown by substituting a wire, or the finger, for one of them, a change which does not at all interfere with the other, though it stops all action at the changed pole. This fact may be observed by turning the machine for some time; for though bubbles will rise from the point left unaltered, in quantity sufficient to cover entirely the wire used for the other communication, if they could be applied to it, yet not a single bubble will appear on that wire.

65. When electro-chemical decomposition takes place, there is great reason to believe that the *quantity* of matter decomposed is not proportionate to the intensity, but to the quantity of electricity passed (56). Of this I shall be able to offer some proofs in a future part of this paper (111, 113). But in the experiment under consideration, this is not the case. If, with

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[1] *Nicholson's Journal*, 4to, vol. i. pp. 241, 299, 349.

a constant pair of points, the electricity be passed from the machine in sparks, a certain proportion of gas is evolved; but if the sparks be rendered shorter, less gas is evolved; and if no sparks be passed, there is scarcely a sensible portion of gases set free. On substituting solution of sulphate of soda for water, scarcely a sensible quantity of gas could be procured even with powerful sparks, and nearly none with the mere current; yet the quantity of electricity in a given time was the same in all these cases.

66. I do not intend to deny that with such an apparatus common electricity can decompose water in a manner analogous to that of the voltaic pile; I believe at present that it can. But when what I consider the true effect only was obtained, the quantity of gas given off was so small that I could not ascertain whether it was, as it ought to be, oxygen at one wire and hydrogen at the other. Of the two streams one seemed more copious than the other, and on turning the apparatus round, still the same side in relation to the machine gave the largest stream. On substituting solution of sulphate of soda for pure water (65), these minute streams were still observed. But the quantities were so small, that on working the machine for half an hour I could not obtain at either pole a bubble of gas larger than a small grain of sand. If the conclusion which I have drawn (113) relating to the amount of chemical action be correct, this ought to be the case.

67. I have been the more anxious to assign the true value of this experiment as a test of electro-chemical action, because I shall have occasion to refer to it in cases of supposed chemical action by magneto-electric and other electric currents (72, 82) and elsewhere. But, independent of it, there cannot be now a doubt that Dr. Wollaston was right in his general conclusion; and that voltaic and common electricity have powers of chemical decomposition, alike in their nature, and governed by the same law of arrangement.

68. iv. *Physiological effects.*—The power of the common electric current to shock and convulse the animal system, and when weak to affect the tongue and the eyes, may be considered as the same with the similar power of voltaic electricity, account being taken of the intensity of the one electricity and duration of the other. When a wet thread was interposed in the course of the current of common electricity from the battery (27) charged by eight or ten[1] revolutions of the machine in good

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[1] Or even from thirty to forty.

action (26), and the discharge made by platina spatulas through the tongue or the gums, the effect upon the tongue and eyes was exactly that of a momentary feeble voltaic circuit.

69. v. *Spark.*—The beautiful flash of light attending the discharge of common electricity is well known. It rivals in brilliancy, if it does not even very much surpass, the light from the discharge of voltaic electricity; but it endures for an instant only, and is attended by a sharp noise like that of a small explosion. Still no difficulty can arise in recognising it to be the same spark as that from the voltaic battery, especially under certain circumstances. The eye cannot distinguish the difference between a voltaic and a common electricity spark, if they be taken between amalgamated surfaces of metal, at intervals only, and through the same distance of air.

70. When the Leyden battery (27) was discharged through a wet string placed in some part of the circuit away from the place where the spark was to pass, the spark was yellowish, flamy, having a duration sensibly longer than if the water had not been interposed, was about three-fourths of an inch in length, was accompanied by little or no noise, and whilst losing part of its usual character had approximated in some degree to the voltaic spark. When the electricity retarded by water was discharged between pieces of charcoal, it was exceedingly luminous and bright upon both surfaces of the charcoal, resembling the brightness of the voltaic discharge on such surfaces. When the discharge of the unretarded electricity was taken upon charcoal, it was bright upon both the surfaces (in that respect resembling the voltaic spark), but the noise was loud, sharp, and ringing.

71. I have assumed, in accordance, I believe, with the opinion of every other philosopher, that atmospheric electricity is of the same nature with ordinary electricity (20), and I might therefore refer to certain published statements of chemical effects produced by the former as proofs that the latter enjoys the power of decomposition in common with voltaic electricity. But the comparison I am drawing is far too rigorous to allow me to use these statements without being fully assured of their accuracy; yet I have no right to suppress them, because, if accurate, they establish what I am labouring to put on an undoubted foundation, and have priority to my results.

72. M. Bonijol of Geneva[1] is said to have constructed very delicate apparatus for the decomposition of water by common

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[1] *Bibliothèque Universelle*, 1830, tome xlv. p. 213.

electricity. By connecting an insulated lightning rod with his apparatus, the decomposition of the water proceeded in a continuous and rapid manner even when the electricity of the atmosphere was not very powerful. The apparatus is not described; but as the diameter of the wire is mentioned as very small, it appears to have been similar in construction to that of Wollaston (63); and as that does not furnish a case of true polar electro-chemical decomposition (64), this result of M. Bonijol does not prove the identity in chemical action of common and voltaic electricity.

73. At the same page of the *Bibliothèque Universelle*, M. Bonijol is said to have decomposed *potash*, and also chloride of silver, by putting them into very narrow tubes and passing electric sparks from an ordinary machine over them. It is evident that these offer no analogy to cases of true voltaic decomposition, where the electricity only decomposes when it is *conducted* by the body acted upon, and ceases to decompose, according to its ordinary laws, when it passes in sparks. These effects are probably partly analogous to that which takes place with water in Pearson's or Wollaston's apparatus, and may be due to very high temperature acting on minute portions of matter; or they may be connected with the results in air (58). As nitrogen can combine directly with oxygen under the influence of the electric spark (60), it is not impossible that it should even take it from the potassium of the potash, especially as there would be plenty of potassa in contact with the acting particles to combine with the nitric acid formed. However distinct all these actions may be from true polar electro-chemical decompositions, they are still highly important, and well worthy of investigation.

74. The late Mr. Barry communicated a paper to the Royal Society[1] last year, so distinct in the details, that it would seem at once to prove the identity in chemical action of common and voltaic electricity; but, when examined, considerable difficulty arises in reconciling certain of the effects with the remainder. He used two tubes, each having a wire within it passing through the closed end, as is usual for voltaic decompositions. The tubes were filled with solution of sulphate of soda, coloured with syrup of violets, and connected by a portion of the same solution, in the ordinary manner; the wire in one tube was connected by a *gilt thread* with the string of an insulated electrical kite, and the wire in the other tube by a similar *gilt thread* with the

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[1] *Philosophical Transactions*, 1831, p. 165.

ground. Hydrogen soon appeared in the tube connected with the kite, and oxygen in the other, and in ten minutes the liquid in the first tube was green from the alkali evolved, and that in the other red from free acid produced. The only indication of the strength or intensity of the atmospheric electricity is in the expression, "the usual shocks were felt on touching the string."

75. That the electricity in this case does not resemble that from any ordinary source of common electricity, is shown by several circumstances. Wollaston could not effect the decomposition of water by such an arrangement, and obtain the gases in *separate* vessels, using common electricity; nor have any of the numerous philosophers, who have employed such an apparatus, obtained any such decomposition, either of water or of a neutral salt, by the use of the machine. I have lately tried the large machine (26) in full action for a quarter of an hour, during which time seven hundred revolutions were made, without producing any sensible effects, although the shocks that it would then give must have been far more powerful and numerous than could have been taken, with any chance of safety, from an electrical kite-string; and by reference to the comparison hereafter to be made (107), it will be seen that for common electricity to have produced the effect, the quantity must have been awfully great, and apparently far more than could have been conducted to the earth by a gilt thread, and at the same time only have produced the "usual shocks."

76. That the electricity was apparently not analogous to voltaic electricity is evident, for the "usual shocks" only were produced, and nothing like the terrible sensation due to a voltaic battery, even when it has a tension so feeble as not to strike through the eighth of an inch of air.

77. It seems just possible that the air which was passing by the kite and string, being in an electrical state sufficient to produce the "usual shocks" only, could still, when the electricity was drawn off below, renew the charge, and so continue the current. The string was 1500 feet long, and contained two double threads. But when the enormous quantity which must have been thus collected is considered (107, 112), the explanation seems very doubtful. I charged a voltaic battery of twenty pairs of plates four inches square with double coppers very strongly, insulated it, connected its positive extremity with the discharging train (28), and its negative pole with an apparatus like that of Mr. Barry, communicating by a wire inserted

three inches into the wet soil of the ground. This battery thus arranged produced feeble decomposing effects, as nearly as I could judge answering the description Mr. Barry has given. Its intensity was, of course, far lower than the electricity of the kite-string, but the supply of quantity from the discharging train was unlimited. It gave no shocks to compare with the "usual shocks" of a kite-string.

78. Mr. Barry's experiment is a very important one to repeat and verify. If confirmed, it will be, as far as I am aware, the first recorded case of true electro-chemical decomposition of water by common electricity, and it will supply a form of electrical current, which, both in quantity and intensity, is exactly intermediate with those of the common electrical machine and the voltaic pile.

III. *Magneto-Electricity*

79. *Tension.*—The attractions and repulsions due to the tension of ordinary electricity have been well observed with that evolved by magneto-electric induction. M. Pixii, by using an apparatus, clever in its construction and powerful in its action,[1] was able to obtain great divergence of the gold leaves of an electrometer.[2]

80. *In motion :* i. *Evolution of heat.*—The current produced by magneto-electric induction can heat a wire in the manner of ordinary electricity. At the British Association of Science at Oxford, in June of the present year, I had the pleasure, in conjunction with Mr. Harris, Professor Daniell, Mr. Duncan, and others, of making an experiment, for which the great magnet in the museum, Mr. Harris's new electrometer and the magneto-electric coil[3] were put in requisition. The latter had been modified in the manner I have elsewhere described,[4] so as to produce an electric spark when its contact with the magnet was made or broken. The terminations of the spiral, adjusted so as to have their contact with each other broken when the spark was to pass, were connected with the wire in the electrometer, and it was found that each time the magnetic contact was made

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[1] *Annales de Chimie*, l. p. 322.

[2] *Ibid.* li. p. 77.

[3] A combination of helices was constructed upon a hollow cylinder of pasteboard: there were eight lengths of copper wire, containing altogether 220 feet; four of these helices were connected end to end, and then with the galvanometer; the other intervening four were also connected end to end, and the battery of one hundred pairs discharged through them.

[4] *Phil. Mag. and Annals*, 1832, vol. xi. p. 405.

and broken, expansion of the air within the instrument occurred, indicating an increase, at the moment, of the temperature of the wire.

81. ii. *Magnetism.*—These currents were discovered by their magnetic power.

82. iii. *Chemical decomposition.*—I have made many endeavours to effect chemical decomposition by magneto-electricity, but unavailingly. In July last I received an anonymous letter (which has since been published)[1] describing a magneto-electric apparatus, by which the decomposition of water was effected. As the term "guarded points" is used, I suppose the apparatus to have been Wollaston's (63, etc.), in which case the results did not indicate polar electro-chemical decomposition. Signor Botto has recently published certain results which he has obtained;[2] but they are, as at present described, inconclusive. The apparatus he used was apparently that of Dr. Wollaston, which gives only fallacious indications (63, etc.). As magneto-electricity can produce sparks, it would be able to show the effects proper to this apparatus. The apparatus of M. Pixii already referred to (79), has however, in the hands of himself[3] and M. Hachette,[4] given decisive chemical results, so as to complete this link in the chain of evidence. Water was decomposed by it, and the oxygen and hydrogen obtained in separate tubes according to the law governing volta-electric and machine-electric decomposition.

83. iv. *Physiological effects.*—A frog was convulsed in the earliest experiments on these currents. The sensation upon the tongue, and the flash before the eyes, which I at first obtained only in a feeble degree, have been since exalted by more powerful apparatus, so as to become even disagreeable.

84. v. *Spark.*—The feeble spark which I first obtained with these currents has been varied and strengthened by Signori Nobili and Antinori, and others, so as to leave no doubt as to its identity with the common electric spark.

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[1] *Lond. and Edinb. Phil. Mag. and Journ.* 1832, vol. i. p. 161.

[2] *Ibid.* 1832, vol. i. p. 441.

[3] *Annales de Chimie,* li. p. 77.

[4] *Ibid.* li. p. 72.

IV. *Thermo-Electricity*

85. With regard to thermo-electricity (that beautiful form of electricity discovered by Seebeck), the very conditions under which it is excited are such as to give no ground for expecting that it can be raised like common electricity to any high degree of tension; the effects, therefore, due to that state are not to be expected. The sum of evidence respecting its analogy to the electricities already described, is, I believe, as follows:—*Tension.* The attractions and repulsions due to a certain degree of tension have not been observed. *In currents :* i. *Evolution of heat.* I am not aware that its power of raising temperature has been observed. ii. *Magnetism.* It was discovered, and is best recognised, by its magnetic powers. iii. *Chemical decomposition* has not been effected by it. iv. *Physiological effects.* Nobili has shown [1] that these currents are able to cause contractions in the limbs of a frog. v. *Spark.* The spark has not yet been seen.

86. Only those effects are weak or deficient which depend upon a certain high degree of intensity; and if common electricity be reduced in that quality to a similar degree with the thermo-electricity, it can produce no effects beyond the latter.

V. *Animal Electricity*

87. After an examination of the experiments of Walsh,[2] Ingenhousz,[3] Cavendish,[4] Sir H. Davy,[5] and Dr. Davy,[6] no doubt remains on my mind as to the identity of the electricity of the torpedo with common and voltaic electricity; and I presume that so little will remain on the minds of others as to justify my refraining from entering at length into the philosophical proofs of that identity. The doubts raised by Sir H. Davy have been removed by his brother Dr. Davy; the results of the latter being the reverse of those of the former. At present the sum of evidence is as follows:—

88. *Tension.*—No sensible attractions or repulsions due to tension have been observed.

89. *In motion :* i. *Evolution of heat ;* not yet observed; I

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[1] *Bibliothèque Universelle*, xxxvii. 15.

[2] *Philosophical Transactions*, 1773, p. 461.

[3] *Ibid.* 1775, p. 1.

[4] *Ibid.* 1776, p. 196.

[5] *Ibid.* 1829, p. 15.

[6] *Ibid.* 1832, p. 259.

have little or no doubt that Harris's electrometer would show it (23, 95).

90. ii. *Magnetism.*—Perfectly distinct. According to Dr. Davy,[1] the current deflected the needle and made magnets under the same law, as to direction, which governs currents of ordinary and voltaic electricity.

91. iii. *Chemical decomposition.*—Also distinct; and though Dr. Davy used an apparatus of similar construction with that of Dr. Wollaston (63), still no error in the present case is involved, for the decompositions were polar, and in their nature truly electro-chemical. By the direction of the magnet, it was found that the under surface of the fish was negative, and the upper positive; and in the chemical decompositions, silver and lead were precipitated on the wire connected with the under surface, and not on the other; and when these wires were either steel or silver, in solution of common salt, gas (hydrogen?) rose from the negative wire, but none from the positive.

92. Another reason for the decomposition being electro-chemical is, that a Wollaston's apparatus constructed with *wires*, coated by sealing-wax, would most probably not have decomposed water, even in its own peculiar way, unless the electricity had risen high enough in intensity to produce sparks in some part of the circuit; whereas the torpedo was not able to produce sensible sparks. A third reason is, that the purer the water in Wollaston's apparatus, the more abundant is the decomposition: and I have found that a machine and wire points which succeeded perfectly well with distilled water, failed altogether when the water was rendered a good conductor by sulphate of soda, common salt, or other saline bodies. But in Dr. Davy's experiments with the torpedo, *strong* solutions of salt, nitrate of silver, and superacetate of lead were used successfully, and there is no doubt with more success than weaker ones.

93. iv. *Physiological effects.*—These are so characteristic, that by them the peculiar powers of the torpedo and gymnotus are principally recognised.

94. v. *Spark.*—The electric spark has not yet been obtained, or at least I think not; but perhaps I had better refer to the evidence on this point. Humboldt, speaking of results obtained by M. Fahlberg, of Sweden, says, "This philosopher has seen an electric spark, as Walsh and Ingenhousz had done before him at London, by placing the gymnotus in the air, and interrupting the conducting chain by two gold leaves pasted upon

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[1] *Philosophical Transactions*, 1832, p. 260.

glass, and a line distant from each other."[1] I cannot, however, find any record of such an observation by either Walsh or Ingenhousz, and do not know where to refer to that by M. Fahlberg. M. Humboldt could not himself perceive any luminous effect.

Again, Sir John Leslie, in his dissertation on the progress of mathematical and physical science, prefixed to the seventh edition of the *Encyclopædia Britannica*, Edinburgh, 1830, p. 622, says, "From a healthy specimen" of the *Silurus electricus*, meaning rather the *gymnotus*, "exhibited in London, vivid sparks were drawn in a darkened room;" but he does not say he saw them himself, nor state who did see them; nor can I find any account of such a phenomenon; so that the statement is doubtful.[2]

95. In concluding this summary of the powers of torpedinal electricity, I cannot refrain from pointing out the enormous absolute quantity of electricity which the animal must put in circulation at each effort. It is doubtful whether any common electrical machine has as yet been able to supply electricity sufficient in a reasonable time to cause true electro-chemical decomposition of water (66, 75), yet the current from the torpedo has done it. The same high proportion is shown by the magnetic effects (32, 107). These circumstances indicate that the torpedo has power (in the way probably that Cavendish describes) to continue the evolution for a sensible time, so that its successive discharges rather resemble those of a voltaic arrangement, intermitting in its action, than those of a Leyden apparatus, charged and discharged many times in succession. In reality, however, there is *no philosophical difference* between these two cases.

96. The *general conclusion* which must, I think, be drawn from this collection of facts is, that *electricity, whatever may be its source, is identical in its nature*. The phenomena in the five kinds of species quoted, differ, not in their character but only in degree; and in that respect vary in proportion to the variable circumstances of *quantity* and *intensity*[3] which can at pleasure be made to change in almost any one of the kinds of electricity, as much as it does between one kind and another.

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[1] *Edinburgh Phil. Journal*, ii. p. 249.

[2] Mr. Brayley, who referred me to these statements, and has extensive knowledge of recorded facts, is unacquainted with any further account relating to them.

[3] The term *quantity* in electricity is perhaps sufficiently definite as to sense; the term *intensity* is more difficult to define strictly. I am using the terms in their ordinary and accepted meaning.

Table of the experimental Effects common to the Electricities derived from different Sources.[1]

	Physiological Effects.	Magnetic Deflection.	Magnets made.	Spark.	Heating Power.	True Chemical Action.	Attraction and Repulsion.	Discharge by Hot Air.
1. Voltaic electricity .	×	×	×	×	×	×	×	×
2. Common electricity	×	×	×	×	×	×	×	×
3. Magneto-electricity	×	×	×	×	×	×	×	
4. Thermo-electricity .	×	×	+	+	+	+		
5. Animal electricity .	×	×	×	+	+	×		

§ 2. *Relation by Measure of Common and Voltaic Electricity* [2]

97. Believing the point of identity to be satisfactorily established, I next endeavoured to obtain a common measure, or a known relation as to quantity, of the electricity excited by a machine, and that from a voltaic pile; for the purpose not only of confirming their identity (114), but also of demonstrating certain general principles (102, 113, etc.), and creating an extension of the means of investigating and applying the chemical powers of this wonderful and subtile agent.

98. The first point to be determined was, whether the same absolute quantity of ordinary electricity, sent through a galvano-

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[1] Many of the spaces in this table originally left blank may now be filled. Thus with *thermo-electricity*, Botto made magnets and obtained polar chemical decomposition: Antinori produced the spark; and if it has not been done before, Mr. Watkins has recently heated a wire in Harris's thermo-electrometer. In respect to *animal electricity*, Matteucci and Linari have obtained the spark from the torpedo, and I have recently procured it from the gymnotus: Dr. Davy has observed the heating power of the current from the torpedo. I have therefore filled up these spaces with crosses, in a different position to the others originally in the table. There remain but five spaces unmarked, two under *attraction* and *repulsion*, and three under *discharge by hot air*; and though these effects have not yet been obtained, it is a necessary conclusion that they must be possible, since the *spark* corresponding to them has been procured. For when a discharge across cold air can occur, that intensity which is the only essential additional requisite for the other effects must be present.—*December* 13, 1838.

[2] In further illustration of this subject, see 590-608 in Part V.—*December* 1838.

meter, under different circumstances, would cause the same deflection of the needle. An arbitrary scale was therefore attached to the galvanometer, each division of which was equal to about 4°, and the instrument arranged as in former experiments (32). The machine (26), battery (27), and other parts of the apparatus were brought into good order, and retained for the time as nearly as possible in the same condition. The experiments were alternated so as to indicate any change in the condition of the apparatus and supply the necessary corrections.

99. Seven of the battery jars were removed, and eight retained for present use. It was found that about forty turns would fully charge the eight jars. They were then charged by thirty turns of the machine, and discharged through the galvanometer, a thick wet string, about ten inches long, being included in the circuit. The needle was immediately deflected five divisions and a half, on the one side of the zero, and in vibrating passed as nearly as possible through five divisions and a half on the other side.

100. The other seven jars were then added to the eight, and the whole fifteen charged by thirty turns of the machine. The Henley's electrometer stood not quite half as high as before; but when the discharge was made through the galvanometer, previously at rest, the needle immediately vibrated, passing *exactly* to the same division as in the former instance. These experiments with eight and with fifteen jars were repeated several times alternately with the same results.

101. Other experiments were then made, in which all the battery was used, and its charge (being fifty turns of the machine) sent through the galvanometer: but it was modified by being passed sometimes through a mere wet thread, sometimes through thirty-eight inches of thin string wetted by distilled water, and sometimes through a string of twelve times the thickness, only twelve inches in length, and soaked in dilute acid (34). With the thick string the charge passed at once; with the thin string it occupied a sensible time, and with the thread it required two or three seconds before the electrometer fell entirely down. The current therefore must have varied extremely in intensity in these different cases, and yet the deflection of the needle was sensibly the same in all of them. If any difference occurred, it was that the thin string and thread caused greatest deflection; and if there is any lateral transmission, as M. Colladon says, through the silk in the galvano-

meter coil, it ought to have been so, because then the intensity is lower and the lateral transmission less.

102. Hence it would appear that *if the same absolute quantity of electricity pass through the galvanometer, whatever may be its intensity, the deflecting force upon the magnetic needle is the same.*

103. The battery of fifteen jars was then charged by sixty revolutions of the machine, and discharged, as before, through the galvanometer. The deflection of the needle was now as nearly as possible to the eleventh division, but the graduation was not accurate enough for me to assert that the arc was exactly double the former arc; to the eye it appeared to be so. The probability is, that *the deflecting force of an electric current is directly proportional to the absolute quantity of electricity passed,* at whatever intensity that electricity may be.[1]

104. Dr. Ritchie has shown that in a case where the intensity of the electricity remained the same, the deflection of the magnetic needle was directly as the quantity of electricity passed through the galvanometer.[2] Mr. Harris has shown that the *heating* power of common electricity on metallic wires is the same for the same quantity of electricity whatever its intensity might have previously been.[3]

105. The next point was to obtain a *voltaic* arrangement producing an effect equal to that just described (103). A platina and a zinc wire were passed through the same hole of a draw-plate, being then one-eighteenth of an inch in diameter; these were fastened to a support, so that their lower ends projected, were parallel, and five-sixteenths of an inch apart. The upper ends were well connected with the galvanometer wires. Some acid was diluted, and, after various preliminary experiments, that adopted as a standard which consisted of one drop strong sulphuric acid in four ounces distilled water. Finally, the time was noted which the needle required in swinging either from right to left or left to right: it was equal to seventeen beats of my watch, the latter giving one hundred and fifty in a minute. The object of these preparations was to arrange a voltaic apparatus, which, by immersion in a given acid for a given time, much less than that required by the needle to swing in one

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[1] The great and general value of the galvanometer, as an actual measure of the electricity passing through it, either continuously or interruptedly, must be evident from a consideration of these two conclusions. As constructed by Professor Ritchie with glass threads (see *Philosophical Transactions*, 1830, p. 218, and *Quarterly Journal of Science*, New Series, vol. i. p. 29), it apparently seems to leave nothing unsupplied in its own department.

[2] *Quarterly Journal of Science*, New Series, vol. i. p. 33.

[3] *Plymouth Transactions*, p. 22.

direction, should give equal deflection to the instrument with the discharge of ordinary electricity from the battery (99, 100); and a new part of the zinc wire having been brought into position with the platina, the comparative experiments were made.

106. On plunging the zinc and platina wires five-eighths of an inch deep into the acid, and retaining them there for eight beats of the watch (after which they were quickly withdrawn), the needle was deflected, and continued to advance in the same direction some time after the voltaic apparatus had been removed from the acid. It attained the five-and-a-half division, and then returned swinging an equal distance on the other side. This experiment was repeated many times, and always with the same result.

107. Hence, as an approximation, and judging from *magnetic force* only at present (112), it would appear 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 oil of vitriol and four ounces distilled water, at a temperature about 60°, and connected at the other extremities by a copper wire eighteen feet long and one-eighteenth of an inch thick (being the wire of the galvanometer coils), yield as much electricity in eight beats of my watch, or in $\frac{8}{150}$ths of a minute, as the electrical battery charged by thirty turns of the large machine, in excellent order (99, 100). Notwithstanding this apparently enormous disproportion, the results are perfectly in harmony with those effects which are known to be produced by variations in the intensity and quantity of the electric fluid.

108. In order to procure a reference to *chemical action*, the wires were now retained immersed in the acid to the depth of five-eighths of an inch, and the needle, when stationary, observed; it stood, as nearly as the unassisted eye could decide, at 5⅓ division. Hence a permanent deflection to that extent might be considered as indicating a constant voltaic current, which in eight beats of my watch (105) could supply as much electricity as the electrical battery charged by thirty turns of the machine.

109. The following arrangements and results are selected from many that were made and obtained relative to chemical action. A platina wire one-twelfth of an inch in diameter, weighing two hundred and sixty grains, had the extremity rendered plain, so as to offer a definite surface equal to a circle of the same diameter as the wire; it was then connected in turn with the conductor of the machine, or with the voltaic apparatus

(105), so as always to form the positive pole, and at the same time retain a perpendicular position, that it might rest, with its whole weight, upon the test paper to be employed. The test paper itself was supported upon a platina spatula, connected either with the discharging train (28), or with the negative wire of the voltaic apparatus, and it consisted of four thicknesses, moistened at all times to an equal degree in a standard solution of hydriodate of potassa (52).

110. When the platina wire was connected with the prime conductor of the machine, and the spatula with the discharging train, ten turns of the machine had such decomposing power as to produce a pale round spot of iodine of the diameter of the wire; twenty turns made a much darker mark, and thirty turns made a dark brown spot penetrating to the second thickness of the paper. The difference in effect produced by two or three turns, more or less, could be distinguished with facility.

111. The wire and spatula were then connected with the voltaic apparatus (105), the galvanometer being also included in the arrangement; and, a stronger acid having been prepared, consisting of nitric acid and water, the voltaic apparatus was immersed so far as to give a permanent deflection of the needle to the 5⅓ division (108), the fourfold moistened paper intervening as before.[1] Then by shifting the end of the wire from place to place upon the test paper, the effect of the current for five, six, seven, or any number of the beats of the watch (105) was observed, and compared with that of the machine. After alternating and repeating the experiments of comparison many times, it was constantly found that this standard current of voltaic electricity, continued for eight beats of the watch, was equal, in chemical effect, to thirty turns of the machine; twenty-eight revolutions of the machine were sensibly too few.

112. Hence it results that both in *magnetic deflection* (107) and in *chemical force,* the current of electricity of the standard voltaic battery for eight beats of the watch was equal to that of the machine evolved by thirty revolutions.

113. It also follows that for this case of electro-chemical decomposition, and it is probable for all cases, that the *chemical power, like the magnetic force* (102), *is in direct proportion to the absolute quantity of electricity* which passes.

114. Hence arises still further confirmation, if any were required, of the identity of common and voltaic electricity,

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[1] Of course the heightened power of the voltaic battery was necessary to compensate for the bad conductor now interposed.

and that the differences of intensity and quantity are quite sufficient to account for what were supposed to be their distinctive qualities.

115. The extension which the present investigations have enabled me to make of the facts and views constituting the theory of electro-chemical decomposition, will, with some other points of electrical doctrine, be almost immediately submitted to the Royal Society in another series of these Researches.

December 15, 1832.

II[1]

§ 3. ON A NEW LAW OF ELECTRIC CONDUCTION. § 4. ON CONDUCTING POWER GENERALLY

§ 3. *On a new Law of Electric Conduction*

116. It was during the progress of investigations relating to electro-chemical decomposition, which I still have to submit to the Royal Society, that I encountered effects due to a very *general law* of electric conduction not hitherto recognised; and though they prevented me from obtaining the condition I sought for, they afforded abundant compensation for the momentary disappointment, by the new and important interest which they gave to an extensive part of electrical science.

117. I was working with ice, and the solids resulting from the freezing of solutions, arranged either as barriers across a substance to be decomposed, or as the actual poles of a voltaic battery, that I might trace and catch certain elements in their transit, when I was suddenly stopped in my progress by finding that ice was in such circumstances a non-conductor of electricity; and that as soon as a thin film of it was interposed, in the circuit of a very powerful voltaic battery, the transmission of electricity was prevented, and all decomposition ceased.

118. At first the experiments were made with common ice, during the cold freezing weather of the latter end of January 1833; but the results were fallacious, from the imperfection

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[1] Fourth Series, original edition, vol. i. p. 110.

of the arrangements, and the following more unexceptionable form of experiment was adopted.

119. Tin vessels were formed, five inches deep, one inch and a quarter wide in one direction, of different widths from three-eighths to five-eighths of an inch in the other, and open at one extremity. Into these were fixed by corks, plates of platina, so that the latter should not touch the tin cases; and copper wires having previously been soldered to the plates, these were easily connected, when required, with a voltaic pile. Then distilled water, previously boiled for three hours, was poured into the vessels, and frozen by a mixture of salt and snow, so that pure transparent solid ice intervened between the platina and tin: and finally these metals were connected with the opposite extremities of the voltaic apparatus, a galvanometer being at the same time included in the circuit.

120. In the first experiment, the platina pole was three inches and a half long, and seven-eighths of an inch wide; it was wholly immersed in the water or ice, and as the vessel was four-eighths of an inch in width, the average thickness of the intervening ice was only a quarter of an inch, whilst the surface of contact with it at both poles was nearly fourteen square inches. After the water was frozen, the vessel was still retained in the frigorific mixture, whilst contact between the tin and platina respectively was made with the extremities of a well-charged voltaic battery, consisting of twenty pairs of four-inch plates, each with double coppers. Not the slightest deflection of the galvanometer needle occurred.

121. On taking the frozen arrangement out of the cold mixture, and applying warmth to the bottom of the tin case, so as to melt part of the ice, the connection with the battery being in the meantime retained, the needle did not at first move; and it was only when the thawing process had extended so far as to liquefy part of the ice touching the platina pole, that conduction took place; but then it occurred effectually, and the galvanometer needle was permanently deflected nearly 70°.

122. In another experiment, a platina spatula, five inches in length and seven-eighths of an inch in width, had four inches fixed in the ice, and the latter was only three-sixteenths of an inch thick between one metallic surface and the other; yet this arrangement insulated as perfectly as the former.

123. Upon pouring a little water in at the top of this vessel on the ice, still the arrangement did not conduct; yet fluid water was evidently there. This result was the consequence

of the cold metals having frozen the water where they touched it, and thus insulating the fluid part; and it well illustrates the non-conducting power of ice, by showing how thin a film could prevent the transmission of the battery current. Upon thawing parts of this thin film, at *both* metals, conduction occurred.

124. Upon warming the tin case and removing the piece of ice, it was found that a cork having slipped, one of the edges of the platina had been all but in contact with the inner surface of the tin vessel; yet, notwithstanding the extreme thinness of the interfering ice in this place, no sensible portion of electricity had passed.

125. These experiments were repeated many times with the same results. At last a battery of fifteen troughs, or one hundred and fifty pairs of four-inch plates, powerfully charged, was used; yet even here no sensible quantity of electricity passed the thin barrier of ice.

126. It seemed at first as if occasional departures from these effects occurred; but they could always be traced to some interfering circumstances. The water should in every instance be well frozen; for though it is not necessary that the ice should reach from pole to pole, since a barrier of it about one pole would be quite sufficient to prevent conduction, yet, if part remain fluid, the mere necessary exposure of the apparatus to the air, or the approximation of the hands, is sufficient to produce, at the *upper surface* of the water and ice, a film of fluid, extending from the platina to the tin; and then conduction occurs. Again, if the corks used to block the platina in its place are damp or wet within, it is necessary that the cold be sufficiently well applied to freeze the water in them, or else when the surfaces of their contact with the tin become slightly warm by handling, that part will conduct, and the interior being ready to conduct also, the current will pass. The water should be pure, not only that unembarrassed results may be obtained, but also that, as the freezing proceeds, a minute portion of concentrated saline solution may not be formed, which remaining fluid, and being interposed in the ice, or passing into cracks resulting from contraction, may exhibit conducting powers independent of the ice itself.

127. On one occasion I was surprised to find that after thawing much of the ice the conducting power had not been restored; but I found that a cork which held the wire just where it joined the platina, dipped so far into the ice, that with the ice itself

it protected the platina from contact with the melted part long after that contact was expected.

128. This insulating power of ice is not effective with electricity of exalted intensity. On touching a diverged gold-leaf electrometer with a wire connected with the platina, whilst the tin case was touched by the hand or another wire, the electrometer was instantly discharged (155).

129. But though electricity of an intensity so low that it cannot diverge the electrometer, can still pass (though in very limited quantities (155)) through ice; the comparative relation of water and ice to the electricity of the voltaic apparatus is not less extraordinary on that account, or less important in its consequences.

130. As it did not seem likely that this *law of the assumption of conducting power during liquefaction, and loss of it during congelation,* would be peculiar to water, I immediately proceeded to ascertain its influence in other cases, and found it to be very general. For this purpose bodies were chosen which were solid at common temperatures, but readily fusible; and of such composition as, for other reasons connected with electrochemical action, led to the conclusion that they would be able when fused to replace water as conductors. A voltaic battery of two troughs, or twenty pairs of four-inch plates (120), was used as the source of electricity, and a galvanometer introduced into the circuit to indicate the presence or absence of a current.

131. On fusing a little chloride of lead by a spirit-lamp on a fragment of a Florence flask, and introducing two platina wires connected with the poles of the battery, there was instantly powerful action, the galvanometer was most violently affected, and the chloride rapidly decomposed. On removing the lamp, the instant the chloride solidified all current and consequent effects ceased, though the platina wires remained inclosed in the chloride not more than the one-sixteenth of an inch from each other. On renewing the heat, as soon as the fusion had proceeded far enough to allow liquid matter to connect the poles, the electrical current instantly passed.

132. On fusing the chloride, with one wire introduced, and then touching the liquid with the other, the latter being cold, caused a little knob to concrete on its extremity, and no current passed; it was only when the wire became so hot as to be able to admit or allow of contact with the liquid matter, that conduction took place, and then it was very powerful.

133. When chloride of silver and chlorate of potassa were

experimented with, in a similar manner, exactly the same results occurred.

134. Whenever the current passed in these cases, there was decomposition of the substances; but the electro-chemical part of this subject I purpose connecting with more general views in a future paper.[1]

135. Other substances, which could not be melted on glass, were fused by the lamp and blowpipe on platina connected with one pole of the battery, and then a wire, connected with the other, dipped into them. In this way chloride of sodium, sulphate of soda, protoxide of lead, mixed carbonates of potash and soda, etc., etc., exhibited exactly the same phenomena as those already described: whilst liquid, they conducted and were decomposed; whilst solid, though very hot, they insulated the battery current even when four troughs were used.

136. Occasionally the substances were contained in small bent tubes of green glass, and when fused, the platina poles introduced, one on each side. In such cases the same general results as those already described were procured; but a further advantage was obtained, namely, that whilst the substance was conducting and suffering decomposition, the final arrangement of the elements could be observed. Thus, iodides of potassium and lead gave iodine at the positive pole, and potassium or lead at the negative pole. Chlorides of lead and silver gave chlorine at the positive, and metals at the negative pole. Nitre and chlorate of potassa gave oxygen, etc., at the positive, and alkali, or even potassium, at the negative pole.

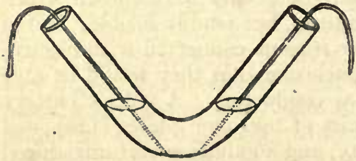

Fig. 7.

137. A fourth arrangement was used for substances requiring very high temperatures for their fusion. A platina wire was connected with one pole of the battery; its extremity bent into a small ring, in the manner described by Berzelius, for blowpipe experiments; a little of the salt, glass, or other substance,

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[1] In 1801, Sir H. Davy knew that "dry nitre, caustic potash, and soda are conductors of galvanism when rendered fluid by a high degree of heat" (*Journals of the Royal Institution*, 1802, p. 53), but was not aware of the general law which I have been engaged in developing. It is remarkable, that eleven years after that, he should say, "There are no fluids known except such as contain water, which are capable of being made the medium of connection between the metal or metals of the voltaic apparatus."—*Elements of Chemical Philosophy*, p. 169.

was melted on this ring by the ordinary blowpipe, or even in some cases by the oxy-hydrogen blowpipe, and when the drop, retained in its place by the ring, was thoroughly hot and fluid, a platina wire from the opposite pole of the battery was made to touch it, and the effects observed.

138. The following are various substances, taken from very different classes chemically considered, which are subject to this law. The list might, no doubt, be enormously extended; but I have not had time to do more than confirm the law by a sufficient number of instances.

First, *Water.*

Amongst *oxides ;*—potassa, protoxide of lead, glass of antimony, protoxide of antimony, oxide of bismuth.

Chlorides of potassium, sodium, barium, strontium, calcium, magnesium, manganese, zinc, copper (proto-), lead, tin (proto-), antimony, silver.

Iodides of potassium, zinc and lead, protiodide of tin, periodide of mercury; *fluoride* of potassium; *cyanide* of potassium; *sulpho-cyanide* of potassium.

Salts. Chlorate of potassa; nitrates of potassa, soda, baryta, strontia, lead, copper, and silver; sulphates of soda and lead, proto-sulphate of mercury; phosphates of potassa, soda, lead, copper, phosphoric glass or acid phosphate of lime; carbonates of potassa and soda, mingled and separate; borax, borate of lead, per-borate of tin; chromate of potassa, bi-chromate of potassa, chromate of lead; acetate of potassa.

Sulphurets. Sulphuret of antimony, sulphuret of potassium made by reducing sulphate of potassa by hydrogen; ordinary sulphuret of potassa.

Silicated potassa; chameleon mineral.

139. It is highly interesting in the instances of those substances which soften before they liquefy, to observe at what period the conducting power is acquired, and to what degree it is exalted by perfect fluidity. Thus, with the borate of lead, when heated by the lamp upon glass, it becomes as soft as treacle, but it did not conduct, and it was only when urged by the blowpipe and brought to a fair red heat, that it conducted. When rendered quite liquid, it conducted with extreme facility.

140. I do not mean to deny that part of the increased conducting power in these cases of softening was probably due to the elevation of temperature (168, 181); but I have no doubt that by far the greater part was due to the influence of the

general law already demonstrated, and which in these instances came gradually, instead of suddenly, into operation.

141. The following are bodies which acquired no conducting power upon assuming the liquid state:—

Sulphur, phosphorus; iodide of sulphur, per-iodide of tin; orpiment, realgar; glacial acetic acid, mixed margaric and oleic acids, artificial camphor; caffeine, sugar, adipocire, stearine of cocoa-nut oil, spermaceti, camphor, naphthaline, resin, gum sandarach, shell lac.

142. Perchloride of tin, chloride of arsenic, and the hydrated chloride of arsenic, being liquids, had no sensible conducting power indicated by the galvanometer, nor were they decomposed.

143. Some of the above substances are sufficiently remarkable as exceptions to the general law governing the former cases. These are orpiment, realgar, acetic acid, artificial camphor, per-iodide of tin, and the chlorides of tin and arsenic. I shall have occasion to refer to these cases in the paper on Electro-chemical Decomposition.

144. Boracic acid was raised to the highest possible temperature by an oxy-hydrogen flame (137), yet it gained no conducting powers sufficient to affect the galvanometer, and underwent no apparent voltaic decomposition. It seemed to be quite as bad a conductor as air. Green bottle-glass, heated in the same manner, did not gain conducting power sensible to the galvanometer. Flint glass, when highly heated, did conduct a little and decompose; and as the proportion of potash or oxide of lead was increased in the glass, the effects were more powerful. Those glasses, consisting of boracic acid on the one hand, and oxide of lead or potassa on the other, show the assumption of conducting power upon fusion and the accompanying decomposition very well.

145. I was very anxious to try the general experiment with sulphuric acid, of about specific gravity 1.783, containing that proportion of water which gives it the power of crystallising at 40° Fahr.; but I found it impossible to obtain it so that I could be sure the whole would congeal even at 0° Fahr. A ten-thousandth part of water, more or less than necessary, would, upon cooling the whole, cause a portion of uncongealable liquid to separate, and that remaining in the interstices of the solid mass, and moistening the planes of division, would prevent the correct observation of the phenomena due to entire solidification and subsequent liquefaction.

146. With regard to the substances on which conducting power is thus conferred by liquidity, the degree of power so given is generally very great. Water is that body in which this acquired power is feeblest. In the various oxides, chlorides, salts, etc., etc., it is given in a much higher degree. I have not had time to measure the conducting power in these cases, but it is apparently some hundred times that of pure water. The increased conducting power known to be given to water by the addition of salts would seem to be in a great degree dependent upon the high conducting power of these bodies when in the liquid state, that state being given them for the time, not by heat but solution in the water.

147. Whether the conducting power of these liquefied bodies is a consequence of their decomposition or not (149), or whether the two actions of conduction and decomposition are essentially connected or not, would introduce no difference affecting the probable accuracy of the preceding statement.

148. This *general assumption of conducting power* by bodies as soon as they pass from the solid to the liquid state, offers a new and extraordinary character, the existence of which, as far as I know, has not before been suspected; and it seems importantly connected with some properties and relations of the particles of matter which I may now briefly point out.

149. In almost all the instances, as yet observed, which are governed by this law, the substances experimented with have been those which were not only compound bodies, but such as contain elements known to arrange themselves at the opposite poles; and were also such as could be *decomposed* by the electrical current. When conduction took place, decomposition occurred; when decomposition ceased, conduction ceased also; and it becomes a fair and an important question, Whether the conduction itself may not, wherever the law holds good, be a consequence not merely of the capability, but of the act of decomposition? And that question may be accompanied by another, namely, Whether solidification does not prevent conduction, merely by chaining the particles to their places, under the influence of aggregation, and preventing their final separation in the manner necessary for decomposition?

150. But, on the other hand, there is one substance (and others may occur), the *per-iodide of mercury*, which, being experimented with like the others (136), was found to insulate when solid, and to acquire conducting power when fluid; yet it did not seem to undergo decomposition in the latter case.

151. Again, there are many substances which contain elements such as would be expected to arrange themselves at the opposite poles of the pile, and therefore in that respect fitted for decomposition, which yet do not conduct. Amongst these are the iodide of sulphur, per-iodide of zinc, per-chloride of tin, chloride of arsenic, hydrated chloride of arsenic, acetic acid, orpiment, realgar, artificial camphor, etc.; and from these it might perhaps be assumed that decomposition is dependent upon conducting power, and not the latter upon the former. The true relation, however, of conduction and decomposition in those bodies governed by the general law which it is the object of this paper to establish, can only be satisfactorily made out from a far more extensive series of observations than those I have yet been able to supply.[1]

152. The relation, under this law, of the conducting power of electricity to that for heat, is very remarkable, and seems to imply a natural dependence of the two. As the solid becomes a fluid, it loses almost entirely the power of conduction for heat, but gains in a high degree that for electricity; but as it reverts back to the solid state, it gains the power of conducting heat, and loses that of conducting electricity. If, therefore, the properties are not incompatible, still they are most strongly contrasted, one being lost as the other is gained. We may hope, perhaps, hereafter to understand the physical reason of this very extraordinary relation of the two conducting powers, both of which appear to be directly connected with the corpuscular condition of the substances concerned.

153. The assumption of conducting power and a decomposable condition by liquefaction, promises new opportunities of, and great facilities in, voltaic decomposition. Thus, such bodies as the oxides, chlorides, cyanides, sulpho-cyanides, fluorides, certain vitreous mixtures, etc., etc., may be submitted to the action of the voltaic battery under new circumstances; and indeed I have already been able, with ten pairs of plates, to decompose common salt, chloride of magnesium, borax, etc., etc., and to obtain sodium, magnesium, boron, etc., in their separate states.

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[1] See 414, etc., etc.—*December* 1838.

§ 4. *On Conducting Power generally* [1]

154. It is not my intention here to enter into an examination of all the circumstances connected with conducting power, but to record certain facts and observations which have arisen during recent inquiries, as additions to the general stock of knowledge relating to this point of electrical science.

155. I was anxious, in the first place, to obtain some idea of the conducting power of ice and solid salts for electricity of high tension (128), that a comparison might be made between it and the large accession of the same power gained upon liquefaction. For this purpose the large electrical machine (26) was brought into excellent action, its conductor connected with a delicate gold-leaf electrometer, and also with the platina inclosed in the ice (119), whilst the tin case was connected with the discharging train (28). On working the machine moderately, the gold leaves barely separated; on working it rapidly, they could be opened nearly two inches. In this instance the tin case was five-eighths of an inch in width; and as, after the experiment, the platina plate was found very nearly in the middle of the ice, the average thickness of the latter had been five-sixteenths of an inch, and the extent of surface of contact with tin and platina fourteen square inches (120). Yet, under these circumstances, it was but just able to conduct the small quantity of electricity which this machine could evolve (107), even when of a tension competent to open the leaves two inches; no wonder, therefore, that it could not conduct any sensible portion of the electricity of the troughs (120), which, though almost infinitely surpassing that of the machine in quantity, had a tension so low as not to be sensible to an electrometer.

156. In another experiment, the tin case was only four-eighths of an inch in width, and it was found afterwards that the platina had been not quite one-eighth of an inch distant in the ice from one side of the tin vessel. When this was introduced into the course of the electricity from the machine (155), the gold leaves could be opened, but not more than half an inch; the thinness of the ice favouring the conduction of the electricity, and permitting the same quantity to pass in the same time, though of a much lower tension.

157. Iodide of potassium which had been fused and cooled

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[1] In reference to this § refer to paragraph 718, and the results connected with it.—*December* 1838.

was introduced into the course of the electricity from the machine. There were two pieces, each about a quarter of an inch in thickness, and exposing a surface on each side equal to about half a square inch; these were placed upon platina plates, one connected with the machine and electrometer (155), and the other with the discharging train, whilst a fine platina wire connected the two pieces, resting upon them by its two points. On working the electrical machine, it was possible to open the electrometer leaves about two-thirds of an inch.

158. As the platina wire touched only by points, the facts show that this salt is a far better conductor than ice; but as the leaves of the electrometer opened, it is also evident with what difficulty conduction, even of the small portion of electricity produced by the machine, is effected by this body in the solid state, when compared to the facility with which enormous quantities at very low tensions are transmitted by it when in the fluid state.

159. In order to confirm these results by others, obtained from the voltaic apparatus, a battery of one hundred and fifty plates, four inches square, was well charged: its action was good; the shock from it strong; the discharge would *continue* from copper to copper through four-tenths of an inch of air, and the gold-leaf electrometer before used could be opened nearly a quarter of an inch.

160. The ice vessel employed (156) was half an inch in width: as the extent of contact of the ice with the tin and platina was nearly fourteen square inches, the whole was equivalent to a plate of ice having a surface of seven square inches of perfect contact at each side, and only one-fourth of an inch thick. It was retained in a freezing mixture during the experiment.

161. The order of arrangement in the course of the electric current was as follows. The positive pole of the battery was connected by a wire with the platina plate in the ice; the plate was in contact with the ice, the ice with the tin jacket, the jacket with a wire, which communicated with a piece of tin foil, on which rested one end of a bent platina wire (48), the other or decomposing end being supported on paper moistened with solution of iodide of potassium (52): the paper was laid flat on a platina spatula connected with the negative end of the battery. All that part of the arrangement between the ice vessel and the decomposing wire point, including both these, was insulated, so that no electricity might pass through the latter which had not traversed the former also.

162. Under these circumstances, it was found that a pale brown spot of iodine was slowly formed under the decomposing platina point, thus indicating that ice could conduct a little of the electricity evolved by a voltaic battery charged up to the degree of intensity indicated by the electrometer. But it is quite evident that notwithstanding the enormous quantity of electricity which the battery could furnish, it was, under present circumstances, a very inferior instrument to the ordinary machine; for the latter could send as much through the ice as it could carry, being of a far higher intensity, *i.e.* able to open the electrometer leaves half an inch or more (155, 156).

163. The decomposing wire and solution of iodide of potassium were then removed, and replaced by a very delicate galvanometer; it was so nearly astatic, that it vibrated to and fro in about sixty-three beats of a watch giving one hundred and fifty beats in a minute. The same feebleness of current as before was still indicated; the galvanometer needle was deflected, but it required to break and make contact three or four times (33) before the effect was decided.

164. The galvanometer being removed, two platina plates were connected with the extremities of the wires, and the tongue placed between them, so that the whole charge of the battery, so far as the ice would let it pass, was free to go through the tongue. Whilst standing on the stone floor, there was shock, etc., but when insulated, I could feel no sensation. I think a frog would have been scarcely, if at all, affected.

165. The ice was now removed, and experiments made with other solid bodies, for which purpose they were placed under the end of the decomposing wire instead of the solution of iodide of potassium (161). For instance, a piece of dry iodide of potassium was placed on the spatula connected with the negative pole of the battery, and the point of the decomposing wire placed upon it, whilst the positive end of the battery communicated with the latter. A brown spot of iodine very slowly appeared, indicating the passage of a little electricity, and agreeing in that respect with the results obtained by the use of the electrical machine (157). When the galvanometer was introduced into the circuit at the same time with the iodide, it was with difficulty that the action of the current on it could be rendered sensible.

166. A piece of common salt previously fused and solidified being introduced into the circuit was sufficient almost entirely to destroy the action on the galvanometer. Fused and cooled

chloride of lead produced the same effect. The conducting power of these bodies, *when fluid*, is very great (131, 138).

167. These effects, produced by using the common machine and the voltaic battery, agree therefore with each other, and with the law laid down in this paper (130); and also with the opinion I have supported, in the First Part of these Researches, of the identity of electricity derived from different sources (96).

168. The effect of heat in increasing the conducting power of many substances, especially for electricity of high tension, is well known. I have lately met with an extraordinary case of this kind, for electricity of low tension, or that of the voltaic pile, and which is in direct contrast with the influence of heat upon metallic bodies, as observed and described by Sir Humphry Davy.[1]

169. The substance presenting this effect is sulphuret of silver. It was made by fusing a mixture of precipitated silver and sublimed sulphur, removing the film of silver by a file from the exterior of the fused mass, pulverising the sulphuret, mingling it with more sulphur, and fusing it again in a green glass tube, so that no air should obtain access during the process. The surface of the sulphuret being again removed by a file or knife, it was considered quite free from uncombined silver.

170. When a piece of this sulphuret, half an inch in thickness, was put between surfaces of platina, terminating the poles of a voltaic battery of twenty pairs of four-inch plates, a galvanometer being also included in the circuit, the needle was slightly deflected, indicating a feeble conducting power. On pressing the platina poles and sulphuret together with the fingers, the conducting power increased as the whole became warm. On applying a lamp under the sulphuret between the poles, the conducting power rose rapidly with the heat, and at last the galvanometer needle jumped into a fixed position, and the sulphuret was found conducting in the manner of a metal. On removing the lamp and allowing the heat to fall, the effects were reversed, the needle at first began to vibrate a little, then gradually left its transverse direction, and at last returned to a position very nearly that which it would take when no current was passing through the galvanometer.

171. Occasionally, when the contact of the sulphuret with the platina poles was good, the battery freshly charged, and the commencing temperature not too low, the mere current of electricity from the battery was sufficient to raise the temperature

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[1] *Philosophical Transactions*, 1821, p. 431.

of the sulphuret; and then, without any application of extraneous heat, it went on increasing conjointly in temperature and conducting power, until the cooling influence of the air limited the effects. In such cases it was generally necessary to cool the whole purposely, to show the returning series of phenomena.

172. Occasionally, also, the effects would sink of themselves, and could not be renewed until a fresh surface of the sulphuret had been applied to the positive pole. This was in consequence of peculiar results of decomposition, to which I shall have occasion to revert in the section on Electro-chemical Decomposition, and was conveniently avoided by inserting the ends of two pieces of platina wire into the opposite extremities of a portion of sulphuret fused in a glass tube, and placing this arrangement between the poles of the battery.

173. The hot sulphuret of silver conducts sufficiently well to give a bright spark with charcoal, etc., etc., in the manner of a metal.

174. The native grey sulphuret of silver, and the ruby silver ore, both presented the same phenomena. The native malleable sulphuret of silver presented precisely the same appearances as the artificial sulphuret.

175. There is no other body with which I am acquainted, that, like sulphuret of silver, can compare with metals in conducting power for electricity of low tension when hot, but which, unlike them, during cooling, loses in power, whilst they, on the contrary, gain. Probably, however, many others may, when sought for, be found.

176. The proto-sulphuret of iron, the native per-sulphuret of iron, arsenical sulphuret of iron, native yellow sulphuret of copper and iron, grey artificial sulphuret of copper, artificial sulphuret of bismuth, and artificial grey sulphuret of tin, all conduct the voltaic battery current when cold, more or less, some giving sparks like the metals, others not being sufficient for that high effect. They did not seem to conduct better when heated than before; but I had not time to enter accurately into the investigation of this point. Almost all of them became much heated by the transmission of the current, and present some very interesting phenomena in that respect. The sulphuret of antimony does not conduct the same current sensibly either hot or cold, but is amongst those bodies acquiring conducting power when fused (138). The sulphuret of silver and perhaps some others decompose whilst in the solid state; but the

phenomena of this decomposition will be reserved for its proper place in the next series of these Researches.

177. Notwithstanding the extreme dissimilarity between sulphuret of silver and gases or vapours, I cannot help suspecting the action of heat upon them to be the same, bringing them all into the same class as conductors of electricity, although with those great differences in degree which are found to exist under common circumstances. When gases are heated, they increase in conducting power, both for common and voltaic electricity (7); and it is probable that if we could compress and condense them at the same time, we should still further increase their conducting power. Cagniard de la Tour has shown that a substance, for instance water, may be so expanded by heat whilst in the liquid state, or condensed whilst in the vaporous state, that the two states shall coincide at one point, and the transition from one to the other be so gradual that no line of demarcation can be pointed out;[1] that, in fact, the two states shall become one;—which one state presents us at different times with differences in degree as to certain properties and relations; and which differences are, under ordinary circumstances, so great as to be equivalent to two different states.

178. I cannot but suppose at present that at that point where the liquid and the gaseous state coincide, the conducting properties are the same for both; but that they diminish as the expansion of the matter into a rarer form takes place by the removal of the necessary pressure; still, however, retaining, as might be expected, the capability of having what feeble conducting power remains increased by the action of heat.

179. I venture to give the following summary of the conditions of electric conduction in bodies, not however without fearing that I may have omitted some important points.

180. All bodies conduct electricity in the same manner from metals to lac and gases, but in very different degrees.

181. Conducting power is in some bodies powerfully increased by heat, and in others diminished, yet without our perceiving any accompanying essential electrical difference, either in the bodies or in the changes occasioned by the electricity conducted.

182. A numerous class of bodies, insulating electricity of low intensity, when solid, conduct it very freely when fluid, and are then decomposed by it.

183. But there are many fluid bodies which do not sensibly

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[1] *Annales de Chimie*, xxi. pp. 127, 178.

conduct electricity of this low intensity; there are some which conduct it and are not decomposed; nor is fluidity essential to decomposition.[1]

184. There is but one body yet discovered [2] which, insulating a voltaic current when solid, and conducting it when fluid, is not decomposed in the latter case (150).

185. There is no strict electrical distinction of conduction which can, as yet, be drawn between bodies supposed to be elementary, and those known to be compounds.

April 15, 1833.

III[3]

§ 5. 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

§ 5. *On Electro-chemical Decomposition*[4]

186. I HAVE in a recent series of these Researches (1) 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 the voltaic battery.

187. 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 (107, 112) 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 (96), 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

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[1] See the next part of these *Experimental Researches*.

[2] It is just possible that this case may, by more delicate experiment, hereafter disappear.

[3] Fifth Series, original edition, vol. i. p. 127.

[4] Refer to the note after paragraph 783.—*December* 1838.

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.

188. 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*

189. 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.

190. 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 (48, 52); and also a particular experiment (55), 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 (28, 52), 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.

191. 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.

192. Experiments were then made both with sulphate of soda and iodide of potassium, to ascertain if any diminution of decomposing effect was produced by such great extension as those just described 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 (113).

193. 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.

194. 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.

195. 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, considered in relation to the *direction* of the electric current.

196. 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 (28) by a decomposing wire (48); 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.

197. These cases are abundantly sufficient to show that electro-chemical decomposition 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.

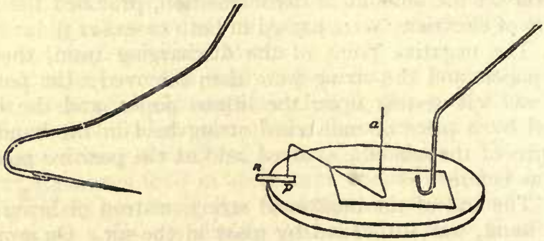

Fig. 8.

198. A piece of turmeric paper, not more than 0.4 of an inch in length and 0.5 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 (fig. 8); 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* (48). 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. 8*a*).

Fig. 8*a*.

199. A similar piece of litmus paper, dipped in solution of

sulphate of soda *n*, fig. 9, was now supported upon the end of the discharging train *a*, and its extremity brought opposite to 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 (58); and these, with the accompanying general facts, are sufficient to show that the acid was really the result of electro-chemical decomposition (202).

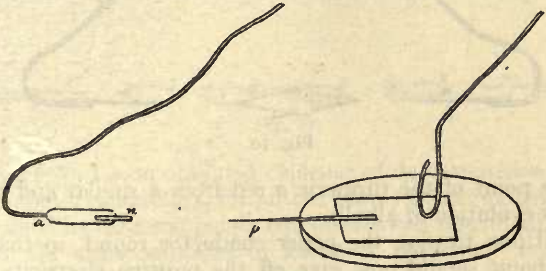

Fig. 9.

200. 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.

201. 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. 10, 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.

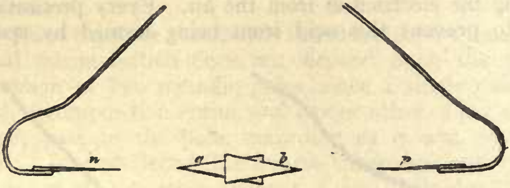

Fig. 10.

202. 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 (199) the effect was not due to the action of brushes or mere electric discharges causing the formation of nitric acid from the air (58).

203. 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.

204. 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.

205. Finally, a series of four small compound conductors, consisting of litmus and turmeric paper (fig. 11) 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 (58), 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.

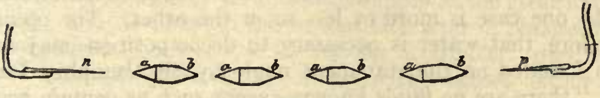

Fig. 11.

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

207. These cases of electro-chemical decomposition are in their nature exactly of the same kind as those affected 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 electrified boundary surfaces (203). 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 (229, 254), that I may previously consider another supposed condition of electro-chemical decomposition.[1]

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[1] 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 (63, 66) 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 part of these Researches (78); 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 (67).

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

208. 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 in 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 connection between the metals or metal of the voltaic apparatus:"[1] 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."[2]

209. 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,[3] 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;[4] 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.

210. I may refer to the last part of these *Experimental Researches* (116, 138) 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 (138) were effective; and that amongst more complicated compounds, cyanides and salts, of equal efficacy, occurred in great numbers (138).

[1] *Elements of Chemical Philosophy*, p. 169, etc.

[2] *Ibid.* pp. 144, 145.

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

[4] *Philosophical Transactions*, 1826, p. 406.

211. 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 (130); 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 a smaller interfering, injurious or complicating action upon the bodies, either dissolved or evolved, than any other substance.

212. 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 (138), 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.[1] 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*

213. The extreme beauty and value of electro-chemical decompositions have given to that power which the voltaic pile possesses of causing their occurrence an interest surpassing that of any other of its properties; for the power is not only intimately connected with the continuance, if not with the

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[1] *Philosophical Transactions*, 1826, p. 406.

production, of the electrical phenomena, but it 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 substances; has given us several new combinations, and sustains us with the hope that when thoroughly understood it will produce many more.

214. What may be considered as the general facts of electrochemical 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.

215. 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.

216. It will be needful that I briefly state the views of electrochemical 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.

217. Grotthuss, in the year 1805, wrote expressly on the decomposition of liquids by voltaic electricity.[1] He considers the pile as an electric magnet, *i.e.* as an attractive and repulsive 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

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

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*.[1] 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,[2] 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.[3]

218. 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.

219. 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;[4] and supposes that the attractive and repellent agencies may be communicated from the metallic surfaces throughout the whole of the menstruum,[5] being communicated from *one particle to another particle of the same kind*,[6] and diminishing in strength from the place of the poles to the middle point, which is necessarily neutral.[7] In reference to this diminution of power at

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[1] *Annales de Chimie*, pp. 66, 67, also tom. lxiii. p. 20.

[2] *Ibid.* tom lviii. p. 68, tom. lxiii. p. 20.

[3] *Ibid.* tom lxiii. p. 34.

[4] *Philosophical Transactions*, 1807, pp. 29, 30.

[5] *Ibid.* p. 39.

[6] *Ibid.* p. 29.

[7] *Ibid.* p. 42.

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.[1]

220. 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,[2] and uses the terms attraction and repulsion apparently in the same sense as before.[3]

221. 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, etc., 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.[4]

222. M. Biot is very cautious in expressing an opinion as to the cause of the separation of the elements of a compound body.[5] 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.[6] When a particle of salt 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.[7]

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[1] *Philosophical Transactions*, 1807, p. 42.

[2] *Ibid.* 1826, p. 383.

[3] *Ibid.* pp. 389, 407, 415.

[4] *Annales de Chimie*, 1807, tom. lxiii. p. 83, etc.

[5] *Précis Elémentaire de Physique*, 3me édition, 1824, tom. i. p. 641.

[6] *Ibid.* p. 637.

[7] *Ibid.* pp. 641, 642.

223. M. Biot does not appear to admit the successive decompositions and recompositions spoken of by Grotthuss, Davy, etc., etc.; but seems to consider the substance whilst in transit as combined with, or rather attached to, the electricity for the time,[1] 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.[2]

224. 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.[3]

225. M. A. de la Rive investigated this subject particularly, and published a paper on it in 1825.[4] He thinks those who have referred the phenomena to the attractive powers of the poles, rather express the general fact 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.[5] 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,[6] 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 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.[7] In this respect M. de la Rive's hypothesis accords in part with that of MM. Riffault and Chompré (221).

226. M. de la Rive considers the portions of matter which are decomposed to be those contiguous to *both* poles.[8] He

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[1] *Précis Elémentaire de Physique*, 3me édition, 1824, tom. i. p. 636.
[2] *Ibid.* p. 642. [3] *Ibid.* pp. 638, 642.
[4] *Annales de Chimie*, tom. xxviii. p. 190. [5] *Ibid.* pp. 200, 202.
[6] *Ibid.* p. 202. [7] *Ibid.* p. 201. [8] *Ibid.* pp. 197, 198.

does not admit with others the successive decompositions and recompositions in the whole course of the electricity through the humid conductor,[1] 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.[2] 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.

227. The latest communication that I am aware of on the subject is by M. Hachette: its date is October 1832.[3] It is incidental to the description of the decomposition of water by the magneto-electric currents (82). 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."

228. 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 apologise to the authors.

229. 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 (48), upon the elements in contact with or near to them, appeared very evident from the experiments made in air (198, 201, etc.), when the substances evolved did not collect about any poles, but, in obedience to the direction 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

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[1] *Annales de Chimie*, tom. xxviii. pp. 192, 199.

[2] *Ibid.* p. 200.

[3] *Ibid.* tom. li. p. 73.

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.

230. A glass basin (fig. 12), 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 comparatively 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

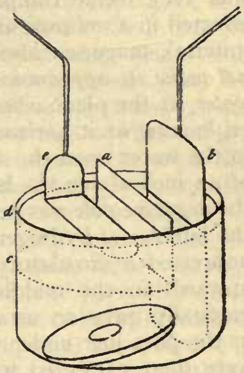

Fig. 12.

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.

231. 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 metallic 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 looked for were satisfactorily ascertained.

232. 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.

233. As, therefore, the substances evolved in cases of electrochemical decomposition may be made to appear against air (201, 205),—which, according to common language, is not a

conductor, nor is decomposed, or against water (231), 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.

234. 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.

235. Grotthuss, for instance, describes the poles as centres of attractive and repulsive forces (217), 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 (238, 241), 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.

236. Sir Humphry Davy, who also speaks of the *diminution* of power with increase of distance from the poles [1] (219), supposes that when both poles are acting on substances to decompose them, still the power of decomposition *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

[1] *Philosophical Transactions*, 1807, p. 42.

theoretically from considering the poles as centres of attraction and repulsion; but I have not found the statement borne out by other experiments (241); 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.

237. 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.[1]

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

239. 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,

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[1] 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 Fourth Part of these Researches.

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.

240. 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 (113), and that the section passes through every part of the current through the decomposing conductor.

241. 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, etc., 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 part but one of these Researches.

242. 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, etc., a consequence which, although perhaps not impossible, seems in the present state of the subject very unlikely.

243. The view which M. de la Rive has taken (225), and also MM. Riffault and Chompré (221), of the manner in which electro-chemical decomposition is effected, is very different to that already considered, and is not affected by either the arguments or facts urged 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 (198, 205) and water (231), 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 analogy of air to metal is, electrically considered, so small, that instead of the former replacing the latter (198), an effect the very reverse might have been expected. Or if even that were allowed, the experiment with water (231) at once sets the matter at rest, the decomposing pole being now of a substance which is admitted as competent to transmit the assumed compound of electricity and matter.

244. With regard to the views of MM. Riffault and Chompré (221), the occurrence of decomposition alone 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.

245. 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.

246. Electro-chemical decomposition is well known to depend essentially upon the *current* of electricity. I have shown that in certain cases (111) 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 (113), even when the utmost generality is taken on the one hand, and great precision of expression on the other (241).

247. In speaking of the current, I find myself obliged to be still more particular than on a former occasion (19), 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.

248. 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,[1] the nitrate of soda being, under similar circumstances, decomposed by the former, but not by the latter.

249. M. Hachette states[2] 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.

250. 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 (226).[3] 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 considered 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 a species of combination can only be conceived to take place between things having independent existences. The two elementary electric currents, moving in opposite directions, from pole to pole, constitute the ordinary *voltaic current*.

251. 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,

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[1] *Annales de Chimie*, 1807, tom. lxiii. p. 84.

[2] *Ibid.* 1832, tom. li. p. 73.

[3] *Ibid.* 1825, tom. xxviii. pp. 197, 201.

according to him, compounds with the electricities; when evolved at the poles, they are de-electrified.

252. 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.[1]

253. *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, 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.*

254. 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 body under decomposition may be considered as a mass of acting particles, all those which are

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

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 neutralised 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.

255. 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. 13, 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. 14, 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.

Fig. 13.

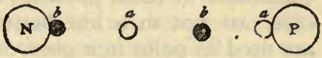

Fig. 14.

256. As far as regards any single compound particle, the case may be considered as analogous to one of ordinary decomposition, for in fig. 14, *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 (253) 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.

257. 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 (255, 256) 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.

258. 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.

259. 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 connection 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.

260. 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 body under decomposition, in the direction of the current, *and that* in larger or smaller quantities, according as the current is more or less powerful (113). I think, therefore, it would be more philosophical, and more directly expressive of the facts, to speak of such a 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, etc., are rendered at its negative extremity, and combustibles, metals, alkalies, bases, etc., at its positive extremity (203). 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 (201), and in water (231), already quoted, for facts illustrating these views in the first instance; to which I will now add others.

261. 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 neutralised by a measure of the prepared sulphuric acid.

262. Four glass cups were then arranged, as in fig. 15; seventeen measures of the free sulphuric acid (261) 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.

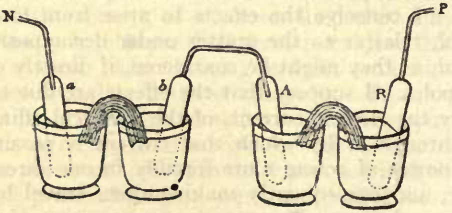

Fig. 15.

263. On breaking the connection with the battery, the por-

tions 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 neutralised by the addition of the soda solution (261), 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*.

264. 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 (261) to neutralise it, and the solution in B required also 3.2 measures of the soda solution (261) to neutralise 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.

265. 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.

266. 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.[1]

267. In some of the experiments the acid from the vessels *a* and *b* was neutralised 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.

268. 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 neutralise 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 brown turmeric point and press them together, when the alkaline effect immediately disappeared.

269. The experiment with sulphate of magnesia already described (231) 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 (263, etc.); and that so soon as the magnesia advanced beyond the reach of

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[1] See the note to 410.—*December* 1838.

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.

270. 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.

271. 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.

272. 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, in accordance with the usual theory, a piece of platina be supposed to have sufficient power 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, magnetism, cohesion, chemical affinity, etc., *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, etc., are left equally at liberty to diffuse themselves through the fluid surrounding the pole, and show no particular tendency to combine with or adhere 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.

273. 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 (254, 255), 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 are sometimes set free, whilst at others they unite to the matter of the poles, according to the chemical nature of the latter, *i.e.* their chemical

relation to those particles which are leaving the substance under operation.

274. 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 (116, 138), 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.

275. Chloride of lead, for instance, fused in a bent tube (136), 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 of platina 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.

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

277. 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 (260).

278. 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.[1] Yet such is not the case, as has been shown by the experiments on free and combined acid (262, 264).

279. 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*.

280. 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 acids and alkalies themselves.[2] Nevertheless the case of sulphate of magnesia is in point (230, 231), and shows that *one element or principle only* has no power of transference or of passing towards either pole.

281. 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 (254, 260), to combine with it; the platina therefore remains where it was first placed, and has no tendency to pass

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[1] Even Sir Humphry Davy considered the attraction of the pole as being communicated from one particle to another of the *same* kind (219).

[2] See the note to 410.—*December* 1838.

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, etc., 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.

282. 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.[1]

283. In support of these arguments, it may be observed that as yet no determination of a substance to a pole, or tendency to obey 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, does not in any case seem to be affected by the electric current.

[1] 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 pile, not the slightest tendency to the negative pole could be perceived.

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 (231, 269), with those of comminuted metals in certain solutions (282), 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 through the surrounding fluid.

284. There are, it is true, many instances of insoluble bodies being acted upon, as glass, sulphate of baryta, marble, slate, basalt, etc., 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.

285. 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, etc., 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, etc., rendered subject to electro-chemical decomposition by fusion (138). 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 (130, 153), we may be able to penetrate much further than at present into the constitution of our chemical elements.

286. Some of the most beautiful and surprising cases of

electro-chemical decomposition and *transfer* which Sir Humphry Davy described in his celebrated paper,[1] were those in which acids were passed through alkalies, and alkalies or earths through acids;[2] 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.

287. The instances in which sulphuric acid could not be passed through baryta, or baryta through sulphuric acid,[3] because of the precipitation of sulphate of baryta, enter within the pale of the law already described (116, 148), by which liquidity is so generally required for conduction and decomposition. In assuming the solid state of sulphate of baryta, these bodies 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.

288. 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.[4] 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 (172), then the sulphur appears at the positive pole; and if a hot platina pole be used so as to vaporise 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,

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[1] *Philosophical Transactions*, 1807, p. 1.

[2] *Ibid.* p. 24, etc.

[3] *Ibid.* p. 25, etc.

[4] At 416 and 492 of Part V. will be found corrections of the statement here made respecting sulphur and sulphuric acid. At present there is no well-ascertained fact which proves that the same body can go directly to *either* of the two poles at pleasure.—*December* 1838.

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. 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.

289. *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 (263), 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.

290. 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.

291. 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.[1]

292. 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 substance suffering decomposition. They limit the extent of that substance in the course of the electric current, being its *terminations* in that direction: hence the elements evolved pass so far and no further.

293. 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 such as are not chemically acted upon by ordinary substances.

294. Water makes a pole of difficult application, except in a few cases (230), 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.

295. Air, however, and some gases are free from the latter objection, and may be used as poles in many cases (197, etc.); 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 (107, 112) to effect electro-chemical decomposition with facility.

296. When 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

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[1] Refer for proof of the truth of this supposition to 483, 487, etc.—*December* 1838.

of the current (254), then they suffer corrosion, and the parts dissolved are subject to transference, in the same manner as the particles of the body originally under decomposition. 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 the transfer and evolution of the elements. Thus platina being made the positive and negative poles in a solution of sulphate of soda, has no affinity or attraction for oxygen, hydrogen, acid, or alkali evolved, and refuses to combine with or retain them. Zinc can combine 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.

297. 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 combines with the silver, and the decomposition of the original sulphuret is rendered evident; whereas in the latter case it is dissipated, and the assurance of its separation at the pole not easily obtained.

298. 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 (201, 205), are explained in the simplest possible manner by the theoretical 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 (260), 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 current.

299. 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.

June 1833.

IV[1]

§ 6. ON THE POWER OF METALS AND OTHER SOLIDS TO INDUCE THE COMBINATION OF GASEOUS BODIES

300. THE conclusion at which I have arrived in the present communication may seem to render the whole of it unfit to form part of a series of researches in electricity; since, remarkable as the phenomena are, the power which produces them is not to be considered as of an electric origin, otherwise than as all attraction of particles may have this subtile agent for their common cause. But as the effects investigated arose out of electrical researches, as they are directly connected with other effects which are of an electric nature, and must of necessity be understood and guarded against in a very extensive series of electro-chemical decompositions (442), I have felt myself fully justified in describing them in this place.

301. Believing that I had proved (by experiments hereafter to be described (440)) the constant and definite chemical action of a certain quantity of electricity, whatever its intensity might be, or however the circumstances of its transmission through either the body under decomposition or the more perfect conductors were varied, I endeavoured upon that result to construct a new measuring instrument, which from its use might be called, at least provisionally, a *Volta-electrometer* (475).[2]

302. During the course of the experiments made to render the instrument efficient, I was occasionally surprised at observing a deficiency of the gases resulting from the decompositions of water, and at last an actual disappearance of portions which had been evolved, collected, and measured. The circumstances of the disappearance were these. A glass tube, about twelve

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[1] Sixth Series, original edition, vol. i. p. 165.

[2] Or Voltameter.—*December* 1838.

inches in length and three-fourths of an inch in diameter, had two platina poles fixed into its upper, hermetically sealed, extremity: the poles, where they passed through the glass, were of wire; but terminated below in plates, which were soldered to the wires with gold (fig. 16). The tube was filled with dilute sulphuric acid, and inverted in a cup of the same fluid; a voltaic battery was connected with the two wires, and sufficient oxygen and hydrogen evolved to occupy four-fifths of the tube, or by the graduation, 116 parts. On separating the tube from the voltaic battery the volume of gas immediately began to diminish, and in about five hours only $13\frac{1}{2}$ parts remained, and these ultimately disappeared.

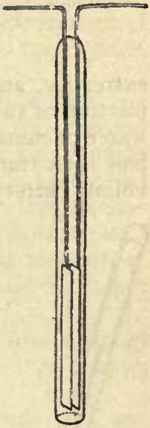

Fig. 16.

303. It was found by various experiments that this effect was not due to the escape or solution of the gas, nor to recombination of the oxygen or hydrogen in consequence of any peculiar condition *they* might be supposed to possess under the circumstances; but to be occasioned by the action of one or both of the poles within the tube upon the gas around them. On disuniting the poles from the pile after they had acted upon dilute sulphuric acid, and introducing them into separate tubes containing mixed oxygen and hydrogen, it was found that the *positive* pole effected the union of the gases, but the negative pole apparently not (324). It was ascertained also that no action of a sensible kind took place between the positive pole with oxygen or hydrogen alone.

304. These experiments reduced the phenomena to the consequence of a power possessed by the platina, after it had been the positive pole of a voltaic pile, of causing the combination of oxygen and hydrogen at common, or even at low, temperatures. This effect is, as far as I am aware, altogether new, and was immediately followed out to ascertain whether it was really of an electric nature, and how far it would interfere with the determination of the quantities evolved in the cases of electro-chemical decomposition.

305. Several platina plates were prepared (fig. 17). They were nearly half an inch wide, and two inches and a half long: some were $\frac{1}{200}$dth of an inch, others not more than $\frac{1}{600}$dth, whilst some were as much as $\frac{1}{70}$th of an inch in thickness. Each had a piece of platina wire, about seven inches long, soldered to

it by pure gold. Then a number of glass tubes were prepared: they were about nine or ten inches in length, five-eighths of an inch in internal diameter, were sealed hermetically at one

Fig. 17.

extremity, and were graduated. Into these tubes was put a mixture of two volumes of hydrogen and one of oxygen, at the water pneumatic trough, and when one of the plates described had been connected with the positive or negative pole of the voltaic battery for a given time, or had been otherwise prepared, it was introduced through the water into the gas within the tube; the whole set aside in a test-glass (fig. 18), and left for a longer or shorter period, that the action might be observed.

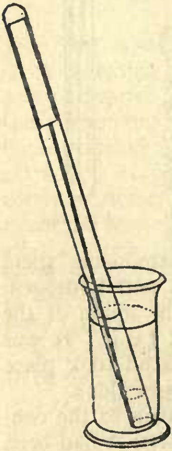

Fig. 18.

306. The following result may be given as an illustration of the phenomenon to be investigated. Diluted sulphuric acid, of the specific gravity 1.336, was put into a glass jar, in which was placed also a large platina plate, connected with the negative end of a voltaic battery of forty pairs of four-inch plates, with double coppers, and moderately charged. One of the plates above described (305) was then connected with the positive extremity, and immersed in the same jar of acid for five minutes, after which it was separated from the battery, washed in distilled water and introduced through the water of the pneumatic trough into a tube containing the mixture of oxygen and hydrogen (305). The volume of gases immediately began to lessen, the diminution proceeding more and more rapidly until about three-fourths of the mixture had disappeared. The upper end of the tube became quite warm, the plate itself so hot that the water boiled as it rose over it; and in less than a minute a cubical inch and a half of the gases were gone, having been combined by the power of the platina, and converted into water.

307. This extraordinary influence acquired by the platina at the positive pole of the pile, is exerted far more readily and

effectively on oxygen and hydrogen than on any other mixture of gases that I have tried. One volume of nitrous gas was mixed with a volume of hydrogen, and introduced into a tube with a plate which had been made positive in the dilute sulphuric acid for four minutes (306). There was no sensible action in an hour: being left for thirty-six hours, there was a diminution of about one-eighth of the whole volume. Action had taken place, but it had been very feeble.

308. A mixture of two volumes of nitrous oxide with one volume of hydrogen was put with a plate similarly prepared into a tube (305, 306). This also showed no action immediately; but in thirty-six hours nearly a fourth of the whole had disappeared, *i.e.* about half of a cubic inch. By comparison with another tube containing the same mixture without a plate, it appeared that a part of the diminution was due to solution, and the other part to the power of the platina; but the action had been very slow and feeble.

309. A mixture of one volume olefiant gas and three volumes oxygen was not affected by such a platina plate, even though left together for several days (376, 377).

310. A mixture of two volumes carbonic oxide and one volume oxygen was also unaffected by the prepared platina plate in several days (381, etc.).

311. A mixture of equal volumes of chlorine and hydrogen was used in several experiments, with plates prepared in a similar manner (306). Diminution of bulk soon took place; but when after thirty-six hours the experiments were examined, it was found that nearly all the chlorine had disappeared, having been absorbed, principally by the water, and that the original volume of hydrogen remained unchanged. No combination of the gases, therefore, had here taken place.

312. Reverting to the action of the prepared plates on mixtures of oxygen and hydrogen (306), I found that the power, though gradually diminishing in all cases, could still be retained for a period, varying in its length with circumstances. When tubes containing plates (305) were supplied with fresh portions of mixed oxygen and hydrogen as the previous portions were condensed, the action was found to continue for above thirty hours, and in some cases slow combination could be observed even after eighty hours; but the continuance of the action greatly depended upon the purity of the gases used (374).

313. Some plates (305) were made positive for four minutes in dilute sulphuric acid of specific gravity 1.336: they were

rinsed in distilled water, after which two were put into a small bottle and closed up, whilst others were left exposed to the air. The plates preserved in the limited portion of air were found to retain their power after eight days, but those exposed to the atmosphere had lost their force almost entirely in twelve hours, and in some situations, where currents existed, in a much shorter time.

314. Plates were made positive for five minutes in sulphuric acid, specific gravity 1.336. One of these was retained in similar acid for eight minutes after separation from the battery: it then acted on mixed oxygen and hydrogen with apparently undiminished vigour. Others were left in similar acid for forty hours, and some even for eight days, after the electrisation, and then acted as well in combining oxygen and hydrogen gas as those which were used immediately after electrisation.

315. The effect of a solution of caustic potassa in preserving the platina plates was tried in a similar manner. After being retained in such a solution for forty hours, they acted exceedingly well on oxygen and hydrogen, and one caused such rapid condensation of the gases, that the plate became much heated, and I expected the temperature would have risen to ignition.

316. When similarly prepared plates (305) had been put into distilled water for forty hours, and then introduced into mixed oxygen and hydrogen, they were found to act but very slowly and feebly as compared with those which had been preserved in acid or alkali. When, however, the quantity of water was but small, the power was very little impaired after three or four days. As the water had been retained in a wooden vessel, portions of it were redistilled in glass, and this was found to preserve prepared plates for a great length of time. Prepared plates were put into tubes with this water and closed up; some of them, taken out at the end of twenty-four days, were found very active on mixed oxygen and hydrogen; others, which were left in the water for fifty-three days, were still found to cause the combination of the gases. The tubes had been closed only by corks.

317. The act of combination always seemed to diminish, or apparently exhaust, the power of the platina plate. It is true, that in most, if not all instances, the combination of the gases, at first insensible, gradually increased in rapidity, and sometimes reached to explosion; but when the latter did not happen, the rapidity of combination diminished; and although fresh portions of gas were introduced into the tubes, the combination

went on more and more slowly, and at last ceased altogether. The first effect of an increase in the rapidity of combination depended in part upon the water flowing off from the platina plate, and allowing a better contact with the gas, and in part upon the heat evolved during the progress of the combination (366). But notwithstanding the effect of these causes, diminution, and at last cessation of the power, always occurred. It must not, however, be unnoticed, that the purer the gases subjected to the action of the plate, the longer was its combining power retained. With the mixture evolved at the poles of the voltaic pile, in pure dilute sulphuric acid, it continued longest; and with oxygen and hydrogen, of perfect purity, it probably would not be diminished at all.

318. Different modes of treatment applied to the platina plate, after it had ceased to be the positive pole of the pile, affected its power very curiously. A plate which had been a positive pole in diluted sulphuric acid of specific gravity 1.336 for four or five minutes, if rinsed in water and put into mixed oxygen and hydrogen, would act very well, and condense perhaps one cubic inch and a half of gas in six or seven minutes; but if that same plate, instead of being merely rinsed, had been left in distilled water for twelve or fifteen minutes, or more, it would rarely fail, when put into the oxygen and hydrogen, of becoming, in the course of a minute or two, ignited, and would generally explode the gases. Occasionally the time occupied in bringing on the action extended to eight or nine minutes, and sometimes even to forty minutes, and yet ignition and explosion would result. This effect is due to the removal of a portion of acid which otherwise adheres firmly to the plate.[1]

319. Occasionally the platina plates (305), after being made the positive pole of the battery, were washed, wiped with filtering-paper or a cloth, and washed and wiped again. Being then introduced into mixed oxygen and hydrogen, they acted apparently as if they had been unaffected by the treatment. Sometimes the tubes containing the gas were opened in the air for an instant, and the plates put in dry; but no sensible difference in action was perceived, except that it commenced sooner.

320. The power of heat in altering the action of the prepared platina plates was also tried (331). Plates which had been rendered positive in dilute sulphuric acid for four minutes were well washed in water, and heated to redness in the flame of a

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[1] In proof that this is the case, refer to 774.—*December* 1838.

spirit-lamp: after this they acted very well on mixed oxygen and hydrogen. Others, which had been heated more powerfully by the blowpipe, acted afterwards on the gases, though not so powerfully as the former. Hence it appears that heat does not take away the power acquired by the platina at the positive pole of the pile: the occasional diminution of force seemed always referable to other causes than the mere heat. If, for instance, the plate had not been well washed from the acid, or if the flame used was carbonaceous, or was that of an alcohol lamp trimmed with spirit containing a little acid, or having a wick on which salt, or other extraneous matter, had been placed, then the power of the plate was quickly and greatly diminished (370, 372).

321. This remarkable property was conferred upon platina when it was made the positive pole in sulphuric acid of specific gravity 1.336, or when it was considerably weaker, or when stronger, even up to the strength of oil of vitriol. Strong and dilute nitric acid, dilute acetic acid, solutions of tartaric, citric, and oxalic acids, were used with equal success. When muriatic acid was used, the plates acquired the power of condensing the oxygen and hydrogen, but in a much inferior degree.

322. Plates which were made positive in solution of caustic potassa did not show any sensible action upon the mixed oxygen and hydrogen. Other plates made positive in solutions of carbonates of potassa and soda exhibited the action, but only in a feeble degree.

323. When a neutral solution of sulphate of soda, or of nitre, or of chlorate of potassa, or of phosphate of potassa, or acetate of potassa, or sulphate of copper, was used, the plates, rendered positive in them for four minutes, and then washed in water, acted very readily and powerfully on the mixed oxygen and hydrogen.

324. It became a very important point, in reference to the *cause* of this action of the platina, to determine whether the *positive* pole *only* could confer it (303), or whether, notwithstanding the numerous contrary cases, the *negative* pole might not have the power when such circumstances as could interfere with or prevent the action were avoided. Three plates were therefore rendered negative, for four minutes in diluted sulphuric acid of specific gravity 1.336, washed in distilled water, and put into mixed oxygen and hydrogen. *All* of them *acted*, though not so strongly as they would have done if they had been rendered positive. Each combined about a cubical inch

and a quarter of the gases in twenty-five minutes. On every repetition of the experiment the same result was obtained; and when the plates were retained in distilled water for ten or twelve minutes, before being introduced into the gas (318), the action was very much quickened.

325. But when there was any metallic or other substance present in the acid, which could be precipitated on the negative plate, then that plate ceased to act upon the mixed oxygen and hydrogen.

326. These experiments led to the expectation that the power of causing oxygen and hydrogen to combine, which could be conferred upon any piece of platina by making it the positive pole of a voltaic pile, was not essentially dependent upon the action of the pile, or upon any structure or arrangement of parts it might receive whilst in association with it, but belonged to the platina *at all times*, and was *always effective* when the surface was *perfectly clean*. And though, when made the *positive* pole of the pile in acids, the circumstances might well be considered as those which would cleanse the surface of the platina in the most effectual manner, it did not seem impossible that ordinary operations should produce the same result, although in a less eminent degree.

327. Accordingly, a platina plate (305) was cleaned by being rubbed with a cork, a little water, and some coal-fire ashes upon a glass plate: being washed, it was put into mixed oxygen and hydrogen, and was found to act at first slowly, and then more rapidly. In an hour, a cubical inch and a half had disappeared.

328. Other plates were cleaned with ordinary sand-paper and water; others with chalk and water; others with emery and water; others, again, with black oxide of manganese and water; and others with a piece of charcoal and water. All of these acted in tubes of oxygen and hydrogen, causing combination of the gases. The action was by no means so powerful as that produced by plates having been in communication with the battery; but from one to two cubical inches of the gases disappeared, in periods extending from twenty-five to eighty or ninety minutes.

329. Upon cleaning the plates with a cork, ground emery, and dilute sulphuric acid, they were found to act still better. In order to simplify the conditions, the cork was dismissed, and a piece of platina foil used instead; still the effect took place. Then the acid was dismissed; and a solution of *potassa* used, but the effect occurred as before.

330. These results are abundantly sufficient to show that the mere mechanical cleansing of the surface of the platina is sufficient to enable it to exert its combining power over oxygen and hydrogen at common temperatures.

331. I now tried the effect of heat in conferring this property upon platina (320). Plates which had no action on the mixture of oxygen and hydrogen were heated by the flame of a freshly trimmed spirit-lamp, urged by a mouth blowpipe, and when cold were put into tubes of the mixed gases: they acted slowly at first, but after two or three hours condensed nearly all the gases.

332. A plate of platina, which was about one inch wide and two and three-quarters in length, and which had not been used in any of the preceding experiments, was curved a little so as to enter a tube, and left in a mixture of oxygen and hydrogen for thirteen hours: not the slightest action or combination of the gases occurred. It was withdrawn at the pneumatic trough from the gas through the water, heated red hot by the spirit-lamp and blowpipe, and then returned when cold into the *same* portion of gas. In the course of a few minutes diminution of the gases could be observed, and in forty-five minutes about one cubical inch and a quarter had disappeared. In many other experiments platina plates when heated were found to acquire the power of combining oxygen and hydrogen.

333. But it happened not unfrequently that plates, after being heated, showed no power of combining oxygen and hydrogen gases, though left undisturbed in them for two hours. Sometimes also it would happen that a plate which, having been heated to dull redness, acted feebly, upon being heated to whiteness ceased to act; and at other times a plate which, having been slightly heated, did not act, was rendered active by a more powerful ignition.

334. Though thus uncertain in its action, and though often diminishing the power given to the plates at the positive pole of the pile (320), still it is evident that heat can render platina active which before was inert (331). The cause of its occasional failure appears to be due to the surface of the metal becoming soiled, either from something previously adhering to it, which is made to adhere more closely by the action of the heat, or from matter communicated from the flame of the lamp, or from the air itself. It often happens that a polished plate of platina, when heated by the spirit-lamp and a blow-pipe, becomes dulled and clouded on its surface by something either

formed or deposited there; and this, and much less than this, is sufficient to prevent it from exhibiting the curious power now under consideration (370, 372). Platina also has been said to combine with carbon; and it is not at all unlikely that in processes of heating, where carbon or its compounds are present, a film of such a compound may be thus formed, and thus prevent the exhibition of the properties belonging to *pure* platina.[1]

335. The action of alkalies and acids in giving platina this property was now experimentally examined. Platina plates (305) having no action on mixed oxygen and hydrogen, being boiled in a solution of caustic potassa, washed, and then put into the gases, were found occasionally to act pretty well, but at other times to fail. In the latter case I concluded that the impurity upon the surface of the platina was of a nature not to be removed by the mere solvent action of the alkali, for when the plates were rubbed with a little emery, and the same solution of alkali (328), they became active.

336. The action of acids was far more constant and satisfactory. A platina plate was boiled in dilute nitric acid: being washed and put into mixed oxygen and hydrogen gases, it acted well. Other plates were boiled in strong nitric acid for periods extending from half a minute to four minutes, and then being washed in distilled water, were found to act very well, condensing one cubic inch and a half of gas in the space of eight or nine minutes, and rendering the tube warm (306).

337. Strong sulphuric acid was very effectual in rendering the platina active. A plate (305) was heated in it for a minute, then washed and put into the mixed oxygen and hydrogen, upon which it acted as well as if it had been made the positive pole of a voltaic pile (306).

338. Plates which, after being heated or electrised in alkali, or after other treatment, were found inert, immediately received power by being dipped for a minute or two, or even only for an instant, into hot oil of vitriol, and then into water.

339. When the plate was dipped into the oil of vitriol, taken out, and then heated so as to drive off the acid, it did not act, in consequence of the impurity left by the acid upon its surface.

340. Vegetable acids, as acetic and tartaric, sometimes rendered inert platina active, at other times not. This, I believe,

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[1] When heat does confer the property it is only by the destruction or dissipation of organic or other matter which had previously soiled the plate (368, 369, 370).—*December* 1838.

depended upon the character of the matter previously soiling the plates, and which may easily be supposed to be sometimes of such a nature as to be removed by these acids, and at other times not. Weak sulphuric acid showed the same difference, but strong sulphuric acid (337) never failed in its action.

341. The most favourable treatment, except that of making the plate a positive pole in strong acid, was as follows. The plate was held over a spirit-lamp flame, and when hot, rubbed with a piece of potassa fusa (caustic potash), which melting, covered the metal with a coat of very strong alkali, and this was retained fused upon the surface for a second or two:[1] it was then put into water for four or five minutes to wash off the alkali, shaken, and immersed for about a minute in hot strong oil of vitriol; from this it was removed into distilled water, where it was allowed to remain ten or fifteen minutes to remove the last traces of acid (318). Being then put into a mixture of oxygen and hydrogen, combination immediately began, and proceeded rapidly; the tube became warm, the platina became red hot, and the residue of the gases was inflamed. This effect could be repeated at pleasure, and thus the maximum phenomenon could be produced without the aid of the voltaic battery.

342. When a solution of tartaric or acetic acid was substituted, in this mode of preparation, for the sulphuric acid, still the plate was found to acquire the same power, and would often produce explosion in the mixed gases; but the strong sulphuric acid was most certain and powerful.

343. If borax, or a mixture of the carbonates of potash and soda, be fused on the surface of a platina plate, and that plate be well washed in water, it will be found to have acquired the power of combining oxygen and hydrogen, but only in a moderate degree; but if, after the fusion and washing, it be dipped in the hot sulphuric acid (337), it will become very active.

344. Other metals than platina were then experimented with. Gold and palladium exhibited the power either when made the positive pole of the voltaic battery (306), or when acted on by hot oil of vitriol (337). When palladium is used, the action of the battery or acid should be moderated, as that metal is soon acted upon under such circumstances. Silver and copper could not be made to show any effect at common temperatures.

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[1] The heat need not be raised so much as to make the alkali tarnish the platina, although if that effect does take place it does not prevent the ultimate action.

345. There can remain no doubt that the property of inducing combination, which can thus be conferred upon masses of platina and other metals by connecting them with the poles of the battery, or by cleansing processes either of a mechanical or chemical nature, is the same as that which was discovered by Dobereiner,[1] in 1823, to belong in so eminent a degree to spongy platina, and which was afterwards so well experimented upon and illustrated by MM. Dulong and Thenard,[2] in 1823. The latter philosophers even quote experiments in which a very fine platina wire, which had been coiled up and digested in nitric, sulphuric, or muriatic acid, became ignited when put into a jet of hydrogen gas.[3] This effect I can now produce at pleasure with either wires or plates by the processes described (306, 337, 341); and by using a smaller plate cut so that it shall rest against the glass by a few points, and yet allow the water to flow off (fig. 19), the loss of heat is less, the metal is assimilated somewhat to the spongy state, and the probability of failure almost entirely removed.

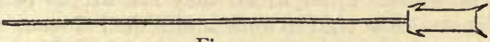

Fig. 19.

346. M. Dobereiner refers the effect entirely to an electric action. He considers the platina and hydrogen as forming a voltaic element of the ordinary kind, in which the hydrogen, being very highly positive, represents the zinc of the usual arrangement, and like it, therefore, attracts oxygen and combines with it.[4]

347. In the two excellent experimental papers by MM. Dulong and Thenard,[5] those philosophers show that elevation of temperature favours the action, but does not alter its character; Sir Humphry Davy's incandescent platina wire being the same phenomenon with Dobereiner's spongy platina. They show that *all* metals have this power in a greater or smaller degree, and that it is even possessed by such bodies as charcoal, pumice, porcelain, glass, rock-crystal, etc., when their temperatures are raised; and that another of Davy's effects, in which oxygen and hydrogen had combined slowly together at a heat below ignition, was really dependent upon the property of the

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[1] *Annales de Chimie*, tom. xxiv. p. 93.

[2] *Ibid.* tom. xxiii. p. 440; tom. xxiv. p. 380.

[3] *Ibid.* tom. xxiv. p. 383.

[4] *Ibid.* tom. xxiv. pp. 94, 95. Also *Bibliothèque Universelle*, tom. xxiv. p. 54.

[5] *Ibid.* tom. xxiii. p. 440; tom. xxiv. p. 380.

heated glass, which it has in common with the bodies named above. They state that liquids do not show this effect, at least that mercury, at or below the boiling point, has not the power; that it is not due to porosity; that the same body varies very much in its action, according to its state; and that many other gaseous mixtures besides oxygen and hydrogen are affected, and made to act chemically, when the temperature is raised. They think it probable that spongy platina acquires its power from contact with the acid evolved during its reduction, or from the heat itself to which it is then submitted.

348. MM. Dulong and Thenard express themselves with great caution on the theory of this action; but, referring to the decomposing power of metals on ammonia when heated to temperatures not sufficient alone to affect the alkali, they remark that those metals which in this case are most efficacious, are the least so in causing the combination of oxygen and hydrogen; whilst platina, gold, etc., which have least power of decomposing ammonia, have most power of combining the elements of water:—from which they are led to believe that amongst gases, some tend to *unite* under the influence of metals, whilst others tend to *separate,* and that this property varies in opposite directions with the different metals. At the close of their second paper they observe, that the action is of a kind that cannot be connected with any known theory; and though it is very remarkable that the effects are transient, like those of most electrical actions, yet they state that the greater number of the results observed by them are inexplicable, by supposing them to be of a purely electric origin.

349. Dr. Fusinieri has also written on this subject, and given a theory which he considers as sufficient to account for the phenomena.[1] He expresses the immediate cause thus: "The platina determines upon its surface a continual renovation of *concrete laminæ* of the combustible substance of the gases or vapours, which flowing over it are burnt, pass away, and are renewed: this combustion at the surface raises and sustains the temperature of the metal." The combustible substance, thus reduced into imperceptible laminæ, of which the concrete parts are in contact with the oxygen, is presumed to be in a state combinable with the oxygen at a much lower temperature than when it is in the gaseous state, and more in analogy with what is called the nascent condition. That combustible gases should lose their elastic state, and become concrete, assuming the form

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[1] *Giornale di Fisica,* etc., 1825, tom. viii. p. 259.

of exceedingly attenuated but solid strata, is considered as proved by facts, some of which are quoted in the *Giornale di Fisica* for 1824;[1] and though the theory requires that they should assume this state at high temperatures, and though the *similar* films of aqueous and other matter are dissipated by the action of heat, still the facts are considered as justifying the conclusion against all opposition of reasoning.

350. The power or force which makes combustible gas or vapour abandon its elastic state in contact with a solid, that it may cover the latter with a thin stratum of its own proper substance, is considered as being neither attraction nor affinity. It is able also to extend liquids and solids in concrete laminæ over the surface of the acting solid body, and consists in a *repulsion*, which is developed from the parts of the solid body by the simple fact of attenuation, and is highest when the attenuation is most complete. The force has a progressive development, and acts most powerfully, or at first, in the direction in which the dimensions of the attenuated mass decrease, and then in the direction of the angles or corners which from any cause may exist on the surface. This force not only causes spontaneous diffusion of gases and other substances over the surface, but is considered as very elementary in its nature, and competent to account for all the phenomena of capillarity, chemical affinity, attraction of aggregation, rarefaction, ebullition, volatilisation, explosion, and other thermometric effects, as well as inflammation, detonation, etc., etc. It is considered as a form of heat to which the term *native caloric* is given, and is still further viewed as the principle of the two electricities and the two magnetisms.

351. I have been the more anxious to give a correct abstract of Dr. Fusinieri's view, both because I cannot form a distinct idea of the power to which he refers the phenomena, and because of my imperfect knowledge of the language in which the memoir is written. I would therefore beg to refer those who pursue the subject to the memoir itself.

352. Not feeling, however, that the problem has yet been solved, I venture to give the view which seems to me sufficient, upon *known principles*, to account for the effect.

353. It may be observed of this action, that, with regard to platina, it cannot be due to any peculiar, temporary condition, either of an electric or of any other nature: the activity of plates rendered either positive or negative by the pole, or cleaned with

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[1] pp. 138, 371.

such different substances as acids, alkalies, or water; charcoal, emery, ashes, or glass; or merely heated, is sufficient to negative such an opinion. Neither does it depend upon the spongy and porous, or upon the compact and burnished, or upon the massive or the attenuated state of the metal, for in any of these states it may be rendered effective, or its action may be taken away. The only essential condition appears to be a *perfectly clean* and *metallic surface*, for whenever that is present the platina acts, whatever its form and condition in other respects may be; and though variations in the latter points will very much affect the rapidity, and therefore the visible appearances and secondary effects, of the action, *i.e.* the ignition of the metal and the inflammation of the gases, they, even in their most favourable state, cannot produce any effect unless the condition of a clean, pure, metallic surface be also fulfilled.

354. The effect is evidently produced by most, if not all, solid bodies, weakly perhaps by many of them, but rising to a high degree in platina. Dulong and Thenard have very philosophically extended our knowledge of the property to its possession by all the metals, and by earths, glass, stones, etc. (347); and every idea of its being a known and recognised electric action is in this way removed.

355. All the phenomena connected with this subject press upon my mind the conviction that the effects in question are entirely incidental and of a secondary nature; that they are dependent upon the *natural conditions* of gaseous elasticity, combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination, though often assuming the condition of adhesion; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction. I am prepared myself to admit (and probably many others are of the same opinion), both with respect to the attraction of aggregation and of chemical affinity, that the sphere of action of particles extends beyond those other particles with which they are immediately and evidently in union (259), and in many cases produces effects rising into considerable importance: and I think that this kind of attraction is a determining cause of Dobereiner's effect, and of the many others of a similar nature.

356. Bodies which become wetted by fluids with which they do not combine chemically, or in which they do not dissolve, are simple and well known instances of this kind of attraction.

357. All those cases of bodies which being insoluble in water and not combining with it are hygrometric, and condense its vapour around or upon their surface, are stronger instances of the same power, and approach a little nearer to the cases under investigation. If pulverised clay, protoxide or peroxide of iron, oxide of manganese, charcoal, or even metals, as spongy platina or precipitated silver, be put into an atmosphere containing vapour of water, they soon become moist by virtue of an attraction which is able to condense the vapour upon, although not to combine it with, the substances; and if, as is well known, these bodies so damped be put into a dry atmosphere, as, for instance, one confined over sulphuric acid, or if they be heated, then they yield up this water again almost entirely, it not being in direct or permanent combination.[1]

358. Still better instances of the power I refer to, because they are more analogous to the cases to be explained, are furnished by the attraction existing between glass and air, so well known to barometer and thermometer makers, for here the adhesion or attraction is exerted between a solid and gases, bodies having very different physical conditions, having no power of combination with each other, and each retaining, during the time of action, its physical state unchanged.[2] When mercury is poured into a barometer tube, a film of air will remain between the metal and glass for months, or, as far as is known, for years, for it has never been displaced except by the action of means especially fitted for the purpose. These consist in boiling the mercury, or in other words, of forming an abundance of vapour, which coming in contact with every part of the glass and every portion of surface of the mercury, gradually mingles with, dilutes, and carries off the air attracted by, and adhering to, those surfaces, replacing it by other vapour, subject to an equal or perhaps greater attraction, but which when cooled condenses into the same liquid as that with which the tube is filled.

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[1] I met at Edinburgh with a case, remarkable as to its extent, of hygrometric action, assisted a little perhaps by very slight solvent power. Some turf had been well dried by long exposure in a covered place to the atmosphere, but being then submitted to the action of a hydrostatic press, it yielded, *by the mere influence of the pressure*, 54 per cent. of water.

[2] Fusinieri and Bellani consider the air as forming solid concrete films in these cases.—*Giornale di Fisica*, 1825, tom. viii. p. 262.

359. Extraneous bodies, which, acting as nuclei in crystallising or depositing solutions, cause deposition of substances on them, when it does not occur elsewhere in the liquid, seem to produce their effects by a power of the same kind, *i.e.* a power of attraction extending to neighbouring particles, and causing them to become attached to the nuclei, although it is not strong enough to make them combine chemically with their substance.

360. It would appear from many cases of nuclei in solutions, and from the effects of bodies put into atmospheres containing the vapours of water, or camphor, or iodine, etc., as if this attraction were in part elective, partaking in its characters both of the attraction of aggregation and chemical affinity: nor is this inconsistent with, but agreeable to, the idea entertained, that it is the power of particles acting, not upon others with which they can immediately and intimately combine, but upon such as are either more distantly situated with respect to them, or which, from previous condition, physical constitution, or feeble relation, are unable to enter into decided union with them.

361. Then, of all bodies, the gases are those which might be expected to show some *mutual* action whilst *jointly* under the attractive influence of the platina or other solid acting substance. Liquids, such as water, alcohol, etc., are in so dense and comparatively incompressible a state, as to favour no expectation that their particles should approach much closer to each other by the attraction of the body to which they adhere, and yet that attraction must (according to its effects) place their particles as near to those of the solid wetted body as they are to each other, and in many cases it is evident that the former attraction is the stronger. But gases and vapours are bodies competent to suffer very great changes in the relative distances of their particles by external agencies; and where they are in immediate contact with the platina, the approximation of the particles to those of the metal may be very great. In the case of the hygrometric bodies referred to (357), it is sufficient to reduce the vapour to the fluid state, frequently from atmospheres so rare that without this influence it would be needful to compress them by mechanical force into a bulk not more than one-tenth or even one-twentieth of their original volume before the vapours would become liquids.

362. Another most important consideration in relation to this action of bodies, and which, as far as I am aware, has not hitherto been noticed, is the condition of elasticity under which the gases are placed against the acting surface. We have but very imperfect notions of the real and intimate conditions of

the particles of a body existing in the solid, the liquid, and the gaseous state; but when we speak of the gaseous state as being due to the mutual repulsions of the particles or of their atmospheres, although we may err in imagining each particle to be a little nucleus to an atmosphere of heat, or electricity, or any other agent, we are still not likely to be in error in considering the elasticity as dependent on *mutuality* of action. Now this mutual relation fails altogether on the side of the gaseous particles next to the platina, and we might be led to expect *à priori* a deficiency of elastic force there to at least one-half; for if, as Dalton has shown, the elastic force of the particles of one gas cannot act against the elastic force of the particles of another, the two being as vacua to each other, so is it far less likely that the particles of the platina can exert any influence on those of the gas against it, such as would be exerted by gaseous particles of its own kind.

363. But the diminution of power to one-half on the side of the gaseous body towards the metal is only a slight result of what seems to me to flow as a necessary consequence of the known constitution of gases. An atmosphere of one gas or vapour, however dense or compressed, is in effect as a vacuum to another; thus, if a little water were put into a vessel containing a dry gas, as air, of the pressure of one hundred atmospheres, as much vapour of the water would *rise* as if it were in a perfect vacuum. Here the particles of watery vapour appear to have no difficulty in approaching within any distance of the particles of air, being influenced solely by relation to particles of their own kind; and if it be so with respect to a body having the same elastic powers as itself, how much more surely must it be so with particles, like those of the platina, or other limiting body, which at the same time that they have not these elastic powers, are also unlike it in nature. Hence it would seem to result that the particles of hydrogen or any other gas or vapour which are next to the platina, etc., must be in such contact with it as if they were in the liquid state, and therefore almost infinitely closer to it than they are to each other, even though the metal be supposed to exert no attractive influence over them.

364. A third and very important consideration in favour of the mutual action of gases under these circumstances is their perfect miscibility. If fluid bodies capable of combining together are also capable of mixture, *they do combine* when they are mingled, not waiting for any other determining circumstance; but if two such gases as oxygen and hydrogen are put together,

though they are elements having such powerful affinity as to unite naturally under a thousand different circumstances, they do not combine by mere mixture. Still it is evident that, from their perfect association, the particles are in the most favourable state possible for combination, upon the supervention of any determining cause, such either as the negative action of the platina in suppressing or annihilating, as it were, their elasticity on its side; or the positive action of the metal in condensing them against its surface by an attractive force; or the influence of both together.

365. Although there are not many distinct cases of combination under the influence of forces external to the combining particles, yet there are sufficient to remove any difficulty which might arise on that ground. Sir James Hall found carbonic acid and lime to remain combined under pressure at temperatures at which they would not have remained combined if the pressure had been removed; and I have had occasion to observe a case of direct combination in chlorine,[1] which being compressed at common temperatures will combine with water, and form a definite crystalline hydrate, incapable either of being formed or of existing if that pressure be removed.

366. The course of events when platina acts upon, and combines oxygen and hydrogen, may be stated, according to these principles, as follows. From the influence of the circumstances mentioned (355, etc.), *i.e.* the deficiency of elastic power and the attraction of the metal for the gases, the latter, when they are in association with the former, are so far condensed as to be brought within the action of their mutual affinities at the existing temperature; the deficiency of elastic power, not merely subjecting them more closely to the attractive influence of the metal, but also bringing them into a more favourable state for union, by abstracting a part of that power (upon which depends their elasticity), which elsewhere in the mass of gases is opposing their combination. The consequence of their combination is the production of the vapour of water and an elevation of temperature. But as the attraction of the platina for the water formed is not greater than for the gases, if so great, (for the metal is scarcely hygrometric), the vapour is quickly diffused through the remaining gases; fresh portions of the latter, therefore, come into juxtaposition with the metal, combine, and the fresh vapour formed is also diffused, allowing new portions of gas to be acted upon. In this way the process

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[1] *Philosophical Transactions*, 1823, p. 161.

advances, but is accelerated by the evolution of heat, which is known by experiment to facilitate the combination in proportion to its intensity, and the temperature is thus gradually exalted until ignition results.

367. The dissipation of the vapour produced at the surface of the platina, and the contact of fresh oxygen and hydrogen with the metal, form no difficulty in this explication. The platina is not considered as causing the combination of any particles with itself, but only associating them closely around it; and the compressed particles are as free to move from the platina, being replaced by other particles, as a portion of dense air upon the surface of the globe, or at the bottom of a deep mine, is free to move by the slightest impulse, into the upper and rarer parts of the atmosphere.

368. It can hardly be necessary to give any reasons why platina does not show this effect under ordinary circumstances. It is then not sufficiently clean (353), and the gases are prevented from touching it, and suffering that degree of effect which is needful to commence their combination at common temperatures, and which they can only experience at its surface. In fact, the very power which causes the combination of oxygen and hydrogen, is competent, under the usual casual exposure of platina, to condense extraneous matters upon its surface, which soiling it, take away for the time its power of combining oxygen and hydrogen, by preventing their contact with it (334).

369. Clean platina, by which I mean such as has been made the positive pole of a pile (306), or has been treated with acid (341), and has then been put into distilled water for twelve or fifteen minutes, has a *peculiar friction* when one piece is rubbed against another. It wets freely with pure water, even after it has been shaken and dried by the heat of a spirit-lamp; and if made the pole of a voltaic pile in a dilute acid, it evolves minute bubbles from every part of its surface. But platina in its common state wants that peculiar friction: it will not wet freely with water as the clean platina does; and when made the positive pole of a pile, it for a time gives off large bubbles which seem to cling or adhere to the metal, and are evolved at distinct and separate points of the surface. These appearances and effects, as well as its want of power on oxygen and hydrogen, are the consequences, and the indications, of a soiled surface.

370. I found also that platina plates which had been cleaned perfectly soon became soiled by mere exposure to the air; for

after twenty-four hours they no longer moistened freely with water, but the fluid ran up into portions, leaving part of the surface bare, whilst other plates which had been retained in water for the same time, when they were dried (316) did moisten, and gave the other indications of a clean surface.

371. Nor was this the case with platina or metals only, but also with earthy bodies. Rock crystal and obsidian would not wet freely upon the surface, but being moistened with strong oil of vitriol, then washed, and left in distilled water to remove all the acid, they did freely become moistened, whether they were previously dry or whether they were left wet; but being dried and left exposed to the air for twenty-four hours, their surface became so soiled that water would not then adhere freely to it, but ran up into partial portions. Wiping with a cloth (even the cleanest) was still worse than exposure to air; the surface either of the minerals or metals immediately became as if it were slightly greasy. The floating upon water of small particles of metals under ordinary circumstances is a consequence of this kind of soiled surface. The extreme difficulty of cleaning the surface of mercury when it has once been soiled or greased is due to the same cause.

372. The same reasons explain why the power of the platina plates in some circumstances soon disappear, and especially upon use: MM. Dulong and Thenard have observed the same effect with the spongy metal,[1] as indeed have all those who have used Dobereiner's instantaneous light machines. If left in the air, if put into ordinary distilled water, if made to act upon ordinary oxygen and hydrogen, they can still find in all these cases *that* minute portion of impurity which, when once in contact with the surface of the platina, is retained there, and is sufficient to prevent its full action upon oxygen and hydrogen at common temperatures: a slight elevation of temperature is again sufficient to compensate this effect, and cause combination.

373. No state of a solid body can be conceived more favourable for the production of the effect than that which is possessed by platina obtained from the ammonia-muriate by heat. Its surface is most extensive and pure, yet very accessible to the gases brought in contact with it: if placed in impurity, the interior, as Thenard and Dulong have observed, is preserved clean by the exterior; and as regards temperature, it is so bad a conductor of heat, because of its divided condition, that almost all which is evolved by the combination of the first por-

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[1] *Annales de Chimie*, tom. xxiv. p. 386.

tions of gas is retained within the mass, exalting the tendency of the succeeding portions to combine.

374. I have now to notice some very extraordinary interferences with this phenomenon, dependent, not upon the nature or condition of the metal or other acting solid, but upon the presence of certain substances mingled with the gases acted upon; and as I shall have occasion to speak frequently of a mixture of oxygen and hydrogen, I wish it always to be understood that I mean a mixture composed of one volume oxygen to two volumes of hydrogen, being the proportions that form water. Unless otherwise expressed, the hydrogen was always that obtained by the action of dilute sulphuric acid on pure zinc, and the oxygen that obtained by the action of heat from the chlorate of potassa.

375. Mixtures of oxygen and hydrogen with *air*, containing one-fourth, one-half, and even two-thirds of the latter, being introduced with prepared platina plates (306, 341) into tubes, were acted upon almost as well as if no air were present: the retardation was far less than might have been expected from the mere dilution and consequent obstruction to the contact of the gases with the plates. In two hours and a half nearly all the oxygen and hydrogen introduced as mixture was gone.

376. But when similar experiments were made with *olefiant gas* (the platina plates having been made the positive poles of a voltaic pile (306) in acid), very different results occurred. A mixture was made of 29.2 volumes hydrogen and 14.6 volumes oxygen, being the proportions for water; and to this was added another mixture of three volumes oxygen and one volume olefiant gas, so that the olefiant gas formed but $\frac{1}{48}$th part of the whole; yet in this mixture the platina plate would not act in forty-five hours. The failure was not for want of any power in the plate, for when after that time it was taken out of this mixture and put into one of oxygen and hydrogen, it immediately acted, and in seven minutes caused explosion of the gas. This result was obtained several times, and when larger proportions of olefiant gas were used, the action seemed still more hopeless.

377. A mixture of forty-nine volumes oxygen and hydrogen (374) with one volume of olefiant gas had a well-prepared platina plate introduced. The diminution of gas was scarcely sensible at the end of two hours, during which it was watched; but on examination twenty-four hours afterwards, the tube was found blown to pieces. The action, therefore, though it had

been very much retarded, had occurred at last, and risen to a maximum.

378. With a mixture of ninety-nine volumes of oxygen and hydrogen (374) with one of olefiant gas, a feeble action was evident at the end of fifty minutes; it went on accelerating (366) until the eighty-fifth minute, and then became so intense that the gas exploded. Here also the retarding effect of the olefiant gas was very beautifully illustrated.

379. Plates prepared by alkali and acid (341) produced effects corresponding to those just described.

380. It is perfectly clear from these experiments that *olefiant gas*, even in small quantities, has a very remarkable influence in preventing the combination of oxygen and hydrogen under these circumstances, and yet without at all injuring or affecting the power of the platina.

381. Another striking illustration of similar interference may be shown in *carbonic oxide;* especially if contrasted with *carbonic acid*. A mixture of one volume oxygen and hydrogen (374) with four volumes of carbonic acid was affected at once by a platina plate prepared with acid, etc. (341), and in one hour and a quarter nearly all the oxygen and hydrogen was gone. Mixtures containing less carbonic acid were still more readily affected.

382. But when carbonic oxide was substituted for the carbonic acid, not the slightest effect of combination was produced; and when the carbonic oxide was only one-eighth of the whole volume, no action occurred in forty and fifty hours. Yet the plates had not lost their power; for being taken out and put into pure oxygen and hydrogen, they acted well and at once.

383. Two volumes of carbonic oxide and one of oxygen were mingled with nine volumes of oxygen and hydrogen (374). This mixture was not affected by a plate which had been made positive in acid, though it remained in it fifteen hours. But when to the same volumes of carbonic oxide and oxygen were added thirty-three volumes of oxygen and hydrogen, the carbonic oxide being then only $\frac{1}{18}$th part of the whole, the plate acted, slowly at first, and at the end of forty-two minutes the gases exploded.

384. These experiments were extended to various gases and vapours, the general results of which may be given as follow. Oxygen, hydrogen, nitrogen, and nitrous oxide, when used to dilute the mixture of oxygen and hydrogen, did not prevent the action of the plates even when they made four-fifths of

the whole volume of gas acted upon. Nor was the retardation so great in any case as might have been expected from the mere dilution of the oxygen and hydrogen, and the consequent mechanical obstruction to its contact with the platina. The order in which carbonic acid and these substances seemed to stand was as follows, the first interfering least with the action; *nitrous oxide, hydrogen, carbonic acid, nitrogen, oxygen:* but it is possible the plates were not equally well prepared in all the cases, and that other circumstances also were unequal; consequently more numerous experiments would be required to establish the order accurately.

385. As to cases of *retardation*, the powers of olefiant gas and carbonic oxide have been already described. Mixtures of oxygen and hydrogen, containing from $\frac{1}{16}$th to $\frac{1}{20}$th of sulphuretted hydrogen or phosphuretted hydrogen, seemed to show a little action at first, but were not further affected by the prepared plates, though in contact with them for seventy hours. When the plates were removed they had lost all power over pure oxygen and hydrogen, and the interference of these gases was therefore of a different nature from that of the two former, having permanently affected the plate.

386. A small piece of cork was dipped in sulphuret of carbon and passed up through water into a tube containing oxygen and hydrogen (374), so as to diffuse a portion of its vapour through the gases. A plate being introduced appeared at first to act a little, but after sixty-one hours the diminution was very small. Upon putting the same plate into a pure mixture of oxygen and hydrogen, it acted at once and powerfully, having apparently suffered no diminution of its force.

387. A little vapour of ether being mixed with the oxygen and hydrogen retarded the action of the plate, but did not prevent it altogether. A little of the vapour of the condensed oil-gas liquor[1] retarded the action still more, but not nearly so much as an equal volume of olefiant gas would have done. In both these cases it was the original oxygen and hydrogen which combined together, the ether and the oil-gas vapour remaining unaffected, and in both cases the plates retained the power of acting on fresh oxygen and hydrogen.

388. Spongy platina was then used in place of the plates, and jets of hydrogen mingled with the different gases thrown against it in air. The results were exactly of the same kind, although presented occasionally in a more imposing form.

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[1] *Philosophical Transactions*, 1825, p. 440.

Thus, mixtures of one volume of olefiant gas or carbonic oxide with three of hydrogen could not heat the spongy platina when the experiments were commenced at common temperatures; but a mixture of equal volumes of nitrogen and hydrogen acted very well, causing ignition. With carbonic acid the results were still more striking. A mixture of three volumes of that gas with one of hydrogen caused *ignition* of the platina, yet that mixture would not continue to burn from the jet when attempts were made to light it by a taper. A mixture even of *seven* volumes of carbonic acid and *one* of hydrogen will thus cause the ignition of cold spongy platina, and yet, as if to supply a contrast, than which none can be greater, *it cannot burn at a taper*, but causes the extinction of the latter. On the other hand, the mixtures of carbonic oxide or olefiant gas, which can do nothing with the platina, are *inflamed* by the taper, burning well.

389. Hydrogen mingled with the vapour of ether or oil-gas liquor causes the ignition of the spongy platina. The mixture with oil-gas burns with a flame far brighter than that of the mixture of hydrogen and olefiant gas already referred to, so that it would appear that the retarding action of the hydrocarbons is not at all in proportion merely to the quantity of carbon present.

390. In connection with these interferences, I must state that hydrogen itself, prepared from steam passed over ignited iron, was found when mingled with oxygen to resist the action of platina. It had stood over water seven days, and had lost all fetid smell; but a jet of it would not cause the ignition of spongy platina, commencing at common temperatures; nor would it combine with oxygen in a tube either under the influence of a prepared plate or of spongy platina. A mixture of one volume of this gas with three of pure hydrogen, and the due proportion of oxygen, was not affected by plates after fifty hours. I am inclined to refer the effect to carbonic oxide present in the gas, but have not had time to verify the suspicion. The power of the plates was not destroyed (376, 382).

391. Such are the general facts of these remarkable interferences. Whether the effect produced by such small quantities of certain gases depends upon any direct action which they may exert upon the particles of oxygen and hydrogen, by which the latter are rendered less inclined to combine, or whether it depends upon their modifying the action of the plate temporarily (for they produce no real change on it), by invest-

ing it through the agency of a stronger attraction than that of the hydrogen, or otherwise, remains to be decided by more extended experiments.

392. The theory of action which I have given for the original phenomena appears to me quite sufficient to account for all the effects by reference to known properties, and dispenses with the assumption of any new power of matter. I have pursued this subject at some length, as one of great consequence, because I am convinced that the superficial actions of matter, whether between two bodies, or of one piece of the same body, and the actions of particles not directly or strongly in combination, are becoming daily more and more important to our theories of chemical as well as mechanical philosophy.[1] In all ordinary cases of combustion it is evident that an action of the kind considered, occurring upon the surface of the carbon in the fire, and also in the bright part of a flame, must have great influence over the combinations there taking place.

393. The condition of elasticity upon the exterior of the gaseous or vaporous mass already referred to (362, 363) must be connected directly with the action of solid bodies, as nuclei, on vapours, causing condensation upon them in preference to any condensation in the vapours themselves; and in the well-known effect of nuclei on solutions a similar condition may have existence (359), for an analogy in condition exists between the parts of a body in solution, and those of a body in the vaporous or gaseous state. This thought leads us to the consideration of what are the respective conditions at the surfaces of contact of two portions of the same substance at the same temperature, one in the solid or liquid, and the other in the vaporous state; as, for instance, steam and water. It would seem that the particles of vapour next to the particles of liquid are in a different relation to the latter to what they would be with respect to any other liquid or solid substance; as, for instance, mercury or

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[1] As a curious illustration of the influence of mechanical forces over chemical affinity, I will quote the refusal of certain substances to effloresce when their surfaces are perfect, which yield immediately upon the surface being broken. If crystals of carbonate of soda, or phosphate of soda, or sulphate of soda, having no part of their surfaces broken, be preserved from external violence, they will not effloresce. I have thus retained crystals of carbonate of soda perfectly transparent and unchanged from September 1827 to January 1833; and crystals of sulphate of soda from May 1832 to the present time, November 1833. If any part of the surface were scratched or broken, then efflorescence began at that part, and covered the whole. The crystals were merely placed in evaporating basins and covered with paper.

platina, if they were made to replace the water, *i.e.* if the view of independent action which I have taken (362, 363) as a consequence of Dalton's principles, be correct. It would also seem that the mutual relation of similar particles, and the indifference of dissimilar particles which Dalton has established as a matter of fact amongst gases and vapours, extends to a certain degree amongst solids and fluids, that is, when they are in relation by contact with vapours, either of their own substance or of other bodies. But though I view these points as of great importance with respect to the relations existing between different substances and their physical constitution in the solid, liquid, or gaseous state, I have not sufficiently considered them to venture any strong opinions or statements here.[1]

394. There are numerous well-known cases, in which substances, such as oxygen and hydrogen, act readily in their *nascent* state, and produce chemical changes which they are not able to effect if once they have assumed the gaseous condition. Such instances are very common at the poles of the voltaic pile, and are, I think, easily accounted for, if it be considered that at the moment of separation of any such particle it is entirely surrounded by other particles of a *different* kind with which it is in close contact, and has not yet assumed those relations and conditions which it has in its fully developed state, and which it can only assume by association with other particles of its own kind. For, at the moment, its elasticity is absent, and it is in the same relation to particles with which it is in contact, and for which it has an affinity, as the particles of oxygen and hydrogen are to each other on the surface of clean platina (362, 363).

395. The singular effects of retardation produced by very small quantities of some gases, and not by large quantities of others (376, 381, 388), if dependent upon any relation of the added gas to the surface of the solid, will then probably be found immediately connected with the curious phenomena which are presented by different gases when passing through narrow tubes at low pressures, which I observed many years ago;[2] and this action of surfaces must, I think, influence the highly interesting phenomena of the diffusion of gases, at least in the form in which it has been experimented upon by Mr. Graham in 1829 and

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[1] In reference to this paragraph and also 362, see a correction by Dr. C. Henry, in his valuable paper on this curious subject—*Philosophical Magazine*, 1835, vol. vi. p. 365.—*December* 1838.

[2] *Quarterly Journal of Science*, 1819, vol. vii. p. 106.

1831,[1] and also by Dr. Mitchell of Philadelphia[2] in 1830. It seems very probable that if such a substance as spongy platina were used, another law for the diffusion of gases under the circumstances would come out than that obtained by the use of plaster of Paris.

396. I intended to have followed this section by one on the secondary piles of Ritter, and the peculiar properties of the poles of the pile, or of metals through which electricity has passed, which have been observed by Ritter, Van Marum, Yelin, De la Rive, Marianini, Berzelius, and others. It appears to me that all these phenomena bear a satisfactory explanation on known principles, connected with the investigation just terminated, and do not require the assumption of any new state or new property. But as the experiments advanced, especially those of Marianini, require very careful repetition and examination, the necessity of pursuing the subject of electro-chemical decomposition obliges me for a time to defer the researches to which I have just referred.

November 30, 1833.

V[3]

§ 5. ON ELECTRO-CHEMICAL DECOMPOSITION, CONTINUED.[4] ¶ iv. ON SOME GENERAL CONDITIONS OF ELECTRO-DECOMPOSITION. ¶ v. ON A NEW MEASURER OF VOLTA-ELECTRICITY. ¶ vi. ON THE PRIMARY OR SECONDARY CHARACTER OF BODIES EVOLVED IN ELECTRO-DECOMPOSITION. ¶ vii. ON THE DEFINITE NATURE AND EXTENT OF ELECTRO-CHEMICAL DECOMPOSITIONS. § 7. ON THE ABSOLUTE QUANTITY OF ELECTRICITY ASSOCIATED WITH THE PARTICLES OR ATOMS OF MATTER

Preliminary

397. THE theory which I believe to be a true expression of the facts of electro-chemical decomposition, and which I have therefore detailed in a former part of these Researches, is so much at variance with those previously advanced, that I find the

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[1] *Quarterly Journal of Science*, vol. xxviii. p. 74, and *Edinburgh Transactions*, 1831.

[2] *Journal of the Royal Institution* for 1831, p. 101.

[3] Seventh Series, original edition, vol. i. p. 195.

[4] Refer to the note after 783, Part VI.—*December* 1838.

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, etc., or more cautiously, that it *determines* their evolution upon its 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 body under decomposition; and the oxygen and acids are rendered at the *negative* extremity of that body, whilst hydrogen, metals, etc., are evolved at the *positive* extremity (254, 260).

398. 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 (292); 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 (201, 207) and water (229), against which I have effected electro-chemical decomposition, is subject to doubt. In place of the term pole, I propose using that of *Electrode*,[1] 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.

399. The surfaces at which, according to 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,

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[1] *ἤλεκτρον*, and ὁδὸς *a way.*

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*,[1] and that towards the west the *cathode*;[2] 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, etc., 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.

400. I shall have occasion in these Researches, also, to class bodies together according to certain relations derived from their electrical actions (557); 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*.[3] Water, therefore, is an electrolyte. The bodies which, like nitric or sulphuric acids, are decomposed in a secondary manner (487, 492), are not included under this term. Then for *electro-chemically decomposed*, I shall often use the term *electrolysed*, 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 *analyse*, which is derived in a similar manner. The term

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[1] *ἄνω upwards*, and *ὁδὸς a way*; the way which the sun rises.

[2] *κατὰ downwards*, and *ὁδὸς a way*; the way which the sun sets.

[3] *ἤλεκτρον*, and *λύω*, *solvo*. N. Electrolyte, V. Electrolyse.

electrolytical will be understood at once: muriatic acid is electrolytical, boracic acid is not.

401. 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 such bodies by calling those *anions* [1] which go to the *anode* of the decomposing body; and those passing to the *cathode*, *cations*; [2] 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 *electrolysed* evolves the two *ions*, chlorine and lead, the former being an *anion*, and the latter a *cation*.

402. 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.[3]

403. 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 former occasions (19, 253); and that though I speak of the current as proceeding from the parts which are positive to those which are negative (399), 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.

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[1] *ἀνιὼν that which goes up.* (Neuter participle.)

[2] *κατιὼν that which goes down.*

[3] 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.

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

404. 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 (285).

405. If this result was evident when water was supposed to be essential to, and was present, in almost every case of such decomposition (208), it is far more evident now that it has been shown and proved that water is not necessarily concerned in the phenomena (210), and that other bodies much surpass it in some of the effects supposed to be peculiar to that substance.

406. 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 electrolysation can occur, where, being present, it is not resolved into its first principles.

407. The various oxides, chlorides, iodides, and salts, which I have shown are decomposable by the electric current when in the liquid state, under the same general law with water (138), illustrate in an equally striking manner the activity, in such decompositions, of elements directly and powerfully opposed to each other by their chemical relations.

408. 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.[1] If bottle-glass be fused, and subjected to the voltaic pile, it does not appear to be at all decomposed (144). 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 (144).

409. But the result which is found to be so striking in the instances quoted is not at all borne out by reference to other

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[1] *Philosophical Transactions*, 1830 p. 49.

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 is supposed to be one presented by the 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 (254, 260): 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 electrolysation which have been considered, and is an addition to those which I have taken against them.

410. Amongst powerful compounds which are not decomposed, boracic acids stands prominent (144). 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 (138, 426), 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 (266, 280), where the affinity must by comparison be very weak, separation takes place.[1]

411. 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 (414, 426); and even water itself, which so easily yields up its elements when the

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[1] 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.

current passes, if rendered quite pure, scarcely suffers change, because it then becomes a very bad conductor.

412. If it should hereafter be proved that the want of decomposition in those cases where, from chemical considerations, it might be so strongly expected (404, 407, 409), is due to the absence or deficiency of conducting power, it would also at the same time be proved that decomposition *depends* upon conduction, and not the latter upon the former (149); 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 (556). I may not, however, stop to discuss this point experimentally at present.

413. 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 (138), but the perchloride neither conducts nor is decomposed (142). The protiodide of tin is decomposed when fluid (138); the periodide is not (143). The periodide of mercury when fused is not decomposed (426), even though it does conduct. I was unable to contrast it with the protiodide, the latter being converted into mercury and periodide by heat.

414. These important differences induced me to look more closely to certain binary compounds, with a view of ascertaining whether a *law* regulating the *decomposability* 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 (138), 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 (141, 142).

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

416. 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 (288). When very strong it is a much worse conductor than if diluted.[1] If then subjected to the action of a powerful battery, oxygen appears at the *anode*, or positive electrode, although much is absorbed (463), 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; and it appeared to me that, when fused, such 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 during the action of the pile on sulphuric acid, it is the result of a secondary action, and that the acid itself is not electrolysable (492).

417. 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 volatilises. Upon subjecting phosphoric acid, fused upon the ring end of a wire (137), 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.

418. *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.

419. Nitrous acid, obtained by distilling nitrate of lead, and keeping it in contact 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 en-

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[1] De la Rive.

deavoured to prepare a perfectly anhydrous portion, but could not spare the time required to procure an unexceptionable result.

420. 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 (487).

421. 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.

422. *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 (414), which does not affirm that *all* compounds of single proportionals of elements are decomposable, but that such as are decomposable are so constituted.

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

424. *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.

425. With regard to the exceptions (414), 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. 28) (524), 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 (130)), 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 (430, 531).

426. *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* (138); 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 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.

427. 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.

428. 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 (138, 536). 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.

429. 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.

430. 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, etc., a true protoxide, consisting also of *single* proportionals, was obtainable. But I could not stop to ascertain this matter strictly by analysis.

431. 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.[1]

432. Upon the whole, it appears probable that all those binary compounds of elementary bodies which are capable of being electrolysed when fluid, but not whilst solid, according to the law of liquido-conduction (130), consist of single proportionals of their elementary principles; and it may be because of their departure from this simplicity of composition, that boracic acid, ammonia, perchlorides, periodides, and many other direct compounds of elements, are indecomposable.

433. 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 salts conducted, and were decomposed; but hydrogen always appeared at the negative electrode.

434. 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 electrolysed, I am not quite satisfied that water was entirely absent.

435. 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.

436. Hence this class of compound combinations does not

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[1] In relation to this and the three preceding paragraphs, and also 536, see Berzelius's correction of the nature of the supposed new sulphuret and oxide, *Phil. Mag.* 1836, vol. viii. 476.—*December* 1838.

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.

437. 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 (477, etc.).

438. It is evident that all the cases in which decomposition *does not occur, may* depend upon the want of conduction (412, 149); 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,[1] 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*

439. I have already said, when engaged in reducing common and voltaic electricity to one standard of measurement (113), and again when introducing my theory of electro-chemical decomposition (240, 241, 246), 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) through which it is passed, or in other circumstances. The conclusive proofs of the truth of these statements shall be given almost immediately (518, etc.).

440. 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 *comparative standard* of effect, or as a *positive measurer* of this subtile agent.

441. There is no substance better fitted, under ordinary circumstances, to be the indicating body in such an instrument

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

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 secondary 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 (578).

442. 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 (307). For this purpose various forms of decomposing apparatus were used. The first consisted of straight tubes, each containing a plate and wire of platina soldered together by gold, and fixed hermetically in the glass at the closed extremity of the tube (fig. 20). 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. 21). When these tubes were used as measurers, they were filled with the dilute sulphuric acid, inverted in a basin of the same liquid (fig. 22), and 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 (455).


Fig. 20.

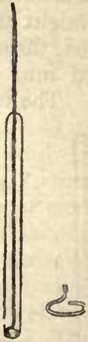
Fig. 21.


Fig. 22.

443. Another form of apparatus is that delineated (fig. 23). 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 (455). 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.

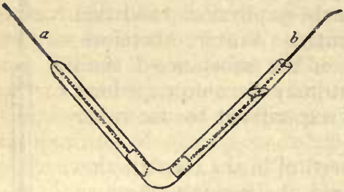

Fig. 23.

444. 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. 24) closed at the upper extremity, and graduated, through the sides of which pass 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 (441), 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.

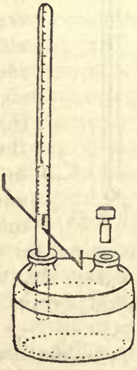

Fig. 24.

445. Another form of the instrument is given at fig. 25.

446. A fifth form is delineated (fig. 26). 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.

447. 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.

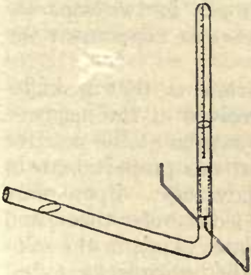

Fig. 25.

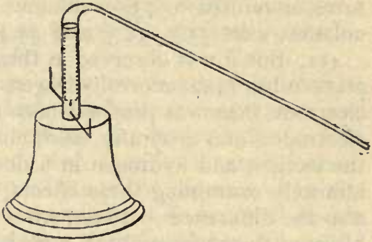

Fig. 26.

448. 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.

449. 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 (444, 445, 446) 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 at the smallest electrodes, namely, those consisting merely of platina wires.

450. Experiments of a similar kind were made with the single-plate, straight tubes (442), and also with the curved tubes (443), 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.

451. But it was observed in these experiments, that in single-plate tubes (442) 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 (449), to the solubility of the gases evolved, especially at the positive electrode.

452. 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 (369); 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 oxywater.

453. 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 amount collected.

454. 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 effect takes place *most extensively* with large plates, because the gas evolved at them is in the most favourable condition for solution.

455. With the intention of avoiding this solubility of the gases as much as possible, I arranged the decomposing plates in a vertical position (442, 443), 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.

456. 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 (463); 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 (552), it can be collected more perfectly and in greater purity.

457. 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.*

458. 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.*

459. 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 (96, *note*); and therefore when large plates were contrasted with wires separated by an equal length of the same decomposing conductor (449), 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.

460. The difference in intensity, under the circumstances described, may be easily shown practically, by arranging two decomposing apparatus as in fig. 27, 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. 26 (446), be connected with the wires at *a b*, fig. 27, 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 connections of P and N with the voltaic battery are of course to be continued during the whole time.

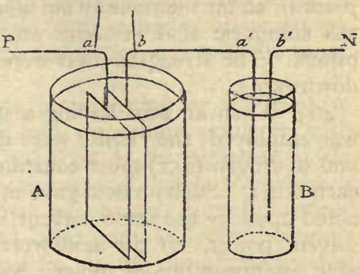

Fig. 27.

461. 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, each of which should traverse one of the remaining instruments, and should then 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 (460).

462. 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 (442); 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 (449). 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 seventy-fold what it was in others. The strengths used were of specific gravity 1.495, and downwards.

463. When an acid having a specific gravity of about 1.336 was employed, the results were most uniform, and the oxygen and hydrogen (451) 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 of 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.

464. 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 (513).

465. 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 (290), 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.*

466. I have already said, respecting large and small electrodes, that change of order caused no change in the general effect (450). 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.

467. 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 (477, etc.), 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.*

468. The forms of instrument which I have given, figs. 24, 25, 26 (444, 445, 446), 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 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 (508, etc.), shall diminish their quantity, or add other gases to them.

469. 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, figs. 22, 23 (442, 443). 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, etc., are employed.

470. 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.

471. 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 (444, 445, 446), and the other in which a single gas, as the hydrogen only, is used (442, 443). 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.

472. 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.[1] For the latter object the volta-electrometer (fig. 26) is most accurate, as its gas can be measured over water, whilst the others retain it over acid or saline solutions.

473. I have not hesitated to apply the term *degree* (471), 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, etc., is there made use of to measure heat, so the equally definite evolution of gases is here turned to a similar use for electricity.

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

474. 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.

475. 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 (526, 578).

476. 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.[1]

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

477. 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 primary 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.

478. 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

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[1] As early as the year 1811, Messrs. Gay Lussac, and Thénard, employed chemical decomposition as a measure of the electricity of the voltaic pile. See *Recherches Physico-chymiques*, p. 12. The principles and precautions by which it becomes an exact measure were of course not then known.—*December* 1838.

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 substances 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.

479. These secondary results occur in two ways, being sometimes due to the mutual action of the evolved substance and the matter of the electrode, and sometimes to its action upon the substances contained in the body itself under decomposition. Thus, when carbon is made the positive electrode in dilute sulphuric acid, carbonic oxide and carbonic acid occasionally 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;*[1] 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 (290). 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.

480. 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.

481. The nature of the substances evolved will often lead to a correct judgment 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 (290, 291), and it is on such occasions evidently viewed as a primary result;[2] but I think I shall show that, when it appears at the positive electrode, or rather at the *anode,* it is a secondary result (483). Thus, also, Sir Humphry

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[1] *Annales de Chimie,* 1804, tom. li. p. 167.

[2] *Ibid.* p. 172.

Davy,[1] and with him the great body of chemical philosophers (including myself), have given the appearance of copper, lead, tin, silver, gold, etc., 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 either of the attraction or of the law announced respecting their places.[2]

482. But when we take to our assistance the law of *constant electro-chemical action* already proved with regard to water (467), and which I hope to extend satisfactorily to all bodies (556), and consider the *quantities* as well as the *nature* of the substances set free, a generally accurate judgment of the primary or secondary character of the results may be formed: and this important point, so essential to the theory of electrolysation, 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.

483. Let us apply these principles to the case of ammonia, and the supposed determination of nitrogen to one or the other *electrode* (290, 291). A pure strong solution of ammonia is as bad a conductor, and therefore as little liable to electrolysation, 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 (442, 471), it was found that the hydrogen obtained was exactly in the proportion

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[1] *Elements of Chemical Philosophy*, pp. 144, 161.

[2] 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*, 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).

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 electrolysed, 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.

484. 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 carbonic 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 (442); 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.

485. 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 (578). In place of oxygen or even the gases already described (484), 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.

486. 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 electrolysed in instances where other substances have been supposed to give way. Some of these results I will give in as few words as possible.

487. *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-electrometer (442), 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 electrolysation, 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.

488. *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.

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

490. *Sulphurous acid.*—Pure liquid sulphurous acid does not conduct nor suffer decomposition by the voltaic current,[1] 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.*

491. A solution containing sulphuric acid in addition to the sulphurous acid 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 voltameter. 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.

492. *Sulphuric acid.*—I have already given my reasons for concluding that sulphuric acid is not electrolysable, *i.e.* not decomposable directly by the electric current, but occasionally suffering by a secondary action at the *cathode* from the hydrogen evolved there (416). In the year 1800, Davy considered the

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[1] See also De la Rive, *Bibliothèque Universelle,* tom. xl. p. 205; or *Quarterly Journal of Science,* vol. xxvii. p. 407.

sulphur from sulphuric acid as the result of the action of the nascent hydrogen.[1] In 1804, Hisinger and Berzelius stated that it was the direct result of the action of the voltaic pile,[2] an opinion which from that time Davy seems to have adopted, and which has since been 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 part of these Researches (288): I do not now think that the appearance of the sulphur at the negative electrode is an immediate consequence of electrolytic action.

493. *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.

494. 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 electrolysable, and if so, whether the decomposition was *definite*.

495. 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.

496. 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 forty pairs of plates or one containing only five pairs were used. With acid of this strength, the oxygen evolved at the *anode* was to the hydrogen at the *cathode,* in volume, as seventeen is to sixty-four; and therefore the chlorine would have been thirty volumes, had it not been dissolved by the fluid.

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[1] Nicholson's *Quarterly Journal,* vol. iv. pp. 280, 281.

[2] *Annales de Chimie,* 1804, tom. li. p. 173.

497. 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.

498. This constancy does not decide whether the muriatic acid is electrolysed 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 (432), 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 (131), which may be justly compared with protoxide of lead (138), and stands in the same relation to it as muriatic acid to water. The chlorides of potassium, sodium, barium, etc., are in the same relation to the protoxides of the same metals and present the same results under the influence of the electric current (138).

499. 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.

500. In the dilute acid (496), 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.

501. *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 electrolysed, 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—524, 529, 549), they are not in the slightest degree opposed to such a conclusion, and do support the *general law.*

502. *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 without 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.

503. I believe the decomposition of the hydriodic acid in this case to be direct, for the reasons already given respecting muriatic acid (498, 499).

504. *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 (501).

505. *Hydro-fluoric acid and fluorides.*—Solution of hydrofluoric 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 electrolysed (153); 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.[1]

506. *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 (501), and because a fused cyanide of potassium evolves cyanogen at the positive electrode,[2] I incline to believe that the cyanide in solution is *directly* decomposed.

507. *Ferro-cyanic acid* and the *ferro-cyanides*, as also *sulpho-cyanic acid* and the *sulpho-cyanides*, presented results corresponding with those just described (506).

508. *Acetic acid.*—Glacial acetic acid, when fused (141), 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 pure water 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

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[1] I have not obtained fluorine: my expectations, amounting to conviction, passed away one by one when subjected to rigorous examination; some very singular results were obtained.—*December* 1838.

[2] 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.

is not electrolysable, but that a portion of it is decomposed by the oxygen evolved at the *anode*, producing secondary results, varying with the strength of the acid, the intensity of the current, and other circumstances.

509. *Acetates.*—One of these has been referred to already, as affording only secondary results relative to the acetic acid (484). With many of the metallic acetates the results at both electrodes are secondary (481, 485).

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 substances; charcoal, sodiuretted hydrogen, etc., being set free at the former, and, as far as I could judge under the circumstances, acetic acid mingled with carbonic oxide, carbonic acid, etc., at the latter.

510. *Tartaric acid.*—Pure solution of tartaric acid is almost as bad a conductor as pure water. On adding sulphuric acid, 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 (487). Alkaline tartrates gave a large proportion of secondary results at the positive electrode. The hydrogen at the negative electrode remained constant unless certain triple metallic salts were used.

511. Solutions, of salts containing other vegetable acids, as the benzoates; of sugar, gum, etc., dissolved in dilute sulphuric acid; of resin, albumen, etc., 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.

512. 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 combination of the evolving substances whilst in their nascent state (394), directly with the matter of the electrode; or else their combination with those bodies, which being contained in, or associated with, the body suffering decomposition, 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 proportions to each other. But it may in a great measure be resolved by attention to the principles already laid down (482).

513. 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.

514. Secondary actions are *not confined to aqueous solutions*, or cases where water is present. For instance, various chlorides acted upon, when fused (138), by platina electrodes, have the chlorine determined electrically to the *anode*. In many cases, as with the chlorides of lead, potassium, barium, etc., 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 (525, 539). These are, therefore, instances of secondary actions of both kinds, produced in bodies containing no water.

515. The production of boron from fused borax (138, 153) is also a case of secondary action; for boracic acid is not decomposable by electricity (144), and it was the sodium evolved at the *cathode* which, re-acting on the boracic acid around it, took oxygen from it and set boron free in the experiments formerly described.

516. 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.[1] 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

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[1] *Annales de Chimie*, tom. xxxv. p. 113.

compounds generally, will probably be obtained by submitting them to the action of nascent oxygen, hydrogen, chlorine, etc., 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, etc., all of which may be expected to have their corresponding influence upon the final result.

517. It is to me a great satisfaction that the extreme variety of secondary results has presented nothing opposed to the doctrine of a constant and definite electro-chemical action, to the particular consideration of which I shall now proceed.

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

518. In the first part 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 (107, 112), 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 a current of electricity is in direct proportion to the absolute quantity of electricity which passes* (113).

519. In the further progress of the successive investigations, I have had frequent occasion to refer to the same law, sometimes in circumstances offering powerful corroboration of its truth (192, 240, 241); and the present series already supplies numerous new cases in which it holds good (439, 457, 461, 467). It is now my object to consider this great principle more closely, and to develop 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.

520. 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 (467). I refer, therefore, to the whole of the

subdivision of this series of Researches which contains the account of the *volta-electrometer* (439, etc.).

521. 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 (493, etc.).

522. 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 (502, 503).

523. 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 (505, 506, 507), and from the close analogy which holds between these bodies and the hydracids of chlorine, iodine, bromine, etc., I consider these also as coming under subjection to the law, and assisting to prove its truth.

524. 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 (116, etc.), I 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. 28). 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 protochloride 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 (446), 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 in fig. 29.


Fig. 28.

525. Under these circumstances the chloride of tin was decomposed: the chlorine evolved at the positive electrode

formed bichloride of tin (514), 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 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 connection 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.

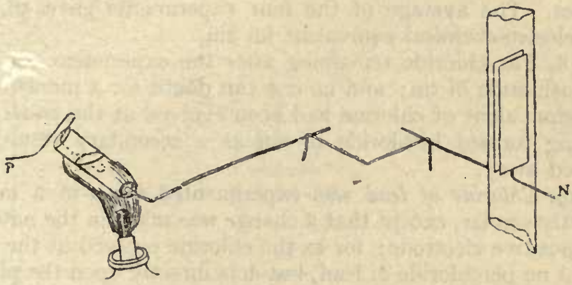

Fig. 29.

526. 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 equvialent 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 (451), etc.), that the numbers leave little doubt of the applicability of the *law of definite action* in this and all similar cases of electro-decomposition.

527. 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.

528. 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.

529. *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, it produces, if that metal be used, 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 would then 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, etc. The chlorine or iodine does not act upon it, but is evolved in the free state; and the plumbago has no re-action, 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.

530. 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 (451) 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 (549, etc.).

531. *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 (425, 428, etc.).

532. 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. 30), 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 in fig. 31.

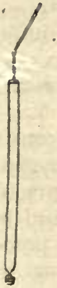

Fig. 30.

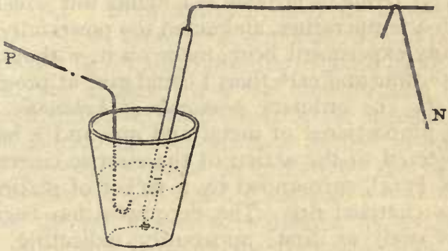

Fig. 31.

533. 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-oxidise 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.

534. In one experiment of this kind I used borate of lead (144, 408). 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 (144) 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.

535. *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.

536. 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 (524), 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 (414, 432), 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 (431, 428). 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 (432). It was a very natural secondary product at the positive electrode (514). 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.[1]

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[1] This paragraph is subject to the corrective note now appended to paragraph 431.—*December* 1838.

537. *Iodide of lead.*—This substance can be experimented with in tubes heated by a spirit-lamp (524); 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 per-compound; nor does crystallisation 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.*

538. This view of the result 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 (553).

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.

539. *Protiodide of tin.*—This substance, when fused (138), conducts and is decomposed by the electric current, tin is evolved at the *anode,* and periodide of tin as a secondary result (514, 525) at the *cathode.* The temperature required for its fusion is too high to allow of the production of any results fit for weighing.

540. *Iodide of potassium* was subjected to electrolytic action in a tube, like that in fig. 28 (524). 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 procuring such results. The iodide was decomposed with the evolution of iodine at the *anode*, and of potassium at the *cathode*, as in former cases.

541. 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.

542. 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 such matters, 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 with 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.

543. The experiment was made thus. Portions of the dilute sulphuric acid were put into three basins. Three volta-electrometer tubes, of the form figs. 20, 22, were filled with the same acid, and one inverted in each basin (442). 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 (446), and that with the negative end of the voltaic battery.

544. 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.*

545. 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 (499); and the results prove that the quantities so decomposed are *perfectly definite* and proportionate to the quantity of electricity which has passed.

546. 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 (130), 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.

547. Charcoal was used as the positive electrode in both sulphuric and muriactic acids (543, 545); 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.

548. Experiments of a similar kind were then made with

bodies altogether in a different state, *i.e.* with *fused* chlorides, iodides, etc. 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.

549. 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 chloride of lead, using a green-glass tube, formed as in fig. 32. A weighed platina wire was fused into the bottom of a small tube, as before described (524). 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 bending up the end of a platina wire into a knot, and fusing about twenty grains of metallic lead on to it, in a small closed tube of glass, which was afterwards

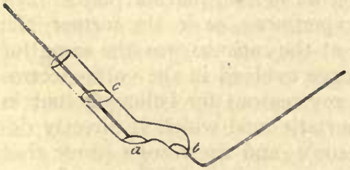

Fig. 32.

broken away. Being so furnished, the wire with its lead was weighed, and the weight recorded.

550. 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 connection with the proper conducting wire of a voltaic battery, was rendered positive. A volta-electrometer was included in the circuit.

551. 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.

552. In this experiment the positive electrode had lost just as much lead as the negative one had gained (530), and the loss and gain were very nearly the equivalents of the water decomposed in the volta-electrometer, giving for lead the number 101.5. It is therefore evident, in this instance, that causing *strong affinity*, or *no affinity*, for the substance evolved at the *anode*, to be active during the experiment (542), produces no variation in the definite action of the electric current.

553. A similar experiment was then made with iodide of lead, and in this manner all confusion from the formation of a periodide avoided (538). 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.

554. 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 (514, 525). 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.

555. 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 cloride or iodide used, which must be removed before the final weight is ascertained. This is more usually the case with lead than tin.

556. 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* (113, 518). 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* (241). 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 ultimately appear.

557. 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.

558. 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.[1] 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

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

one class and another to the other class; but probably on the proportions also (432). It is further remarkable, that with very few, if any, exceptions (150, 426), these decomposable bodies are exactly those governed by the remarkable law of conduction I have before described (130); 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* (400).

559. 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* (401); 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.

560. 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.

561. 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 part of these Researches (254, etc.).

562. ii. If one *ion* be combined in right proportions (432) with another strongly 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 (266, 278, 283).

563. 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 (478).

564. 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.

565. v. There is but one *electrolyte* composed of the same two elementary *ions;* at least such appears to be the fact (432), dependent upon a law, that *only single electro-chemical equivalents of elementary ions can go to the electrodes, and not multiples.*

566. vi. A body not decomposable when alone, as boracic acid, is not directly decomposable by the electric current when in combination (515). 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.

567. 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 (542, 548): but it seriously influences, by secondary action (479), 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.[1]

568. viii. A substance which, being used as the electrode, can combine 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 (479), the same consequence follows, will require more extended investigation to determine.

569. 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*.

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[1] 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 body suffering decomposition, will produce its own definite electrolytic action.

570. 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.

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

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

573. 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.

574. 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 (131), 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 (529), 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, etc., are *ions*, and that their *electro-chemical equivalents* are the same as their *ordinary chemical equivalents*.

575. 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 (478, 512) at one of the electrodes, be ascertained, the electro-chemical equivalent of that body may be deduced from the known con-

stant composition of the substance evolved. Thus, when fused protiodide of tin is decomposed by the voltaic current (539), 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 (540), it is an electrolyte; and the chemical equivalents will also be the electro-chemical equivalents.

576. 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.

577. In many instances, the *secondary results* obtained by the action of the evolved *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 accurately the number representing its electro-chemical equivalent.

578. Upon this principle it is that secondary results may occasionally be used as measurers of the volta-electric current (441, 475); 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 crystallise across the solution and touch the positive electrode, similar vitiated results are obtained. I expect to find in some salts, as the acetates of mercury and zinc, solutions favourable for this use.

579. 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 electrolytic 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.

580. 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 judgment, 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.

581. 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.

582. TABLE OF IONS.

Anions.

Oxygen	8	Selenic acid	64	Tartaric acid	66
Chlorine	35.5	Nitric acid	54	Citric acid	58
Iodine	126	Chloric acid	75.5	Oxalic acid	36
Bromine	78.3	Phosphoric acid	35.7	Sulphur (?)	16
Fluorine	18.7	Carbonic acid	22	Selenium (?)	
Cyanogen	26	Boracic acid	24	Sulpho-cyanogen	
Sulphuric acid	40	Acetic acid	51		

Cations.

Hydrogen	1	Cadmium	55.8	Soda	31.3
Potassium	39.2	Cerium	46	Lithia	18
Sodium	23.3	Cobalt	29.5	Baryta	76.7
Lithium	10	Nickel	29.5	Strontia	51.8
Barium	68.7	Antimony	64.6?	Lime	28.5
Strontium	43.8	Bismuth	71	Magnesia	20.7
Calcium	20.5	Mercury	200	Alumina	(?)
Magnesium	12.7	Silver	108	Protoxides generally.	
Manganese	27.7	Platina	98.6?	Quinia	171.6
Zinc	32.5	Gold	(?)	Cinchona	160
Tin	57.9			Morphia	290
Lead	103.5	Ammonia	17	Vegeto-alkalies generally.	
Iron	28	Potassa	47.2		
Copper	31.6				

583. 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.

584. 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, aluminium, 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.

585. 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 develop that which ought to replace it.

586. 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 expres-

sion, the equivalent number or atomic weight of oxygen is 8, of chlorine 36, of bromine 78.4, of lead 103.5, of tin 59, etc., notwithstanding that a very high authority doubles several of these numbers.

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

587. 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.

588. 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 $\frac{1}{104}$th of an inch in thickness,[1] red hot, in the air during the whole time; and if interrupted anywhere by charcoal points, will produce a very 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,[2] and to what I have said elsewhere on the relation of common and voltaic electricity (107, 111), 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 electrolysation, it has only separated the elements of *a single grain of water*.

589. 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 (149, 438), still the relation of the two functions is equally intimate and inseparable.

590. 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,

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[1] 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 all cases. This I have proved by the volta-electrometer. I found that whether half an inch or eight inches were retained at one constant temperature of dull redness, equal quantities of water were decomposed in equal times. 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.

[2] *Literary Gazette*, 1833, March 1 and 8. *Philosophical Magazine*, 1833, p. 204. *L'Institut*, 1833, p. 261.

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.

591. 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.[1]

592. 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.

593. Those bodies which, being interposed between the metals of the voltaic pile, render it active, *are all of them electrolytes* (212); 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 (138, 212). If, then, a voltaic trough have its extremities connected by a body capable of being decomposed, as water, we shall have a continuous current through the apparatus; and whilst it remains in this state we may look at the part where the acid is acting upon the plates, and that where the current is acting upon the water, as

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[1] 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 (212), 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.

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.

594. But the difference in the two parts of the connected battery, that is, the decomposition 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 (597, etc.).

595. Let us apply this in support of what I have surmised respecting the enormous electric power of each particle or atom of matter (591). I showed in a former part 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 (107). This quantity, though sufficient if passed at once through the head of a rat or 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.

596. 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 sus-

tain a platina wire $\frac{1}{104}$th of an inch in thickness, red hot, in contact with the air, for three minutes and three-quarters (588), 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 (595, 107). 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 (597); 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.

597. 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.

598. 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 zinc plate in its ordinary and simple state: but, as Mr. Sturgeon has shown,[1] 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 oxidised 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 or tow 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.[2]

599. 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 grains. They

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[1] *Recent Experimental Researches*, etc., 1830, p. 74, etc.

[2] 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.

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 (598), and a gas jar, also filled with the acid, inverted in it.[1] 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.

600. 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 oxidised and dissolved during the experiment.

601. 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 (526), 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 oxidised, 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 oxidised an equivalent of water must be decomposed.[2]

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[1] 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.

[2] The experiment was repeated several times with the same results.

602. But let us observe *how* the water is decomposed. It is electrolysed, *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 body under decomposition, 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 pass to the *cathode*, I need only refer to the results which I have given (542, 548) 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.

603. 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.*

604. 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 electrochemical 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.

605. I cannot refrain from recalling here the beautiful idea put forth, I believe, by Berzelius (438) 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.

606. 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, etc., 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, though much may yet 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.

607. The definite production of electricity (603) 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 (592), 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 whether it is an exciting cause of the current, or merely necessary to allow of the conduction of electricity, otherwise generated, from one metal to the other.

608. 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 (595) 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 (603, 596). Nor is it merely true that the quantity is active; it can be directed and made to perform its full equivalent duty (602, etc.). 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?

609. 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* (102, 103, 112, 113); 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.

December 31, 1833.

VI[1]

§ 8. ON THE ELECTRICITY OF THE VOLTAIC PILE; ITS SOURCE, QUANTITY, INTENSITY, AND GENERAL CHARACTERS. ¶ i. ON SIMPLE VOLTAIC CIRCLES. ¶ ii. ON THE INTENSITY NECESSARY FOR ELECTROLYSATION. ¶ iii. ON ASSOCIATED VOLTAIC CIRCLES, OR THE VOLTAIC BATTERY. ¶ iv. ON THE RESISTANCE OF AN ELECTROLYTE TO ELECTROLYTIC ACTION. ¶ v. GENERAL REMARKS ON THE ACTIVE VOLTAIC BATTERY

¶ i. *On simple Voltaic Circles*

610. THE great question of the source of electricity in the voltaic pile has engaged the attention of so many eminent philosophers, that a man of liberal mind and able to appreciate their powers would probably conclude, although he might not have studied the question, that the truth was somewhere revealed. But if in pursuance of this impression he were induced to enter upon the work of collating results and conclusions, he would find such contradictory evidence, such equilibrium of opinion, such variation and combination of theory, as would leave him in complete doubt respecting what he should accept as the true interpretation of nature: he would be forced to take upon himself the labour of repeating and examining the facts, and then use his own judgment on them in preference to that of others.

611. This state of the subject must, to those who have made up their minds on the matter, be my apology for entering upon its investigation. The views I have taken of the definite action of electricity in decomposing bodies (518), and the identity of the power so used with the power to be overcome (590), founded not on a mere opinion or general notion, but on facts which, being altogether new, were to my mind precise and conclusive, gave me, as I conceived, the power of examining the question with advantages not before possessed by any, and which might compensate, on my part, for the superior clearness and extent of intellect on theirs. Such are the considerations which have induced me to suppose I might help in deciding the question,

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[1] Eighth Series, original edition, vol. i. p. 259.

and be able to render assistance in that great service of removing *doubtful knowledge.* Such knowledge is the early morning light of every advancing science, and is essential to its development; but the man who is engaged in dispelling that which is deceptive in it, and revealing more clearly that which is true, is as useful in his place, and as necessary to the general progress of the science, as he who first broke through the intellectual darkness, and opened a path into knowledge before unknown to man.

612. The identity of the force constituting the voltaic current or electrolytic agent, with that which holds the elements of electrolytes together (590), or in other words with chemical affinity, seemed to indicate that the electricity of the pile itself was merely a mode of exertion, or exhibition, or existence of *true chemical action*, or rather of its cause; and I have consequently already said that I agree with those who believe that the *supply* of electricity is due to chemical powers (592).

613. But the great question of whether it is originally due to metallic contact or to chemical action, *i.e.* whether it is the first or the second which *originates* and determines the current, was to me still doubtful; and the beautiful and simple experiment with amalgamated zinc and platina, which I have described minutely as to its results (598, etc.), did not decide the point; for in that experiment the chemical action does not take place without the contact of the metals, and the metallic contact is inefficient without the chemical action. Hence either might be looked upon as the *determining* cause of the current.

614. I thought it essential to decide this question by the simplest possible forms of apparatus and experiment, that no fallacy might be inadvertently admitted. The well-known difficulty of effecting decomposition by a single pair of plates, except in the fluid exciting them into action (598), seemed to throw insurmountable obstruction in the way of such experiments; but I remembered the easy decomposability of the solution of iodide of potassium (52), and seeing no theoretical reason, if metallic contact was not *essential*, why true electro-decomposition should not be obtained without it, even in a single circuit, I persevered and succeeded.

615. A plate of zinc, about eight inches long and half an inch wide, was cleaned and bent in the middle to a right angle, fig. 33, *a*. A plate of platina, about three inches long and half an inch wide, was fastened to a platina wire, and the latter bent as in the figure, *b*. These two pieces of metal were arranged together as delineated, but as yet without the vessel *c*, and

its contents, which consisted of dilute sulphuric acid mingled with a little nitric acid. At *x* a piece of folded bibulous paper, moistened in a solution of iodide of potassium, was placed on the zinc, and was pressed upon by the end of the platina wire. When under these circumstances the plates were dipped into the acid of the vessel *c*, there was an immediate effect at *x*, the iodide being decomposed, and iodine appearing at the *anode* (399), *i.e.* against the end of the platina wire.

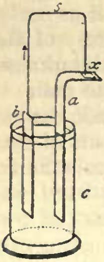

Fig. 33.

616. As long as the lower ends of the plates remained in the acid the electric current continued, and the decomposition proceeded at *x*. On removing the end of the wire from place to place on the paper, the effect was evidently very powerful; and on placing a piece of turmeric paper between the white paper and zinc, both papers being moistened with the solution of iodide of potassium, alkali was evolved at the *cathode* (399) against the zinc, in proportion to the evolution of iodine at the *anode*. Hence the decomposition was perfectly polar, and decidedly dependent upon a current of electricity passing from the zinc through the acid to the platina in the vessel *c*, and back from the platina through the solution to the zinc at the paper *x*.

617. That the decomposition at *x* was a true electrolytic action, due to a current determined by the state of things in the vessel *c*, and not dependent upon any mere direct chemical action of the zinc and platina on the iodide, or even upon any *current* which the solution of iodide might by its action on those metals tend to form at *x*, was shown, in the first place, by removing the vessel *c* and its acid from the plates, when all decomposition at *x* ceased, and in the next by connecting the metals, either in or out of the acid, together, when decomposition of the iodide at *x* occurred, but in a *reverse order;* for now alkali appeared against the end of the platina wire, and the iodine passed to the zinc, the current being the contrary of what it was in the former instance, and produced directly by the difference of action of the solution in the paper on the two metals. The iodine of course *combined* with the zinc.

618. When this experiment was made with pieces of zinc amalgamated over the whole surface (598), the results were obtained with equal facility and in the same direction, even when only dilute surphuric acid was contained in the vessel *c* (fig. 33). Whichsoever end of the zinc was immersed in the

acid, still the effects were the same: so that if, for a moment, the mercury might be supposed to supply the metallic contact, the inversion of the amalgamated piece destroys that objection. The use of *unamalgamated zinc* (615) removes all possibility of doubt.[1]

619. When in pursuance of other views (665), the vessel *c* was made to contain a solution of caustic potash in place of acid, still the same results occurred. Decomposition of the iodide was effected freely, though there was no metallic contact of dissimilar metals, and the current of electricity was in the *same direction* as when acid was used at the place of excitement.

620. Even a solution of common salt in the glass *c* could produce all these effects.

621. Having made a galvanometer with platina wires, and introduced it into the course of the current between the platina plate and the place of decomposition *x*, it was affected, giving indications of currents in the same direction as those shown to exist by the chemical action.

622. If we consider these results generally, they lead to very important conclusions. In the first place, they prove, in the most decisive manner, that *metallic contact is not necessary for the production of the voltaic current*. In the next place, they show a most extraordinary mutual relation of the chemical affinities of the fluid which *excites* the current, and the fluid which is *decomposed* by it.

623. For the purpose of simplifying the consideration, let us take the experiment with amalgamated zinc. The metal so prepared exhibits no effect until the current can pass: it at the same time introduces no new action, but merely removes an influence which is extraneous to those belonging either to the production or the effect of the electric current under investigation (736); an influence also which, when present, tends only to confuse the results.

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[1] The following is a more striking mode of making the above elementary experiment. Prepare a plate of zinc, ten or twelve inches long and two inches wide, and clean it thoroughly: provide also two discs of clean platina, about one inch and a half in diameter:—dip three or four folds of bibulous paper into a strong solution of iodide of potassium, place them on the clean zinc at one end of the plate, and put on them one of the platina discs: finally dip similar folds of paper or a piece of linen cloth into a mixture of equal parts nitric acid and water, and place it at the other end of the zinc plate with the second platina disc upon it. In this state of things no change at the solution of the iodide will be perceptible; but if the two discs be connected by a platina (or any other) wire for a second or two, and then that over the iodide be raised, it will be found that the *whole* of the surface beneath is deeply stained with *evolved iodine.—December* 1838.

624. Let two plates, one of amalgamated zinc and the other of platina, be placed parallel to each other (fig. 34), and introduce a drop of dilute sulphuric acid, *y*, between them at one end: there will be no sensible chemical action at that spot unless the two plates are connected somewhere else, as at P Z, by a body capable of conducting electricity. If that body be a metal or certain forms of carbon, then the current passes, and, as it circulates through the fluid at *y*, decomposition ensues.

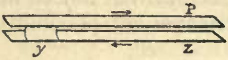

Fig. 34.

625. Then remove the acid from *y*, and introduce a drop of the solution of iodide of potassium at *x* (fig. 35). Exactly the same set of effects occur, except that when the metallic communication is made at P Z, the electric current is in the opposite direction to what it was before, as is indicated by the arrows, which show the courses of the currents (403).

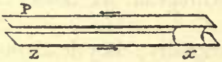

Fig. 35.

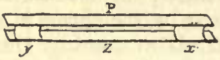

Fig. 36.

626. Now *both* the solutions used are conductors, but the conduction in them is essentially connected with decomposition (593) in a certain constant order, and therefore the appearance of the elements in certain places *shows* in what direction a current has passed when the solutions are thus employed. Moreover, we find that when they are used at opposite ends of the plates, as in the last two experiments (624, 625), metallic contact being allowed at the other extremities, the currents are in opposite directions. We have evidently, therefore, the power of opposing the actions of the two fluids simultaneously to each other at the opposite ends of the plates, using each one as a conductor for the discharge of the current of electricity, which the other tends to generate; in fact, substituting them for metallic contact, and combining both experiments into one (fig. 36). Under these circumstances, there is an opposition of forces: the fluid, which brings into play the stronger set of chemical affinities for the zinc (being the dilute acid), overcomes the force of the other, and determines the formation and direction of the electric current; not merely making that current pass through the weaker liquid, but actually reversing the tendency which the elements of the latter have in relation to the zinc and platina if not thus counteracted, and forcing them

in the contrary direction to that they are inclined to follow, that its own current may have free course. If the dominant action at *y* be removed by making metallic contact there, then the liquid at *x* resumes its power; or if the metals be not brought into contact at *y*, but the affinities of the solution there weakened, whilst those active at *x* are strengthened, then the latter gains the ascendency, and the decompositions are produced in a contrary order.

627. Before drawing a *final* conclusion from this mutual dependence and state of the chemical affinities of two distant portions of acting fluids (651), I will proceed to examine more minutely the various circumstances under which the reaction of the body suffering decomposition is rendered evident upon the action of the body, also undergoing decomposition, which produces the voltaic current.

628. The use of *metallic contact* in a single pair of plates, and the cause of its great superiority above contact made by other kinds of matter, become now very evident. When an amalgamated zinc plate is dipped into dilute sulphuric acid, the force of chemical affinity exerted between the metal and the fluid is not sufficiently powerful to cause sensible action at the surfaces of contact, and occasion the decomposition of water by the oxidation of the metal, although it *is* sufficient to produce such a condition of the electricity (or the power upon which chemical affinity depends) as would produce a current if there were a path open for it (651, 691); and that current would complete the conditions necessary, under the circumstances, for the decomposition of the water.

629. Now the presence of a piece of platina touching both the zinc and the fluid to be decomposed, opens the path required for the electricity. Its *direct communication* with the zinc is effectual, far beyond any communication made between it and that metal (*i.e.* between the platina and zinc), by means of decomposable conducting bodies, or, in other words, *electrolytes*, as in the experiment already described (626); because, when *they* are used, the chemical affinities between them and the zinc produce a contrary and opposing action to that which is influential in the dilute sulphuric acid; or if that action be but small, still the affinity of their component parts for each other has to be overcome, for they cannot conduct without suffering decomposition; and this decomposition is found *experimentally* to react back upon the forces which in the acid tend to produce the current (639, 645, etc.), and in numerous cases

entirely to neutralise them. Where direct contact of the zinc and platina occurs, these obstructing forces are not brought into action, and therefore the production and the circulation of the electric current and the concomitant action of decomposition are then highly favoured.

630. It is evident, however, that one of these opposing actions may be dismissed, and yet an electrolyte be used for the purpose of completing the circuit between the zinc and platina immersed separately into the dilute acid; for if, in fig. 33, the platina wire be retained in metallic contact with the zinc plate *a*, at *x*, and a division of the platina be made elsewhere, as at *s*, then the solution of iodide placed there, being in contact with the platina at both surfaces, exerts no chemical affinities for that metal; or if it does, they are equal on both sides. Its power, therefore, of forming a current in opposition to that dependent upon the action of the acid in the vessel *c*, is removed, and only its resistance to decomposition remains as the obstacle to be overcome by the affinities exerted in the dilute sulphuric acid.

631. This becomes the condition of a single pair of active plates where *metallic contact* is allowed. In such cases, only one set of opposing affinities are to be overcome by those which are dominant in the vessel *c*; whereas, when metallic contact is not allowed, two sets of opposing affinities must be conquered (629).

632. It has been considered a difficult, and by some an impossible thing, to decompose bodies by the current from a single pair of plates, even when it was so powerful as to heat bars of metal red hot, as in the case of Hare's calorimeter, arranged as a single voltaic circuit, or of Wollaston's powerful single pair of metals. This difficulty has arisen altogether from the antagonism of the chemical affinity engaged in producing the current with the chemical affinity to be overcome, and depends entirely upon their relative intensity; for when the sum of forces in one has a certain degree of superiority over the sum of forces in the other, the former gain the ascendency, determine the current, and overcome the latter so as to make the substance exerting them yield up its elements in perfect accordance, both as to direction and quantity, with the course of those which are exerting the most intense and dominant action.

633. Water has generally been the substance, the decomposition of which has been sought for as a chemical test of the passage of an electric current. But I now began to perceive a reason for its failure, and for a fact which I had observed long

before (51, 52) with regard to the iodide of potassium, namely, that bodies would differ in facility of decomposition by a given electric current, according to the condition and intensity of their ordinary chemical affinities. This reason appeared in their *reaction upon the affinities* tending to cause the current; and it appeared probable that many substances might be found which could be decomposed by the current of a single pair of zinc and platina plates immersed in dilute sulphuric acid, although water resisted its action. I soon found this to be the case, and as the experiments offer new and beautiful proofs of the direct relation and opposition of the chemical affinities concerned in producing and in resisting the stream of electricity, I shall briefly describe them.

634. The arrangement of the apparatus was as in fig. 37. The vessel *v* contained dilute sulphuric acid; Z and P are the zinc and platina plates; *a*, *b*, and *c* are platina wires; the decompositions were effected at *x*, and occasionally, indeed generally, a galvanometer was introduced into the circuit at *g*: its place only is here given, the circle at *g* having no reference to the size of the instrument. Various arrangements were made at *x*, according to the kind of decomposition to be effected. If a drop of liquid was to be acted upon, the two ends were merely dipped into it; if a solution contained in the pores of paper was to be decomposed, one of the extremities was connected with a platina plate supporting the paper, whilst the other extremity rested on the paper, *e*, fig. 44: or sometimes, as with sulphate of soda, a plate of platina sustained two portions of paper, one of the ends of the wires resting upon each piece, *c*, fig. 46. The darts represent the direction of the electric current (403).

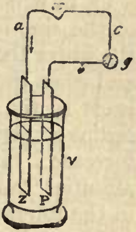

Fig. 37.

635. Solution of *iodide of potassium*, in moistened paper, being placed at the interruption of the circuit at *x*, was readily decomposed. Iodine was evolved at the *anode*, and alkali at the *cathode*, of the decomposing body.

636. *Protochloride of tin*, when fused and placed at *x*, was also readily decomposed, yielding perchloride of tin at the *anode* (514), and tin at the *cathode*.

637. Fused chloride of silver, placed at *x*, was also easily decomposed; chlorine was evolved at the *anode*, and brilliant metallic silver, either in films upon the surface of the liquid, or in crystals beneath, evolved at the *cathode*.

638. Water acidulated with sulphuric acid, solution of muriatic acid, solution of sulphate of soda, fused nitre, and the fused chloride and iodide of lead were not decomposed by this single pair of plates, excited only by dilute sulphuric acid.

639. These experiments give abundant proofs that a single pair of plates can electrolyse bodies and separate their elements. They also show in a beautiful manner the direct relation and opposition of the chemical affinities concerned at the two points of action. In those cases where the sum of the opposing affinities at *x* was sufficiently beneath the sum of the acting affinities in *v*, decomposition took place; but in those cases where they rose higher, decomposition was effectually resisted and the current ceased to pass (626).

640. It is, however, evident that the sum of acting affinities in *v* may be increased by using other fluids than dilute sulphuric acid, in which latter case, as I believe, it is merely the affinity of the zinc for the oxygen already combined with hydrogen in the water that is exerted in producing the electric current (654): and when the affinities are so increased, the view I am supporting leads to the conclusion that bodies which resisted in the preceding experiments would then be decomposed, because of the increased difference between their affinities and the acting affinities thus exalted. This expectation was fully confirmed in the following manner.

641. A little nitric acid was added to the liquid in the vessel *v*, so as to make a mixture which I shall call diluted nitro-sulphuric acid. On repeating the experiments with this mixture, all the substances before decomposed again gave way, and much more readily. But, besides that, many which before resisted electrolysation now yielded up their elements. Thus, solution of sulphate of soda, acted upon in the interstices of litmus and turmeric paper, yielded acid at the *anode* and alkali at the *cathode;* solution of muriatic acid tinged by indigo yielded chlorine at the *anode* and hydrogen at the *cathode;* solution of nitrate of silver yielded silver at the *cathode*. Again, fused nitre and the fused iodide and chloride of lead were decomposable by the current of this single pair of plates, though they were not by the former (638).

642. A solution of acetate of lead was apparently not decomposed by this pair, nor did water acidulated by sulphuric acid seem at first to give way (708).

643. The increase of intensity or power of the current produced by a simple voltaic circle, with the increase of the force of the

chemical action at the exciting place, is here sufficiently evident. But in order to place it in a clearer point of view, and to show that the decomposing effect was not at all dependent, in the latter cases, upon the mere capability of evolving *more* electricity, experiments were made in which the quantity evolved could be increased without variation in the intensity of the exciting cause. Thus the experiments in which dilute sulphuric acid was used (634) were repeated, using large plates of zinc and platina in the acid; but still those bodies which resisted decomposition before, resisted it also under these new circumstances. Then again, where nitro-sulphuric acid was used (641), mere wires of platina and zinc were immersed in the exciting acid; yet, notwithstanding this change, those bodies were now decomposed which resisted any current tending to be formed by the dilute sulphuric acid. For instance, muriatic acid could not be decomposed by a single pair of plates when immersed in dilute sulphuric acid; nor did making the solution of sulphuric acid strong, nor enlarging the size of the zinc and platina plates immersed in it, increase the power; but if to a weak sulphuric acid a very little nitric acid was added, then the electricity evolved had power to decompose the muriatic acid, evolving chlorine at the *anode* and hydrogen at the *cathode,* even when mere wires of metals were used. This mode of increasing the intensity of the electric current, as it excludes the effect dependent upon many pairs of plates, or even the effect of making any one acid stronger or weaker, is at once referable to the condition and force of the chemical affinities which are brought into action, and may, both in principle and practice, be considered as perfectly distinct from any other mode.

644. The direct reference which is thus experimentally made in the simple voltaic circle of the *intensity* of the electric current to the *intensity* of the chemical action going on at the place where the existence and direction of the current is determined, leads to the conclusion that by using selected bodies, as fused chlorides, salts, solutions of acids, etc., which may act upon the metals employed with different degrees of chemical force; and using also metals in association with platina, or with each other, which shall differ in the degree of chemical action exerted between them and the exciting fluid of electrolyte, we shall be able to obtain a series of comparatively constant effects due to electric currents of different intensities, which will serve to assist in the construction of a scale competent to supply the

means of determining relative degrees of intensity with accuracy in future researches.

645. I have already expressed the view which I take of the decomposition in the experimental place, as being the direct consequence of the superior exertion at some other spot of the same kind of power as that to be overcome, and therefore as the result of an antagonism of forces of the *same* nature (626, 639). Those at the place of decomposition have a re-action upon, and a power over, the exerting or determining set proportionate to what is needful to overcome their own power; and hence a curious result of *resistance* offered by decompositions to the original determining force, and consequently to the current. This is well shown in the cases where such bodies as chloride of lead, iodide of lead, and water would not decompose with the current produced by a single pair of zinc and platina plates in sulphuric acid (638), although they would with a current of higher intensity produced by stronger chemical powers. In such cases no sensible portion of the current passes (702); the action is stopped; and I am now of opinion that in the case of the law of conduction which I described in the second part of these Researches (149), the bodies which are electrolytes in the fluid state cease to be such in the solid form, because the attractions of the particles by which they are retained in combination and in their relative position, are then too powerful for the electric current. The particles retain their places; and as decomposition is prevented, the transmission of the electricity is prevented also; and although a battery of many plates may be used, yet if it be of that perfect kind which allows of no extraneous or indirect action (736), the whole of the affinities concerned in the activity of that battery are at the same time also suspended and counteracted.

646. But referring to the *resistance* of each single case of decomposition, it would appear that as these differ in force according to the affinities by which the elements in the substance tend to retain their places, they also would supply cases constituting a series of degrees by which to measure the initial intensities of simple voltaic or other currents of electricity, and which, combined with the scale of intensities determined by different degrees of *acting force* (644), would probably include a sufficient set of differences to meet almost every important case where a reference to intensity would be required.

647. According to the experiments I have already had occasion to make, I find that the following bodies are electrolytic

in the order in which I have placed them, those which are first being decomposed by the current of lowest intensity. These currents were always from a single pair of plates, and may be considered as elementary *voltaic forces*.

Iodide of potassium (solution).
Chloride of silver (fused).
Protochloride of tin (fused).
Chloride of lead (fused).
Iodide of lead (fused).
Muriatic acid (solution).
Water, acidulated with sulphuric acid.

648. It is essential that, in all endeavours to obtain the relative electrolytic intensity necessary for the decomposition of different bodies, attention should be paid to the nature of the electrodes and the other bodies present which may favour secondary actions (721). If in electro-decomposition one of the elements separated has an affinity for the electrode, or for bodies present in the surrounding fluid, then the affinity resisting decomposition is in part balanced by such power, and the true place of the electrolyte in a table of the above kind is not obtained: thus, chlorine combines with a positive platina electrode freely, but iodine scarcely at all, and therefore I believe it is that the fused chlorides stand first in the preceding table. Again, if in the decomposition of water not merely sulphuric but also a little nitric acid be present, then the water is more freely decomposed, for the hydrogen at the *cathode* is not ultimately expelled, but finds oxygen in the nitric acid, with which it can combine to produce a secondary result; the affinities opposing decomposition are in this way diminished, and the elements of the water can then be separated by a current of lower intensity.

649. Advantage may be taken of this principle to interpolate more minute degrees into the scale of initial intensities already referred to (644, 646) than is there spoken of; for by combining the force of a current *constant* in its intensity, with the use of electrodes consisting of matter, having more or less affinity for the elements evolved from the decomposing electrolyte, various intermediate degrees may be obtained.

650. Returning to the consideration of the source of electricity (613, etc.), there is another proof of the most perfect kind that metallic contact has nothing to do with the *production* of electricity in the voltaic circuit, and further, that electricity

is only another mode of the exertion of chemical forces. It is, the production of the *electric spark* before any contact of metals is made, and by the exertion of *pure and unmixed chemical forces*. The experiment, which will be described further on (691), consists in obtaining the spark upon making contact between a plate of zinc and a plate of copper plunged into dilute sulphuric acid. In order to make the arrangement as elementary as possible, mercurial surfaces were dismissed, and the contact made by a copper wire connected with the copper plate, and then brought to touch a clean part of the zinc plate. The electric spark appeared, and it must of necessity have existed and passed *before the zinc and the copper were in contact.*

651. In order to render more distinct the principles which I have been endeavouring to establish, I will restate them in their simplest form, according to my present belief. The electricity of the voltaic pile (591, *note*) is not dependent either in its origin or its continuance upon the contact of the metals with each other (615, 650). It is entirely due to chemical action (617), and is proportionate in its intensity to the intensity of the affinities concerned in its production (643); and in its quantity to the quantity of matter which has been chemically active during its evolution (604). This definite production is again one of the strongest proofs that the electricity is of chemical origin.

652. As *volta-electro-generation* is a case of mere chemical action, so *volta-electro-decomposition* is simply a case of the preponderance of one set of chemical affinities more powerful in their nature, over another set which are less powerful: and if the instance of two opposing sets of such forces (626) be considered, and their mutual relation and dependence borne in mind, there appears no necessity for using, in respect to such cases, any other term than chemical affinity (though that of electricity may be very convenient) or supposing any new agent to be concerned in producing the results; for we may consider that the powers at the two places of action are in direct communion and balanced against each other through the medium of the metals (626), fig. 36, in a manner analogous to that in which mechanical forces are balanced against each other by the intervention of the lever (767).

653. All the facts show us that that power commonly called chemical affinity, can be communicated to a distance through the metals and certain forms of carbon; that the electric cur-

rent is only another form of the forces of chemical affinity; that its power is in proportion to the chemical affinities producing it; that when it is deficient in force it may be helped by calling in chemical aid, the want in the former being made up by an equivalent of the latter; that, in other words, *the forces termed chemical affinity and electricity are one and the same.*

654. When the circumstances connected with the production of electricity in the ordinary voltaic circuit are examined and compared, it appears that the source of that agent, always meaning the electricity which circulates and completes the current in the voltaic apparatus, and gives that apparatus power and character (682, 732), exists in the chemical action which takes place directly between the metal and the body with which it combines, and not at all in the subsequent action of the substance so produced with the acid present.[1] Thus, when zinc, platina, and dilute sulphuric acid are used, it is the union of the zinc with the oxygen of the water which determines the current; and though the acid is essential to the removal of the oxide so formed, in order that another portion of zinc may act on another portion of water, it does not, by combination with that oxide, produce any sensible portion of the current of electricity which circulates; for the quantity of electricity is dependent upon the quantity of zinc oxidised, and in definite proportion to it: its intensity is in proportion to the intensity of the chemical affinity of the zinc for the oxygen under the circumstances, and is scarcely, if at all, affected by the use of either strong or weak acid (643).

655. Again, if zinc, platina, and muriatic acid are used, the electricity appears to be dependent upon the affinity of the zinc for the chlorine, and to be circulated in exact proportion to the number of particles of zinc and chlorine which unite, being in fact an equivalent to them.

656. But in considering this oxidation, or other direct action upon the METAL itself, as the cause and source of the electric current, it is of the utmost importance to observe that the oxygen or other body must be in a peculiar condition, namely, in the state of *combination;* and not only so, but limited still further to such a state of combination and in such proportions as will constitute an *electrolyte* (558). A pair of zinc and platina plates cannot be so arranged in oxygen gas as to produce a current of electricity, or act as a voltaic circle, even though the

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[1] Wollaston, *Philosophical Transactions*, 1801, p. 427.

temperature may be raised so high as to cause oxidation of the zinc far more rapidly than if the pair of plates were plunged into dilute sulphuric acid; for the oxygen is not part of an electrolyte, and cannot therefore conduct the forces onwards by decomposition, or even as metals do by itself. Or if its gaseous state embarrass the minds of some, then liquid chlorine may be taken. It does not excite a current of electricity through the two plates by combining with the zinc, for its particles cannot transfer the electricity active at the point of combination across to the platina. It is not a conductor of itself, like the metals; nor is it an electrolyte, so as to be capable of conduction during decomposition, and hence there is simple chemical action at the spot, and no electric current.[1]

657. It might at first be supposed that a conducting body, not electrolytic, might answer as the third substance between the zinc and the platina; and it is true that we have some such capable of exerting chemical action upon the metals. They must, however, be chosen from the metals themselves, for there are no bodies of this kind except those substances and charcoal. To decide the matter by experiment, I made the following arrangement. Melted tin was put into a glass tube bent into the form of the letter V, fig. ,38 so as to fill the half of each limb, and two pieces of thick platina wire, *p*, *w*, inserted, so as to have their ends immersed some depth in the tin: the whole was then allowed to cool, and the ends *p* and *w* connected with a delicate galvanometer. The part of the tube at *x* was now reheated, whilst the portion *y* was retained cool. The galvanometer was immediately influenced by the thermo-electric current produced. The heat was steadily increased at *x*, until at last the tin and platina combined there; an effect which is known to take place with strong chemical action and high ignition; but not the slightest additional effect occurred at the galvanometer. No other deflection than that due to the thermo-electric current

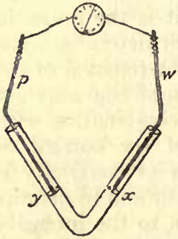

Fig. 38.

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[1] I do not mean to affirm that no traces of electricity ever appear in such cases. What I mean is, that no electricity is evolved in any way, due or related to the causes which excite voltaic electricity, or proportionate to them. That which does appear occasionally is the smallest possible fraction of that which the acting matter could produce if arranged so as to act voltaically, probably not the one-hundred-thousandth, or even the millionth part, and is very probably altogether different in its source.

was observable the whole time. Hence, though a conductor, and one capable of exerting chemical action on the tin, was used, yet, not being an *electrolyte*, not the slightest effect of an electrical current could be observed (682).

658. From this it seems apparent that the peculiar character and condition of an electrolyte is *essential* in one part of the voltaic circuit; and its nature being considered, good reasons appear why it and it alone should be effectual. An electrolyte is always a compound body: it can conduct, but only whilst decomposing. Its conduction depends upon its decomposition and the *transmission of its particles* in directions parallel to the current; and so intimate is this connection, that if their transition be stopped, the current is stopped also; if their course be changed, its course and direction changes with them; if they proceed in one direction, it has no power to proceed in any other than a direction invariably dependent on them. The particles of an electrolytic body are all so mutually connected, are in such relation with each other through their whole extent in the direction of the current, that if the last is not disposed of, the first is not at liberty to take up its place in the new combination which the powerful affinity of the most active metal tends to produce; and then the current itself is stopped; for the dependencies of the current and the decomposition are so mutual, that whichsoever be originally determined, *i.e.* the motion of the particles or the motion of the current, the other is invariable in its concomitant production and its relation to it.

659. Consider, then, water as an electrolyte and also as an oxidising body. The attraction of the zinc for the oxygen is greater, under the circumstances, than that of the oxygen for the hydrogen; but in combining with it, it tends to throw into circulation a current of electricity in a certain direction. This direction is consistent (as is found by innumerable experiments) with the transfer of the hydrogen from the zinc towards the platina, and the transfer in the opposite direction of fresh oxygen from the platina towards the zinc; so that the current *can pass* in that one line, and, whilst it passes, can consist with and favour the renewal of the conditions upon the surface of the zinc, which at first determined both the combination and circulation. Hence the continuance of the action there, and the continuation of the current. It therefore appears quite as essential that there should be an electrolyte in the circuit, in order that the action may be transferred forward, in a *certain constant direction,* as that there should be an oxidising or other

body capable of acting directly on the metal; and it also appears to be essential that these two should merge into one, or that the principle directly active on the metal by chemical action should be one of the *ions* of the electrolyte used. Whether the voltaic arrangement be excited by solution of acids, or alkalies, or sulphurets, or by fused substances (212), this principle has always hitherto, as far as I am aware, been an *anion* (678); and I anticipate, from a consideration of the principles of electric action, that it must of necessity be one of that class of bodies.

660. If the action of the sulphuric acid used in the voltaic circuit be considered, it will be found incompetent to produce any sensible portion of the electricity of the current by its combination with the oxide formed, for this simple reason, it is deficient in a most essential condition: it forms no part of an electrolyte, nor is it in relation with any other body present in the solution which will permit of the mutual transfer of the particles and the consequent transfer of the electricity. It is true, that as the plane at which the acid is dissolving the oxide of zinc formed by the action of the water is in contact with the metal zinc, there seems no difficulty in considering how the oxide there could communicate an electrical state, proportionate to its own chemical action on the acid, to the metal, which is a conductor without decomposition. But on the side of the acid there is no substance to complete the circuit: the water, as water, cannot conduct it, or at least only so small a proportion that it is merely an incidental and almost inappreciable effect (705); and it cannot conduct it as an electrolyte, because an electrolyte conducts in consequence of the *mutual* relation and action of its particles; and neither of the elements of the water, nor even the water itself, as far as we can perceive, are *ions* with respect to the sulphuric acid (583).[1]

661. This view of the secondary character of the sulphuric acid as an agent in the production of the voltaic current, is further confirmed by the fact, that the current generated and transmitted is directly and exactly proportional to the quantity of water decomposed and the quantity of zinc oxidised (603, 727), and is the same as that required to decompose the same quantity of water. As, therefore, the decomposition of the water shows that the electricity has passed by its means, there

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[1] It will be seen that I here agree with Sir Humphry Davy, who has experimentally supported the opinion that acids and alkalies in combining do not produce any current of electricity.—*Philosophical Transactions*, 1826, p. 398.

remains no other electricity to be accounted for or to be referred to any action other than that of the zinc and the water on each other.

662. The general case (for it includes the former one (659)) of acids and bases may theoretically be stated in the following manner. Let *a*, fig. 39, be supposed to be a dry oxacid, and *b* a dry base, in contact at *c*, and in electric communication at their extremities by plates of platina *p p*, and a platina wire *w*. If this acid and base were fluid, and combination took place at *c*, with an affinity ever so vigorous, and capable of originating an electric current, the current could not circulate in any important degree; because, according to the experimental results, neither *a* nor *b* could conduct without being decomposed, for they are either electrolytes or else insulators, under all circumstances, except to very feeble and unimportant currents (705, 721). Now the affinities at *c* are not such as tend to cause the *elements* either of *a* or *b* to separate, but only such as would make the two bodies combine together as a whole; the point of action is, therefore, insulated, the action itself local (656, 682), and no current can be formed.

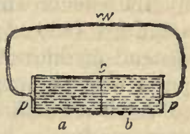

Fig. 39.

663. If the acid and base be dissolved in water, then it is possible that a small portion of the electricity due to chemical action may be conducted by the water without decomposition (701, 719); but the quantity will be so small as to be utterly disproportionate to that due to the equivalents of chemical force; will be merely incidental; and, as it does not involve the essential principles of the voltaic pile, it forms no part of the phenomena at present under investigation.[1]

664. If for the oxacid a hydracid be substituted (662)—as one analogous to the muriatic, for instance—then the state of things changes altogether, and a current due to the chemical action of the acid on the base is possible. But now both the bodies act as electrolytes, for it is only one principle of each which combine mutually—as, for instance, the chlorine with the metal—and the hydrogen of the acid and the oxygen of the base are ready to traverse with the chlorine of the acid and the metal

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[1] It will I trust be fully understood that in these investigations I am not professing to take an account of every small, incidental, or barely possible effect, dependent upon slight disturbances of the electric fluid during chemical action, but am seeking to distinguish and identify those actions on which the power of the voltaic battery essentially depends.

of the base in conformity with the current and according to the general principles already so fully laid down.

665. This view of the oxidation of the metal, or other *direct* chemical action upon it, being the sole cause of the production of the electric current in the ordinary voltaic pile, is supported by the effects which take place when alkaline or sulphuretted solutions (666, 678) are used for the electrolytic conductor instead of dilute sulphuric acid. It was in elucidation of this point that the experiments without metallic contact, and with solution of alkali as the exciting fluid, already referred to (619), were made.

666. Advantage was then taken of the more favourable condition offered, when metallic contact is allowed (630), and the experiments upon the decomposition of bodies by a single pair of plates (634) were repeated, solution of caustic potassa being employed in the vessel *v*, fig. 37, in place of dilute sulphuric acid. All the effects occurred as before: the galvanometer was deflected; the decompositions of the solutions of iodide of potassium, nitrate of silver, muriatic acid, and sulphate of soda ensued at *x*; and the places where the evolved principles appeared, as well as the deflection of the galvanometer, indicated a current in the *same direction* as when acid was in the vessel *v*; *i.e.* from the zinc through the solution to the platina, and back by the galvanometer and substance suffering decomposition to the zinc.

667. The similarity in the action of either dilute sulphuric acid or potassa goes indeed far beyond this, even to the proof of identity in *quantity* as well as in *direction* of the electricity produced. If a plate of amalgamated zinc be put into a solution of potassa, it is not sensibly acted upon; but if touched in the solution by a plate of platina, hydrogen is evolved on the surface of the latter metal, and the zinc is oxidised exactly as when immersed in dilute sulphuric acid (598). I accordingly repeated the experiment before described with weighed plates of zinc (599, etc.), using however solution of potassa instead of dilute sulphuric acid. Although the time required was much longer than when acid was used, amounting to three hours for the oxidisement of 7.55 grains of zinc, still I found that the hydrogen evolved at the platina plate was the equivalent of the metal oxidised at the surface of the zinc. Hence the whole of the reasoning which was applicable in the former instance applies also here, the current being in the same direction, and

its decomposing effect in the same degree, as if acid instead of alkali had been used (603).

668. The proof, therefore, appears to me complete, that the combination of the acid with the oxide, in the former experiment, had nothing to do with the production of the electric current; for the same current is here produced when the action of the acid is absent, and the reverse action of an alkali is present. I think it cannot be supposed for a moment that the alkali acted chemically as an acid to the oxide formed; on the contrary, our general chemical knowledge leads to the conclusion that the ordinary metallic oxides act rather as acids to the alkalies; yet that kind of action would tend to give a reverse current in the present case, if any were due to the union of the oxide of the exciting metal with the body which combines with it. But instead of any variation of this sort, the direction of the electricity was constant, and its quantity also directly proportional to the water decomposed, or the zinc oxidised. There are reasons for believing that acids and alkalies, when in contact with metals upon which they cannot act directly, still have a power of influencing their attractions for oxygen (676); but all the effects in these experiments prove, I think, that it is the oxidation of the metal necessarily dependent upon, and associated as it is with, the electrolysation of the water (656, 658) that produces the current; and that the acid or alkali merely act as solvents, and by removing the oxidised zinc, allow other portions to decompose fresh water, and so continue the evolution or determination of the current.

669. The experiments were then varied by using solution of ammonia instead of solution of potassa; and as it, when pure, is like water, a bad conductor (290), it was occasionally improved in that power by adding sulphate of ammonia to it. But in all the cases the results were the same as before; decompositions of the same kind were effected, and the electric current producing these was in the same direction as in the experiments just described.

670. In order to put the equal and similar action of acid and alkali to stronger proof, arrangements were made as in fig. 40; the glass vessel A contained dilute sulphuric acid, the corresponding glass vessel B solution of potassa, P P was a plate of platina dipping into both solutions, and Z Z two plates of amalgamated zinc connected with a delicate galvanometer. When these were plunged at the same time into the two vessels, there was generally a first feeble effect, and that in favour of

the alkali, *i.e.* the electric current tended to pass through the vessels in the direction of the arrow, being the reverse direction of that which the acid in A would have produced alone: but the effect instantly ceased, and the action of the plates in the vessels was so equal, that, being contrary because of the contrary position of the plates, no permanent current resulted.

671. Occasionally a zinc plate was substituted for the plate P P, and platina plates for the plates Z Z; but this caused no difference in the results: nor did a further change of the middle plate to copper produce any alteration.

672. As the opposition of electro-motive pairs of plates produces results other than those due to the mere difference of their independent actions (747, 781), I devised another form of apparatus, in which the action of acid and alkali might be more directly compared. A cylindrical glass cup, about two inches deep within, an inch in internal diameter, and at least a quarter of an inch in thickness, was cut down the middle into halves, fig. 41. A broad brass ring, larger in diameter than the cup, was supplied with a screw at one side; so that when the two halves of the cup were within the ring, and the screw was made to press tightly against the glass, the cup held any fluid put into it. Bibulous paper of different degrees of permeability was then cut into pieces of such a size as to be easily introduced between the loosened halves of the cup, and served when the latter were tightened again to form a porous division down the middle of the cup, sufficient to keep any two fluids on opposite sides of the paper from mingling, except very slowly, and yet allowing them to act freely as one *electrolyte*. The two spaces thus produced I will call the cells A and B, fig. 42. This instrument I have found of most general application in the investigation of the relation of fluids and metals amongst themselves and to each other. By combining its use

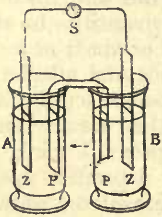

Fig. 40.

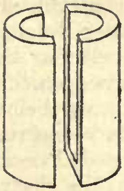

Fig. 41.

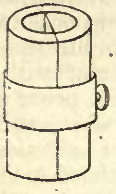

Fig. 42.

with that of the galvanometer, it is easy to ascertain the relation of one metal with two fluids, or of two metals with one fluid, or of two metals and two fluids upon each other.

673. Dilute sulphuric acid, sp. gr. 1.25, was put into the cell A, and a strong solution of caustic potassa into the cell B; they mingled slowly through the paper, and at last a thick crust of sulphate of potassa formed on the side of the paper next to the alkali. A plate of clean platina was put into each cell and connected with a delicate galvanometer, but no electric current could be observed. Hence the *contact* of acid with one platina plate, and alkali with the other, was unable to produce a current; nor was the combination of the acid with the alkali. more effectual (660).

674. When one of the platina plates was removed and a zinc plate substituted, either amalgamated or not, a strong electric current was produced. But, whether the zinc were in the acid whilst the platina was in the alkali, or whether the reverse order were chosen, the electric current was always from the zinc through the electrolyte to the platina, and back through the galvanometer to the zinc, the current seeming to be strongest when the zinc was in the alkali and the platina in the acid.

675. In these experiments, therefore, the acid seems to have no power over the alkali, but to be rather inferior to it in force. Hence there is no reason to suppose that the combination of the oxide formed with the acid around it has any direct influence in producing the electricity evolved, the whole of which appears to be due to the oxidation of the metal (654).

676. The alkali, in fact, is superior to the acid in bringing a metal into what is called the positive state; for if plates of the same metal, as zinc, tin, lead, or copper, be used both in the acid or alkali, the electric current is from the alkali across the cell to the acid, and back through the galvanometer to the alkali, as Sir Humphry Davy formerly stated.[1] This current is so powerful, that if amalgamated zinc, or tin, or lead be used, the metal in the acid evolves hydrogen the moment it is placed in communication with that in the alkali, not from any direct action of the acid upon it, for if the contact be broken the action ceases, but because it is powerfully negative with regard to the metal in the alkali.

677. The superiority of alkali is further proved by this, that if zinc and tin be used, or tin and lead, whichsoever metal is

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[1] *Elements of Chemical Philosophy*, p. 149: or *Philosophical Transactions*, 1826, p. 403.

put into the alkali becomes positive, that in the acid being negative. Whichsoever is in the alkali is oxidised, whilst that in the acid remains in the metallic state, as far as the electric current is concerned.

678. When sulphuretted solutions are used (665) in illustration of the assertion that it is the chemical action of the metal and one of the *ions* of the associated electrolyte that produces all the electricity of the voltaic circuit, the proofs are still the same. Thus, as Sir Humphry Davy[1] has shown, if iron and copper be plunged into dilute acid, the current is from the iron through the liquid to the copper; in solution of potassa it is in the same direction, but in solution of sulphuret of potassa it is reversed. In the two first cases it is oxygen which combines with the iron, in the latter sulphur which combines with the copper, that produces the electric current; but both of these are *ions*, existing as such in the electrolyte, which is at the same moment suffering decomposition; and, what is more, both of these are *anions*, for they leave the electrolytes at their *anodes*, and act just as chlorine, iodine, or any other *anion* would act which might have been previously chosen as that which should be used to throw the voltaic circle into activity.

679. The following experiments complete the series of proofs of the origin of the electricity in the voltaic pile. A fluid amalgam of potassium, containing not more than a hundredth of that metal, was put into pure water, and connected through the galvanometer with a plate of platina in the same water. There was immediately an electric current from the amalgam through the electrolyte to the platina. This must have been due to the oxidation only of the metal, for there was neither acid nor alkali to combine with, or in any way act on, the body produced.

680. Again, a plate of clean lead and a plate of platina were put into *pure* water. There was immediately a powerful current produced from the lead through the fluid to the platina: it was even intense enough to decompose solution of the iodide of potassium when introduced into the circuit in the form of apparatus already described (615), fig. 33. Here no action of acid or alkali on the oxide formed from the lead could supply the electricity: it was due solely to the oxidation of the metal.

681. There is no point in electrical science which seems to

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[1] *Elements of Chemical Philosophy*, p. 148.

me of more importance than the state of the metals and the electrolytic conductor in a simple voltaic circuit *before and at* the moment when metallic contact is first completed. If clearly understood, I feel no doubt it would supply us with a direct key to the laws under which the great variety of voltaic excitements, direct and incidental, occur, and open out new fields of research for our investigation.

682. We seem to have the power of deciding to a certain extent in numerous cases of chemical affinity (as of zinc with the oxygen of water, etc., etc.) which of *two modes of action of the attractive power* shall be exerted (732). In the one mode we can transfer the power onwards, and make it produce elsewhere its equivalent of action (602, 652); in the other, it is not transferred, but exerted wholly at the spot. The first is the case of volta-electric excitation, the other ordinary chemical affinity: but both are chemical actions and due to one force or principle.

683. The general circumstances of the former mode occur in all instances of voltaic currents, but may be considered as in their perfect condition, and then free from those of the second mode, in some only of the cases; as in those of plates of zinc and platina in solution of potassa, or of amalgamated zinc and platina in dilute sulphuric acid.

684. Assuming it sufficiently proved, by the preceding experiments and considerations, that the electro-motive action depends, when zinc, platina, and dilute sulphuric acid are used, upon the mutual affinity of the metal zinc and the oxygen of the water (656, 659), it would appear that the metal, when alone, has not power enough, under the circumstances, to take the oxygen and expel the hydrogen from the water; for, in fact, no such action takes place. But it would also appear that it has power so far to act, by its attraction for the oxygen of the particles in contact with it, as to place the similar forces already active between these and the other particles of oxygen and the particles of hydrogen in the water, in a peculiar state of tension or polarity, and probably also at the same time to throw those of its own particles which are in contact with the water into a similar but opposed state. Whilst this state is retained, no further change occurs; but when it is relieved, by completion of the circuit, in which case the forces determined in opposite directions, with respect to the zinc and the electrolyte, are found exactly competent to neutralise each other, then a series of decompositions and recompositions takes place amongst the particles of oxygen and hydrogen constituting the water,

between the place of contact with the platina and the place where the zinc is active; these intervening particles being evidently in close dependence upon and relation to each other. The zinc forms a direct compound with those particles of oxygen which were, previously, in divided relation to both it and the hydrogen: the oxide is removed by the acid, and a fresh surface of zinc is presented to the water, to renew and repeat the action.

685. Practically, the state of tension is best relieved by dipping a metal which has less attraction for oxygen than the zinc, into the dilute acid, and making it also touch the zinc. The force of chemical affinity, which has been influenced or polarised in the particles of the water by the dominant attraction of the zinc for the oxygen, is then transferred, in a most extraordinary manner, through the two metals, so as to re-enter upon the circuit in the electrolytic conductor, which, unlike the metals in that respect, cannot convey or transfer it without suffering decomposition; or rather, probably, it is exactly balanced and neutralised by the force which at the same moment completes the combination of the zinc with the oxygen of the water. The forces, in fact, of the two particles which are acting towards each other, and which are therefore in opposite directions, are the origin of the two opposite forces, or directions of force, in the current. They are of necessity equivalent to each other. Being transferred forward in contrary directions, they produce what is called the voltaic current: and it seems to me impossible to resist the idea that it must be preceded by a *state of tension* in the fluid, and between the fluid and the zinc; the *first consequence* of the affinity of the zinc for the oxygen of the water.

686. I have sought carefully for indications of a state of tension in the electrolytic conductor; and conceiving that it might produce something like structure, either before or during its discharge, I endeavoured to make this evident by polarised light. A glass cell, seven inches long, one inch and a half wide, and six inches deep, had two sets of platina electrodes adapted to it, one set for the ends, and the other for the sides. Those for the *sides* were seven inches long by three inches high, and when in the cell were separated by a little frame of wood covered with calico; so that when made active by connection with a battery upon any solution in the cell, the bubbles of gas rising from them did not obscure the central parts of the liquid.

687. A saturated solution of sulphate of soda was put into the cell, and the electrodes connected with a battery of 150 pairs of 4-inch plates: the current of electricity was conducted across the cell so freely, that the discharge was as good as if a wire had been used. A ray of polarised light was then transmitted through this solution, directly across the course of the electric current, and examined by an analysing plate; but though it penetrated seven inches of solution thus subject to the action of the electricity, and though contact was sometimes made, sometimes broken, and occasionally reversed during the observations, not the slightest trace of action on the ray could be perceived.

688. The large electrodes were then removed, and others introduced which fitted the *ends* of the cell. In each a slit was cut, so as to allow the light to pass. The course of the polarised ray was now parallel to the current, or in the direction of its axis (253); but still no effect, under any circumstances of contact or disunion, could be perceived upon it.

689. A strong solution of nitrate of lead was employed instead of the sulphate of soda, but no effects could be detected.

690. Thinking it possible that the discharge of the electric forces by the successive decompositions and recompositions of the particles of the electrolyte might neutralise and therefore destroy any effect which the first state of tension could by possibility produce, I took a substance which, being an excellent electrolyte when fluid, was a perfect insulator when solid, namely, borate of lead, in the form of a glass plate, and connecting the sides and the edges of this mass with the metallic plates, sometimes in contact with the poles of a voltaic battery, and sometimes even with the electric machine, for the advantage of the much higher intensity then obtained, I passed a polarised ray across it in various directions, as before, but could not obtain the slightest appearance of action upon the light. Hence I conclude, that notwithstanding the new and extraordinary state which must be assumed by an electrolyte, either during decomposition (when a most enormous quantity of electricity must be traversing it), or in the state of tension which is assumed as preceding decomposition, and which might be supposed to be retained in the solid form of the electrolyte, still it has no power of affecting a polarised ray of light; for no kind of structure or tension can in this way be rendered evident.

691. There is, however, one beautiful experimental proof of a state of tension acquired by the metals and the electrolyte

before the electric current is produced, and *before contact* of the different metals is made (650); in fact, at that moment when chemical forces only are efficient as a cause of action. I took a voltaic apparatus, consisting of a single pair of large plates, namely, a cylinder of amalgamated zinc, and a double cylinder of copper. These were put into a jar containing dilute sulphuric acid,[1] and could at pleasure be placed in metallic communication by a copper wire adjusted so as to dip at the extremities into two cups of mercury connected with the two plates.

692. Being thus arranged, there was no chemical action whilst the plates were not connected. On *making* the connection, a spark was obtained,[2] and the solution was immediately decomposed. On breaking it, the usual spark was obtained, and the decomposition ceased. In this case it is evident that the first spark must have occurred before metallic contact was made, for it passed through an interval of air; and also that it must have tended to pass before the electrolytic action began; for the latter could not take place until the current passed, and the current could not pass before the spark appeared. Hence I think there is sufficient proof, that as it is the zinc and water which by their mutual action produce the electricity of this apparatus, so these, by their first contact with each other, were placed in a state of powerful tension (687), which, though it could not produce the actual decomposition of the water, was able to make a spark of electricity pass between the zinc and a fit discharger as soon as the interval was rendered sufficiently small. The experiment demonstrates the direct production of the electric spark from pure chemical forces.

693. There are a few circumstances connected with the production of this spark by a single pair of plates, which should be known, to ensure success to the experiment. When the amalgamated surfaces of contact are quite clean and dry, the spark, on making contact, is quite as brilliant as on breaking it, if not even more so. When a film of oxide or dirt was present at either mercurial surface, then the first spark was often feeble,

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[1] When nitro-sulphuric acid is used, the spark is more powerful, but local chemical action can then commence, and proceed without requiring metallic contact.

[2] It has been universally supposed that no spark is produced on making the contact between a single pair of plates. I was led to expect one from the considerations already advanced in this paper. The wire of communication should be short; for with a long wire, circumstances strongly affecting the spark are introduced.

and often failed, the breaking spark, however, continuing very constant and bright. When a little water was put over the mercury, the spark was greatly diminished in brilliancy, but very regular both on making and breaking contact. When the contact was made between clean platina, the spark was also very small, but regular both ways. The true electric spark is, in fact, very small, and when surfaces of mercury are used, it is the combustion of the metal which produces the greater part of the light. The circumstances connected with the burning of the mercury are most favourable on breaking contact; for the act of separation exposes clean surfaces of metal, whereas, on making contact, a thin film of oxide, or soiling matter, often interferes. Hence the origin of the general opinion that it is only when the contact is broken that the spark passes.

694. With reference to the other set of cases, namely, those of local action (682) in which chemical affinity being exerted causes no transference of the power to a distance where no electric current is produced, it is evident that forces of the most intense kind must be active, and in some way balanced in their activity, during such combinations; these forces being directed so immediately and exclusively towards each other, that no signs of the powerful electric current they can produce become apparent, although the same final state of things is obtained as if that current had passed. It was Berzelius, I believe, who considered the heat and light evolved in cases of combustion as the consequences of this mode of exertion of the electric powers of the combining particles. But it will require a much more exact and extensive knowledge of the nature of electricity, and the manner in which it is associated with the atoms of matter, before we can understand accurately the action of this power in thus causing their union, or comprehend the nature of the great difference which it presents in the two modes of action just distinguished. We may imagine, but such imaginations must for the time be classed with the great mass of *doubtful knowledge* (611) which we ought rather to strive to diminish than to increase; for the very extensive contradictions of this knowledge by itself shows that but a small portion of it can ultimately prove true.

695. Of the two modes of action in which chemical affinity is exerted, it is important to remark, that that which produces the electric current is as *definite* as that which causes ordinary chemical combination; so that in examining the *production* or

evolution of electricity in cases of combination or decomposition, it will be necessary, not merely to observe certain effects dependent upon a current of electricity, but also their *quantity:* and though it may often happen that the forces concerned in any particular case of chemical action may be partly exerted in one mode and partly in the other, it is only those which are efficient in producing the current that have any relation to voltaic action. Thus, in the combination of oxygen and hydrogen to produce water, electric powers to a most enormous amount are for the time active (596, 608); but any mode of examining the flame which they form during energetic combination, which has as yet been devised, has given but the feeblest traces. These therefore may not, cannot, be taken as evidences of the nature of the action; but are merely incidental results, incomparably small in relation to the forces concerned, and supplying no information of the way in which the particles are active on each other, or in which their forces are finally arranged.

696. That such cases of chemical action produce no *current of electricity*, is perfectly consistent with what we know of the voltaic apparatus, in which it is essential that one of the combining elements shall form part of, or be in direct relation with, an electrolytic conductor (656, 658). That such cases produce no *free electricity of tension*, and that when they are converted into cases of voltaic action they produce a current in which the opposite forces are so equal as to neutralise each other, prove the equality of the forces in the opposed acting particles of matter, and therefore the equality of electric power in those quantities of matter which are called *electro-chemical equivalents* (559). Hence another proof of the definite nature of electro-chemical action (518, etc.), and that chemical affinity and electricity are forms of the same power (652, etc).

697. The direct reference of the effects produced by the voltaic pile at the place of experimental decomposition to the chemical affinities active at the place of excitation (626, 652), gives a very simple and natural view of the cause why the bodies (or *ions*) evolved pass in certain directions; for it is only when they pass in those directions that their forces can consist with and compensate (in direction at least) the superior forces which are dominant at the place where the action of the whole is determined. If, for instance, in a voltaic circuit, the activity of which is determined by the attraction of zinc for the oxygen of water, the zinc move from right to left, then any other *cation* included in the circuit, being part of an electrolyte, or forming

part of it at the moment, will also move from right to left: and as the oxygen of the water, by its natural affinity for the zinc, moves from left to right, so any other body of the same class with it (*i.e.* any other *anion*), under its government for the time, will move from left to right.

698. This I may illustrate by reference to fig. 43, the double circle of which may represent a complete voltaic circuit, the direction of its forces being determined by supposing for a

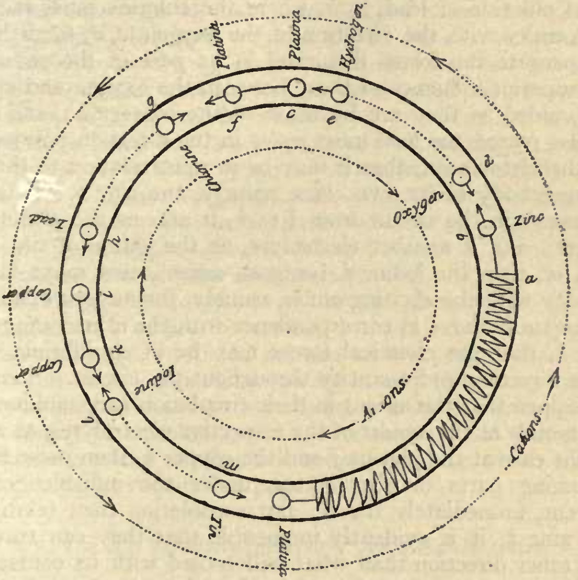

Fig. 43.

moment the zinc *b* and the platina *c* as representing plates of those metals acting upon water, *d*, *e*, and other substances, but having their energy exalted so as to effect several decompositions by the use of a battery at *a* (725). This supposition may be allowed, because the action in the battery will only consist of repetitions of what would take place between *b* and *c*, if they really constituted but a single pair. The zinc *b*, and the oxygen *d* by their mutual affinity, tend to unite; but as the oxygen is already in association with the hydrogen *e*, and has its inherent chemical or electric powers neutralised for the time by those of the latter, the hydrogen *e* must leave the oxygen *d*, and advance in the direction of the arrow head, or else the zinc *b* cannot move in the same direction to unite to the oxygen *d*, nor the oxygen *d* move in the contrary direction to unite to the zinc *b*, the relation of the *similar* forces of *b* and *e*, in contrary directions, to the *opposite* forces of *d* being the preventive. As the hydrogen *e* advances, it, on coming against the platina *c*, *f*, which forms a part of the circuit, communicates its electric or chemical forces through it to the next electrolyte in the circuit, fused chloride of lead, *g*, *h*, where the chlorine must move in conformity with the direction of the oxygen at *d*, for it has to compensate the forces disturbed in its part of the circuit by the superior influence of those between the oxygen and zinc at *d*, *b*, aided as they are by those of the battery *a*; and for a similar reason the lead must move in the direction pointed out by the arrow head, that it may be in right relation to the first moving body of its own class, namely, the zinc *b*. If copper intervene in the circuit from *i* to *k*, it acts as the platina did before; and if another electrolyte, as the iodide of tin, occur at *l*, *m*, then the iodine *l*, being an *anion*, must move in conformity with the exciting *anion*, namely, the oxygen *d*, and the *cation* tin *m* move in correspondence with the other *cations* *b*, *e*, and *h*, that the chemical forces may be in equilibrium as to their direction and quantity throughout the circuit. Should it so happen that the anions in their circulation can combine with the metals at the *anodes* of the respective electrolytes, as would be the case at the platina *f* and the copper *k*, then those bodies becoming parts of electrolytes, under the influence of the current, immediately travel; but considering their relation to the zinc *b*, it is evidently impossible that they can travel in any other direction than what will accord with its course, and therefore can never tend to pass otherwise than *from* the anode and *to* the cathode.

699. In such a circle as that delineated, therefore, all the known *anions* may be grouped within, and all the *cations* without. If any number of them enter as *ions* into the constitution of *electrolytes*, and, forming one circuit, are simultaneously subject to one common current, the anions must move in accordance with each other in one direction, and the cations in the other. Nay, more than that, equivalent portions of these bodies must so advance in opposite directions: for the advance of every 32.5 parts of the zinc *b* must be accompanied by a motion in the opposite direction of 8 parts of oxygen at *d*, of 36 parts of chlorine at *g*, of 126 parts of iodine at *l*; and in the

same direction by electro-chemical equivalents of hydrogen, lead, copper, and tin, at *e*, *h*, *k*, and *m*.

700. If the present paper be accepted as a correct expression of facts, it will still only prove a confirmation of certain general views put forth by Sir Humphry Davy in his Bakerian Lecture for 1806,[1] and revised and re-stated by him in another Bakerian Lecture, on electrical and chemical changes, for the year 1826.[2] His general statement is, that "*chemical and electrical attractions were produced by the same cause, acting in one case on particles, in the other on masses, of matter; and that the same property, under different modifications, was the cause of all the phenomena exhibited by different voltaic combinations.*"[3] This statement I believe to be true; but in admitting and supporting it, I must guard myself from being supposed to assent to all that is associated with it in the two papers referred to, or as admitting the experiments which are there quoted as decided proofs of the truth of the principle. Had I thought them so, there would have been no occasion for this investigation. It may be supposed by some that I ought to go through these papers, distinguishing what I admit from what I reject, and giving good experimental or philosophical reasons for the judgment in both cases. But then I should be equally bound to review, for the same purpose, all that has been written both for and against the necessity of metallic contact,—for and against the origin of voltaic electricity in chemical action,—a duty which I may not undertake in the present paper.[4]

¶ ii. *On the Intensity necessary for Electrolysation*

701. It became requisite, for the comprehension of many of the conditions attending voltaic action, to determine positively, if possible, whether electrolytes could resist the action of an electric current when beneath a certain intensity? whether

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[1] *Philosophical Transactions*, 1807.

[2] *Ibid.* 1826, p. 383.

[3] *Ibid.* 1826, p. 389.

[4] I at one time intended to introduce here, in the form of a note, a table of reference to the papers of the different philosophers who have referred the origin of the electricity in the voltaic pile to contact, or to chemical action, or to both; but on the publication of the first volume of M. Becquerel's highly important and valuable *Traité de l'Electricité et du Magnétism*, I thought it far better to refer to that work for these references, and the views held by the authors quoted. See pages 86, 91, 104, 110, 112, 117, 118, 120, 151, 152, 224, 227, 228, 232, 233, 252, 255, 257, 258, 290, etc.—*July* 3, 1834.

the intensity at which the current ceased to act would be the same for all bodies? and also whether the electrolytes thus resisting decomposition would conduct the electric current as a metal does, after they ceased to conduct as electrolytes, or would act as perfect insulators?

702. It was evident from the experiments described (639, 641) that different bodies were decomposed with very different facilities, and apparently that they required for their decomposition currents of different intensities, resisting some, but giving way to others. But it was needful, by very careful and express experiments, to determine whether a current could really pass through, and yet not decompose an electrolyte (645).

703. An arrangement (fig. 44) was made, in which two glass vessels contained the same dilute sulphuric acid, sp. gr. 1.25. The plate *z* was amalgamated zinc, in connection, by a platina wire *a*, with the platina plate *e*; *b* was a platina wire connecting the two platina plates P P′; *c* was a platina wire connected with the platina plate P″. On the plate *e* was placed a piece of paper moistened in solution of iodide of potassium: the wire *c* was so curved that its end could be made to rest at pleasure on this paper, and show, by the evolution of iodine there, whether a current was passing; or, being placed in the dotted position, it formed a direct communication with the platina plate *e*, and the electricity could pass without causing decomposition. The object was to produce a current by the action of the acid on the amalgamated zinc in the first vessel A; to pass it through the acid in the second vessel B by platina electrodes, that its power of decomposing water might, if existing, be observed; and to verify the existence of the current at pleasure, by decomposition at *e*, without involving the continual obstruction to the current which would arise from making the decomposition there constant. The experiment, being arranged, was examined and the existence of a current ascertained by the decomposition at *e*; the whole was then left with an end of the wire *c* resting on the plate *e*, so as to form a constant metallic communication there.

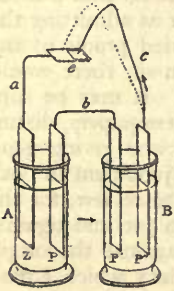

Fig. 44.

704. After several hours, the end of the wire *c* was replaced on the test paper at *e*: decomposition occurred, and *the proof* of a passing current was therefore complete. The current was

very feeble compared to what it had been at the beginning of the experiment, because of a peculiar state acquired by the metal surfaces in the second vessel, which caused them to oppose the passing current by a force which they possess under these circumstances (776). Still it was proved, by the decomposition, that this state of the plates in the second vessel was not able entirely to stop the current determined in the first, and that was all that was needful to be ascertained in the present inquiry.

705. This apparatus was examined from time to time, and an electric current always found circulating through it, until twelve days had elapsed, during which the water in the second vessel had been constantly subject to its action. Notwithstanding this lengthened period, not the slightest appearance of a bubble upon either of the plates in that vessel occurred. From the results of the experiment, I conclude that a current *had* passed, but of so low an intensity as to fall beneath that degree at which the elements of water, unaided by any secondary force resulting from the capability of combination with the matter of the electrodes, or of the liquid surrounding them, separated from each other.

706. It may be supposed, that the oxygen and hydrogen had been evolved in such small quantities as to have entirely dissolved in the water, and finally to have escaped at the surface, or to have reunited into water. That the hydrogen can be so dissolved was shown in the first vessel; for after several days minute bubbles of gas gradually appeared upon a glass rod, inserted to retain the zinc and platina apart, and also upon the platina plate itself, and these were hydrogen. They resulted principally in this way:—notwithstanding the amalgamation of the zinc, the acid exerted a little direct action upon it, so that a small stream of hydrogen bubbles was continually rising from its surface; a little of this hydrogen gradually dissolved in the dilute acid, and was in part set free against the surfaces of the rod and the plate, according to the well-known action of such solid bodies in solutions of gases (359, etc.).

707. But if the gases had been evolved in the second vessel by the decomposition of water, and had tended to dissolve, still there would have been every reason to expect that a few bubbles should have appeared on the electrodes, especially on the negative one, if it were only because of its action as a nucleus on the solution supposed to be formed; but none appeared even after twelve days.

708. When a few drops only of nitric acid were added to the vessel A, fig. 44, then the results were altogether different. In less than five minutes bubbles of gas appeared on the plates P′ and P″ in the second vessel. To prove that this was the effect of the electric current (which by trial at *e* was found at the same time to be passing), the connection at *e* was broken, and plates P′ P″ cleared from bubbles and left in the acid of the vessel B, for fifteen minutes: during that time no bubbles appeared upon them; but on restoring the communication at *e*, a minute did not elapse before gas appeared in bubbles upon the plates. The proof, therefore, is most full and complete, that the current excited by dilute sulphuric acid with a little nitric acid in vessel A, has intensity enough to overcome the chemical affinity exerted between the oxygen and hydrogen of the water in the vessel B, whilst that excited by dilute sulphuric acid alone has *not* sufficient intensity.

709. On using a strong solution of caustic potassa in the vessel A, to excite the current, it was found by the decomposing effects at *e*, that the current passed. But it had not intensity enough to decompose the water in the vessel B; for though left for fourteen days, during the whole of which time the current was found to be passing, still not the slightest appearance of gas appeared on the plates P′ P″, nor any other signs of the water having suffered decomposition.

710. Sulphate of soda in solution was then experimented with, for the purpose of ascertaining with respect to it, whether a certain electrolytic intensity was also required for its decomposition in this state, in analogy with the result established with regard to water (709). The apparatus was arranged as in fig. 45; P and Z are the platina and zinc plates dipping into a solution of common salt; *a* and *b* are platina plates connected by wires of platina (except in the galvanometer *g*) with P and Z; *c* is a connecting wire of platina, the ends of which can be made to rest either on the plates *a*, *b*, or on the papers moistened in solutions which are placed upon them; so that the passage of the current without decomposition, or with one or two decompositions, was under ready command, as far as arrangement was concerned. In order to change the *anodes* and *cathodes* at the places of decomposition, the form of apparatus, fig. 46, was

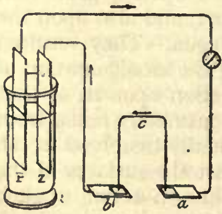

Fig. 45.

occasionally adopted. Here only one platina plate, *c*, was used; both pieces of paper on which decomposition was to be effected were placed upon it, the wires from P and Z resting upon these pieces of paper, or upon the plate *c*, according as the current with or without decomposition of the solutions was required.

711. On placing solution of iodide of potassium in paper at one of the decomposing localities, and solution of sulphate of soda at the other, so that the electric current should pass through both at once, the solution of iodide was slowly decomposed, yielding iodine at the *anode* and alkali at the *cathode*; but the solution of sulphate of soda exhibited no signs of decomposition, neither acid nor alkali being evolved from it. On placing the wires so that the iodide alone was subject to the action of the current (635), it was quickly and powerfully decomposed; but on arranging them so that the sulphate of soda alone was subject to action, it still refused to yield up its elements. Finally, the apparatus was so arranged under a wet bell-glass, that it could be left for twelve hours, the current passing during the whole time through a solution of sulphate of soda, retained in its place by only two thicknesses of bibulous litmus and turmeric paper. At the end of that time it was ascertained by the decomposition of iodide of potassium at the second place of action, that the current was passing and had passed for the twelve hours, and yet no trace of acid or alkali from the sulphate of soda appeared.

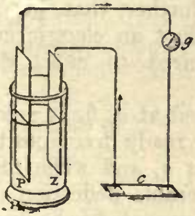

Fig. 46.

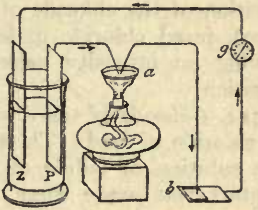

Fig. 47.

712. From these experiments it may, I think, be concluded that a solution of sulphate of soda can conduct a current of electricity, which is unable to decompose the neutral salt present; that this salt in the state of solution, like water, requires a certain electrolytic intensity for its decomposition; and that the necessary intensity is much higher for this sub-

stance than for the iodide of potassium in a similar state of solution.

713. I then experimented on bodies rendered decomposable by fusion, and first on *chloride of lead*. The current was excited by dilute sulphuric acid without any nitric acid between zinc and platina plates, fig. 47, and was then made to traverse a little chloride of lead fused upon glass at *a*, a paper moistened in solution of iodide of potassium at *b*, and a galvanometer at *g*. The metallic terminations at *a* and *b* were of platina. Being thus arranged, the decomposition at *b* and the deflection at *g* showed that an electric current was passing, but there was no appearance of decomposition at *a*, not even after a *metallic* communication at *b* was established. The experiment was repeated several times, and I am led to conclude that in this case the current has not intensity sufficient to cause the decomposition of the chloride of lead; and further, that, like water (709), fused chloride of lead can conduct an electric current having an intensity below that required to effect decomposition.

714. *Chloride of silver* was then placed at *a*, fig. 47, instead of chloride of lead. There was a very ready decomposition of the solution of iodide of potassium at *b*, and when metallic contact was made there, very considerable deflection of the galvanometer needle at *g*. Platina also appeared to be dissolved at the anode of the fused chloride at *a*, and there was every appearance of a decomposition having been effected there.

715. A further proof of decomposition was obtained in the following manner. The platina wires in the fused chloride at *a* were brought very near together (metallic contact having been established at *b*), and left so; the deflection at the galvanometer indicated the passage of a current, feeble in its force, but constant. After a minute or two, however, the needle would suddenly be violently affected, and indicate a current as strong as if metallic contact had taken place at *a*. This I actually found to be the case, for the silver reduced by the action of the current crystallised in long delicate spiculæ, and these at last completed the metallic communication; and at the same time that they transmitted a more powerful current than the fused chloride, they proved that electro-chemical decomposition of that chloride had been going on. Hence it appears that the current excited by dilute sulphuric acid between zinc and platina has an intensity above that required to electrolyse the fused chloride of silver when placed between platina electrodes,

although it has not intensity enough to decompose chloride of lead under the same circumstances.

716. A drop of *water* placed at *a* instead of the fused chlorides, showed as in the former case (705), that it could conduct a current unable to decompose it, for decomposition of the solution of iodide at *b* occurred after some time. But its conducting power was much below that of the fused chloride of lead (713).

717. Fused *nitre* at *a* conducted much better than water: I was unable to decide with certainty whether it was electrolysed, but I incline to think not, for there was no discoloration against the platina at the *cathode*. If sulpho-nitric acid had been used in the exciting vessel, both the nitre and the chloride of lead would have suffered decomposition like the water (641).

718. The results thus obtained of conduction without decomposition, and the necessity of a certain electrolytic intensity for the separation of the *ions* of different electrolytes, are immediately connected with the experiments and results given in § 4 of the second part of these Researches (154, 159, 180, 185). But it will require a more exact knowledge of the nature of intensity, both as regards the first origin of the electric current, and also the manner in which it may be reduced, or lowered by the intervention of longer or shorter portions of bad conductors, whether decomposable or not, before their relation can be minutely and fully understood.

719. In the case of water, the experiments I have as yet made appear to show that, when the electric current is reduced in intensity below the point required for decomposition, then the degree of conduction is the same whether sulphuric acid, or any other of the many bodies which can affect its transferring power as an electrolyte, are present or not. Or, in other words, that the necessary electrolytic intensity for water is the same whether it be pure, or rendered a better conductor by the addition of these substances; and that for currents of less intensity than this, the water, whether pure or acidulated, has equal conducting power. An apparatus, fig. 44, was arranged with dilute sulphuric acid in the vessel A, and pure distilled water in the vessel B. By the decomposition at *e*, it appeared as if water was a *better* conductor than dilute sulphuric acid for a current of such low intensity as to cause no decomposition. I am inclined, however, to attribute this apparent superiority of water to variations in that peculiar condition of the platina electrodes which is referred to further on in this part (776), and

which is assumed, as far as I can judge, to a greater degree in dilute sulphuric acid than in pure water. The power, therefore, of acids, alkalies, salts, and other bodies in solution, to increase conducting power, appears to hold good only in those cases where the electrolyte subject to the current suffers decomposition, and loses all influence when the current transmitted has too low an intensity to affect chemical change. It is probable that the ordinary conducting power of an electrolyte in the solid state (155) is the same as that which it possesses in the fluid state for currents the tension of which is beneath the due electrolytic intensity.

720. Currents of electricity, produced by less than eight or ten series of voltaic elements, can be reduced to that intensity at which water can conduct them without suffering decomposition, by causing them to pass through three or four vessels in which water shall be successively interposed between platina surfaces. The principles of interference upon which this effect depends will be described hereafter (745, 754), but the effect may be useful in obtaining currents of standard intensity, and is probably applicable to batteries of any number of pairs of plates.

721. As there appears every reason to expect that all electrolytes will be found subject to the law which requires an electric current of a certain intensity for their decomposition, but that they will differ from each other in the degree of intensity required, it will be desirable hereafter to arrange them in a table, in the order of their electrolytic intensities. Investigations on this point must, however, be very much extended, and include many more bodies than have been here mentioned before such a table can be constructed. It will be especially needful in such experiments to describe the nature of the electrodes used, or, if possible, to select such as, like platina or plumbago in certain cases, shall have no power of assisting the separation of the *ions* to be evolved (648).

722. Of the two modes in which bodies can transmit the electric forces, namely, that which is so characteristically exhibited by the metals, and usually called conduction, and that in which it is accompanied by decomposition, the first appears common to all bodies, although it occurs with almost infinite degrees of difference; the second is at present distinctive of the electrolytes. It is, however, just possible that it may hereafter be extended to the metals; for their power of conducting without decomposition may, perhaps justly, be ascribed to their

requiring a very high electrolytic intensity for their decomposition.

723. The establishment of the principle that a certain electrolytic intensity is necessary before decomposition can be effected, is of great importance to all those considerations which arise regarding the probable effects of weak currents, such for instance as those produced by natural thermo-electricity, or natural voltaic arrangements in the earth. For to produce an effect of decomposition or of combination, a current must not only exist, but have a certain intensity before it can overcome the quiescent affinities opposed to it, otherwise it will be conducted, producing no permanent chemical effects. On the other hand, the principles are also now evident by which an opposing action can be so weakened by the juxtaposition of bodies not having quite affinity enough to cause direct action between them (648), that a very weak current shall be able to raise the sum of actions sufficiently high, and cause chemical changes to occur.

724. In concluding this division *on the intensity necessary for electrolysation*, I cannot resist pointing out the following remarkable conclusion in relation to intensity generally. It would appear that when a voltaic current is produced, having a certain intensity, dependent upon the strength of the chemical affinities by which that current is excited (651), it can decompose a particular electrolyte without relation to the quantity of electricity passed, the *intensity* deciding whether the electrolyte shall give way or not. If that conclusion be confirmed, then we may arrange circumstances so that the *same quantity* of electricity may pass in the *same time*, in at the *same surface*, into the *same decomposing body in the same state*, and yet, differing in intensity, will *decompose in one case and in the other not*:—for taking a source of too low an intensity to decompose, and ascertaining the quantity passed in a given time, it is easy to take another source having a sufficient intensity, and reducing the quantity of electricity from it by the intervention of bad conductors to the same proportion as the former current, and then all the conditions will be fulfilled which are required to produce the result described.

¶ iii. *On associated Voltaic Circles, or the Voltaic Battery*

725. Passing from the consideration of single circles (610, etc.) to their association in the voltaic battery, it is a very

evident consequence, that if matters are so arranged that two sets of affinities, in place of being opposed to each other as in figs. 33, 36 (615, 626), are made to act in conformity, then, instead of either interfering with the other, it will rather assist it. This is simply the case of two voltaic pairs of metals arranged so as to form one circuit. In such arrangements the activity of the whole is known to be increased, and when ten, or a hundred, or any larger number of such alternations are placed in conformable association with each other, the power of the whole becomes proportionably exalted, and we obtain that magnificent instrument of philosophic research, the *voltaic battery*.

726. But it is evident from the principles of definite action already laid down, that the *quantity* of electricity in the current cannot be increased with the increase of the *quantity of metal* oxidised and dissolved at each new place of chemical action. A single pair of zinc and platina plates throws as much electricity into the form of a current, by the oxidation of 32.5 grains of the zinc (603), as would be circulated by the same alteration of a thousand times that quantity, or nearly five pounds of metal oxidised at the surface of the zinc plates of a thousand pairs placed in regular battery order. For it is evident that the electricity which passes across the acid from the zinc to the platina in the first cell, and which has been associated with, or even evolved by, the decomposition of a definite portion of water in that cell, cannot pass from the zinc to the platina across the acid in the second cell, without the decomposition of the same quantity of water there, and the oxidation of the same quantity of zinc by it (659, 684). The same result recurs in every other cell; the electro-chemical equivalent of water must be decomposed in each, before the current can pass through it; for the quantity of electricity passed and the quantity of electrolyte decomposed *must* be the equivalents of each other. The action in each cell, therefore, is not to increase the quantity set in motion in any one cell, but to aid in urging forward that quantity, the passing of which is consistent with the oxidation of its own zinc; and in this way it exalts that peculiar property of the current which we endeavour to express by the term *intensity*, without increasing the *quantity* beyond that which is proportionate to the quantity of zinc oxidised in any single cell of the series.

727. To prove this, I arranged ten pairs of amalgamated zinc and platina plates with dilute sulphuric acid in the form of a battery. On completing the circuit, all the pairs acted and

evolved gas at the surfaces of the platina. This was collected and found to be alike in quantity for each plate; and the quantity of hydrogen evolved at any one platina plate was in the same proportion to the quantity of metal dissolved from any one zinc plate, as was given in the experiment with a single pair (599, etc.). It was therefore certain that just as much electricity and no more had passed through the series of ten pair of plates as had passed through, or would have been put into motion by, any single pair, notwithstanding that ten times the quantity of zinc had been consumed.

728. This truth has been proved also long ago in another way, by the action of the evolved current on a magnetic needle; the deflecting power of one pair of plates in a battery being equal to the deflecting power of the whole, provided the wires used be sufficiently large to carry the current of the single pair freely; but the *cause* of this equality of action could not be understood whilst the definite action and evolution of electricity (518, 604) remained unknown.

729. The superior decomposing power of a battery over a single pair of plates is rendered evident in two ways. Electrolytes held together by an affinity so strong as to resist the action of the current from a single pair, yield up their elements to the current excited by many pairs; and that body which is decomposed by the action of one or of few pairs of metals, etc., is resolved into its *ions* the more readily as it is acted upon by electricity urged forward by many alternations.

730 Both these effects are, I think, easily understood. Whatever *intensity* may be (and that must of course depend upon the nature of electricity, whether it consist of a fluid or fluids, or of vibrations of an ether, or any other kind or condition of matter), there seems to be no difficulty in comprehending that the *degree* of intensity at which a current of electricity is evolved by a first voltaic element, shall be increased when that current is subjected to the action of a second voltaic element, acting in conformity and possessing equal powers with the first: and as the decompositions are merely opposed actions, but exactly of the same kind as those which generate the current (652), it seems to be a natural consequence that the affinity which can resist the force of a single decomposing action may be unable to oppose the energies of many decomposing actions, operating conjointly, as in the voltaic battery.

731. That a body which can give way to a current of feeble intensity should give way more freely to one of stronger force,

and yet involve no contradiction to the law of definite electrolytic action, is perfectly consistent. All the facts and also the theory I have ventured to put forth, tend to show that the act of decomposition opposes a certain force to the passage of the electric current; and, that this obstruction should be overcome more or less readily, in proportion to the greater or less intensity of the decomposing current, is in perfect consistency with all our notions of the electric agent.

732. I have elsewhere (682) distinguished the chemical action of zinc and dilute sulphuric acid into two portions; that which, acting effectually on the zinc, evolves hydrogen at once upon its surface, and that which, producing an arrangement of the chemical forces throughout the electrolyte present (in this case water), tends to take oxygen from it, but cannot do so unless the electric current consequent thereon can have free passage, and the hydrogen be delivered elsewhere than against the zinc. The electric current depends altogether upon the second of these; but when the current can pass, by favouring the electrolytic action it tends to diminish the former and increase the latter portion.

733. It is evident, therefore, that when ordinary zinc is used in a voltaic arrangement, there is an enormous waste of that power which it is the object to throw into the form of an electric current; a consequence which is put in its strongest point of view when it is considered that three ounces and a half of zinc, properly oxydised, can circulate enough electricity to decompose nearly one ounce of water, and cause the evolution of about 2400 cubic inches of hydrogen gas. This loss of power not only takes place during the time the electrodes of the battery are in communication, being then proportionate to the quantity of hydrogen evolved against the surface of any one of the zinc plates, but includes also *all* the chemical action which goes on when the extremities of the pile are not in communication.

734. This loss is far greater with ordinary zinc than with the pure metal, as M. de la Rive has shown.[1] The cause is, that when ordinary zinc is acted upon by dilute sulphuric acid, portions of copper, lead, cadmium, or other metals which it may contain, are set free upon its surface; and these, being in contact with the zinc, form small but very active voltaic circles, which cause great destruction of the zinc and evolution of hydrogen, apparently upon the zinc surface, but really upon the

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[1] *Quarterly Journal of Science*, 1831, p. 388; or *Bibliothèque Universelle*, 1830, p. 391.

surface of these incidental metals. In the same proportion as they serve to discharge or convey the electricity back to the zinc, do they diminish its power of producing an electric current which shall extend to a greater distance across the acid, and be discharged only through the copper or platina plate which is associated with it for the purpose of forming a voltaic apparatus.

735. All these evils are removed by the employment of an amalgam of zinc in the manner recommended by Mr. Kemp,[1] or the use of the amalgamated zinc plates of Mr. Sturgeon (598), who has himself suggested and objected to their application in galvanic batteries; for he says, "Were it not on account of the brittleness and other inconveniences occasioned by the incorporation of the mercury with the zinc, amalgamation of the zinc surfaces in galvanic batteries would become an important improvement; for the metal would last much longer, and remain bright for a considerable time, even for several successive hours; essential considerations in the employment of this apparatus." [2]

736. Zinc so prepared, even though impure, does not sensibly decompose the water of dilute sulphuric acid, but still has such affinity for the oxygen, that the moment a metal which, like copper or platina, has little or no affinity, touches it in the acid, action ensues, and a powerful and abundant electric current is produced. It is probable that the mercury acts by bringing the surface, in consequence of its fluidity, into one uniform condition, and preventing those differences in character between one spot and another which are necessary for the formation of the minute voltaic circuits referred to (734). If any difference does exist at the first moment, with regard to the proportion of zinc and mercury, at one spot on the *surface*, as compared with another, that spot having the least mercury is first acted on, and, by solution of the zinc, is soon placed in the same condition as the other parts, and the whole plate rendered superficially uniform. One part cannot, therefore, act as a discharger to another; and hence *all* the chemical power upon the water at its surface is in that equable condition (684), which, though it tends to produce an electric current through the liquid to another plate of metal which can act as a discharger (685), presents no irregularities by which any one part, having weaker

[1] Jameson's *Edinburgh Journal*, October 1828.

[2] *Recent Experimental Researches*, p. 42, etc. Mr. Sturgeon is of course unaware of the definite production of electricity by chemical action, and is in fact quoting the experiment as the strongest argument *against* the chemical theory of galvanism.

affinities for oxygen, can act as a discharger to another. Two excellent and important consequences follow upon this state of the metal. The first is, that the *full equivalent* of electricity is obtained for the oxidation of a certain quantity of zinc; the second, that a battery constructed with the zinc so prepared, and charged with dilute sulphuric acid, is active only whilst the electrodes are connected, and ceases to act or be acted upon by the acid the instant the communication is broken.

737. I have had a small battery of ten pairs of plates thus constructed, and am convinced that arrangements of this kind will be very important, especially in the development and illustration of the philosophical principles of the instrument. The metals I have used are amalgamated zinc and platina, connected together by being soldered to platina wires, the whole apparatus having the form of the *couronne des tasses.* The liquid used was dilute sulphuric acid of sp. gr. 1.25. No action took place upon the metals except when the electrodes were in communication, and then the action upon the zinc was only in proportion to the decomposition in the experimental cell; for when the current was retarded there, it was retarded also in the battery, and no waste of the powers of the metal was incurred.

738. In consequence of this circumstance, the acid in the cells remained active for a very much longer time than usual. In fact, time did not tend to lower it in any sensible degree: for whilst the metal was preserved to be acted upon at the proper moment, the acid also was preserved almost at its first strength. Hence a constancy of action far beyond what can be obtained by the use of common zinc.

739. Another excellent consequence was the renewal, during the interval of rest, between two experiments of the first and most efficient state. When an amalgamated zinc and a platina plate, immersed in dilute sulphuric acid, are first connected, the current is very powerful, but instantly sinks very much in force, and in some cases actually falls to only an eighth or a tenth of that first produced (772). This is due to the acid which is in contact with the zinc becoming neutralised by the oxide formed; the continued quick oxidation of the metal being thus prevented. With ordinary zinc, the evolution of gas at its surface tends to mingle all the liquid together, and thus bring fresh acid against the metal, by which the oxide formed there can be removed. With the amalgamated zinc battery, at every cessation of the current, the saline solution against the zinc is gradually diffused amongst the rest of the liquid; and

upon the renewal of contact at the electrodes, the zinc plates are found most favourably circumstanced for the production of a ready and powerful current.

740. It might at first be imagined that amalgamated zinc would be much inferior in force to common zinc, because of the lowering of its energy, which the mercury might be supposed to occasion over the whole of its surface; but this is not the case. When the electric currents of two pairs of platina and zinc plates were opposed, the difference being that one of the zincs was amalgamated and the other not, the current from the amalgamated zinc was most powerful, although no gas was evolved against it, and much was evolved at the surface of the unamalgamated metal. Again, as Davy has shown,[1] if amalgamated and unamalgamated zinc be put in contact, and dipped into dilute sulphuric acid, or other exciting fluids, the former is positive to the latter, *i.e.* the current passes from the amalgamated zinc, through the fluid, to the unprepared zinc. This he accounts for by supposing that "there is not any inherent and specific property in each metal which gives it the electrical character, but that it depends upon its peculiar state—on that form of aggregation which fits it for chemical change."

741. The superiority of the amalgamated zinc is not, however, due to any such cause, but is a very simple consequence of the state of the fluid in contact with it; for as the unprepared zinc acts directly and alone upon the fluid, whilst that which is amalgamated does not, the former (by the oxide it produces) quickly neutralises the acid in contact with its surface, so that the progress of oxidation is retarded, whilst at the surface of the amalgamated zinc, any oxide formed is instantly removed by the free acid present, and the clean metallic surface is always ready to act with full energy upon the water. Hence its superiority (773).

742. The progress of improvement in the voltaic battery and its applications, is evidently in the contrary direction at present to what it was a few years ago; for in place of increasing the number of plates, the strength of acid, and the extent altogether of the instrument, the change is rather towards its first state of simplicity, but with a far more intimate knowledge and application of the principles which govern its force and action. Effects of decomposition can now be obtained with ten pairs of plates (153), which required five hundred or a thousand pairs for their production in the first instance. The capability of

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[1] *Philosophical Transactions*, 1826, p. 405.

decomposing fused chlorides, iodides, and other compounds, according to the law before established (116, etc.), and the opportunity of collecting certain of the products, without any loss, by the use of apparatus of the nature of those already described (524, 549, etc.), render it probable that the voltaic battery may become a useful and even economical manufacturing instrument; for theory evidently indicates that an equivalent of a rare substance may be obtained at the expense of three or four equivalents of a very common body, namely, zinc: and practice seems thus far to justify the expectation. In this point of view I think it very likely that plates of platina or silver may be used instead of plates of copper with advantage, and that then the evil arising occasionally from solution of the copper, and its precipitation on the zinc (by which the electromotive power of the zinc is so much injured), will be avoided (783).

¶ iv. *On the Resistance of an Electrolyte to Electrolytic Action, and on Interpositions*

743. I have already illustrated, in the simplest possible form of experiment (626, 645), the resistance established at the place of decomposition to the force active at the exciting place. I purpose examining the effects of this resistance more generally; but it is rather with reference to their practical interference with the action and phenomena of the voltaic battery, than with any intention at this time to offer a strict and philosophical account of their nature. Their general and principal cause is the resistance of the chemical affinities to be overcome; but there are numerous other circumstances which have a joint influence with these forces (770, 776, etc.), each of which would require a minute examination before a correct account of the whole could be given.


Fig. 48.

744. As it will be convenient to describe the experiments in a form different to that in which they were made, both forms shall first be explained. Plates of platina, copper, zinc, and other metals, about three-quarters of an inch wide and three inches long, were associated together in pairs by means of platina wires to which they were soldered, fig. 48, the plates of one pair being either alike or different, as might be required. These were arranged in glasses, fig. 49, so as to form Volta's crown of cups. The acid or fluid in the cups never covered

the whole of any plate; and occasionally small glass rods were put into the cups, between the plates, to prevent their contact. Single plates were used to terminate the series and complete the connection with a galvanometer, or with a decomposing apparatus (634, 703, etc.), or both. Now if fig. 50 be examined and compared with fig. 51, the latter may be admitted as representing the former in its simplest condition; for the cups, I, II, and III of the former, with their contents, are represented by the cells I, II, and III of the latter, and the metal plates Z and P of the former by the similar plates represented Z and P in the latter. The only difference, in fact, between the apparatus, fig. 50, and the trough represented fig. 51, is that twice the quantity of surface of contact between the metal and acid is allowed in the first to what would occur in the second.

Fig. 49.

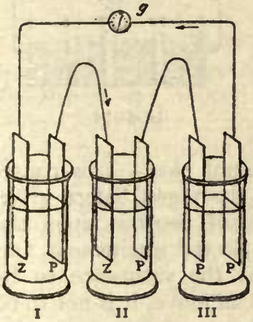

Fig. 50.

745. When the extreme plates of the arrangement just described, fig. 50, are connected metallically through the galvanometer *g*, then the whole represents a battery consisting of two pairs of zinc and platina plates urging a current forward, which has, however, to decompose water unassisted by any direct chemical affinity before it can be transmitted across the cell III, and therefore before it can circulate. This decomposition of water, which is opposed to the passage of the current, may, as a matter of convenience, be considered as taking place either against the surfaces of the two platina plates which constitute the electrodes in the cell III, or against the two surfaces of that platina plate which separates the cells II and III, fig. 51, from each other. It is evident that if that plate were away, the battery would consist of two pairs of plates and two cells, arranged in the most favourable position for the production of a current. The platina plate therefore, which being introduced as at *x*, has oxygen evolved at one surface and hydrogen at the other (that is, if the decomposing current passes), may be considered as the cause of any obstruction arising from the decomposition of water by

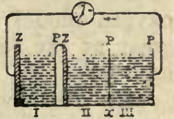

Fig. 51.

the electrolytic action of the current; and I have usually called it the interposed plate.

746. In order to simplify the conditions, dilute sulphuric acid was first used in all the cells, and platina for the interposed plates; for then the initial intensity of the current which tends to be formed is constant, being due to the power which zinc has of decomposing water; and the opposing force of decomposition is also constant, the elements of the water being unassisted in their separation at the interposed plates by any affinity or secondary action at the electrodes (479), arising either from the nature of the plate itself or the surrounding fluid.

747. When only one voltaic pair of zinc and platina plates was used, the current of electricity was entirely stopped to all practical purposes by interposing one platina plate, fig. 52, *i.e.* by requiring of the current that it should decompose water. and evolve both its elements, before it should pass. This consequence is in perfect accordance with the views before given (645, 652, 708). For as the whole result depends upon the opposition of forces at the places of electric excitement and electro-decomposition, and as water is the substance to be decomposed at both before the current can move, it is not to be expected that the zinc should have such powerful attraction for the oxygen, as not only to be able to take it from its associated hydrogen, but leave such a surplus of force as, passing to the second place of decomposition, should be there able to effect a second separation of the elements of water. Such an effect would require that the force of attraction between zinc and oxygen should under the circumstances be *at least* twice as great as the force of attraction between the oxygen and hydrogen.

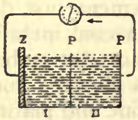

Fig. 52.

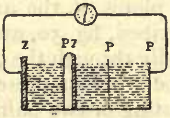

Fig. 53.

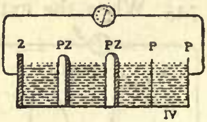

Fig. 54.

748. When two pairs of zinc and platina exciting plates were used, the current was also practically stopped by one interposed platina plate, fig. 53. There was a very feeble effect of a current at first, but it ceased almost immediately. It will be referred to, with many other similar effects, hereafter (753).

749. Three pairs of zinc and platina plates, fig. 54, were able to produce a current which could pass an interposed platina plate, and effect the electrolysation of water in cell IV. The current was evident, both by the continued deflection of the galvanometer, and the production of bubbles of oxygen and hydrogen at the electrodes in cell IV. Hence the accumulated surplus force of three plates of zinc, which are active in decomposing water, is more than equal, when added together, to the force with which oxygen and hydrogen are combined in water, and is sufficient to cause the separation of these elements from each other.

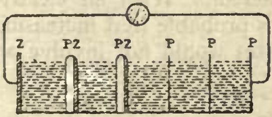

Fig. 55.

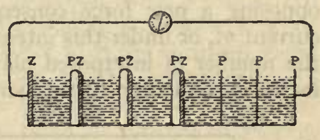

Fig. 56.

750. The three pairs of zinc and platina plates were now opposed by two intervening platina plates, fig. 55. In this case the current was stopped.

751. Four pairs of zinc and platina plates were also neutralised by two interposed platina plates, fig. 56.

752. Five pairs of zinc and platina, with two interposed platina plates, fig. 57, gave a feeble current; there was permanent deflection at the galvanometer, and decomposition in the cells VI and VII. But the current was very feeble; very much less than when all the intermediate plates were removed and the two extreme ones only retained: for when they were placed six inches asunder in one cell, they gave a powerful current. Hence five exciting pairs, with two interposed obstructing plates, do not give a current at all comparable to that of a single unobstructed pair.

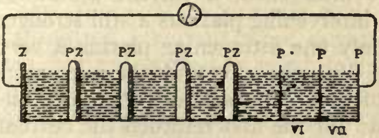

Fig. 57.

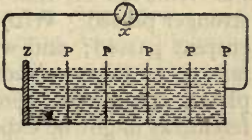

Fig. 58.

753. I have already said that a *very feeble current* passed when the series included one interposed platina and two pairs

of zinc and platina plates (748). A similarly feeble current passed in every case, and even when only one exciting pair and four intervening platina plates were used, fig. 58, a current passed which could be detected at x, both by chemical action on the solution of iodide of potassium, and by the galvanometer. This current I believe to be due to electricity reduced in intensity below the point requisite for the decomposition of water (705, 719); for water can conduct electricity of such low intensity by the same kind of power which it possesses in common with metals and charcoal, though it cannot conduct electricity of higher intensity without suffering decomposition, and then opposing a new force consequent thereon. With an electric current of, or under this intensity, it is probable that increasing the number of interposed platina plates would not involve an increased difficulty of conduction.

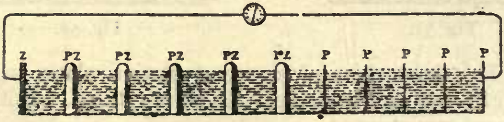

Fig. 59.

754. In order to obtain an idea of the additional interfering power of each added platina plate, six voltaic pairs and four intervening platinas were arranged as in fig. 59; a very feeble current then passed (720, 753). When one of the platinas was removed so that three intervened, a current somewhat stronger passed. With two intervening platinas a still stronger current passed; and with only one intervening platina a very fair current was obtained. But the effect of the successive plates, taken in the order of their interposition, was very different, as might be expected; for the first retarded the current more powerfully than the second, and the second more than the third.

755. In these experiments both amalgamated and unamalgamated zinc were used, but the results generally were the same.

756. The effects of retardation just described were altered altogether when changes were made in the *nature of the liquid* used between the plates, either in what may be called the *exciting* or the *retarding* cells. Thus, retaining the exciting force the same, by still using pure dilute sulphuric acid for that

purpose, if a little nitric acid were added to the liquid in the *retarding* cells, then the transmission of the current was very much facilitated. For instance, in the experiment with one pair of exciting plates and one intervening plate (747), fig. 52, when a few drops of nitric acid were added to the contents of cell 11, then the current of electricity passed with considerable strength (though it soon fell from other causes (772, 776)), and the same increased effect was produced by the nitric acid when many interposed plates were used.

757. This seems to be a consequence of the diminution of the difficulty of decomposing water when its hydrogen, instead of being absolutely expelled, as in the former cases, is transferred to the oxygen of the nitric acid, producing a secondary result at the *cathode* (487); for in accordance with the chemical views of the electric current and its action already advanced (648), the water, instead of opposing a resistance to decomposition equal to the full amount of the force of mutual attraction between its oxygen and hydrogen, has that force counteracted in part, and therefore diminished by the attraction of the hydrogen at the *cathode* for the oxygen of the nitric acid which surrounds it, and with which it ultimately combines instead of being evolved in its free state.

758. When a little nitric acid was put into the exciting cells, then again the circumstances favouring the transmission of the current were strengthened, for the *intensity* of the current itself was increased by the addition (641). When therefore a little nitric acid was added to both the *exciting* and the *retarding* cells, the current of electricity passed with very considerable freedom.

759. When dilute muriatic acid was used, it produced and transmitted a current more easily than pure dilute sulphuric acid, but not so readily as dilute nitric acid. As muriatic acid appears to be decomposed more freely than water (500), and as the affinity of zinc for chlorine is very powerful, it might be expected to produce a current more intense than that from the use of dilute sulphuric acid; and also to transmit it more freely by undergoing decomposition at a lower intensity (647).

760. In relation to the effect of these interpositions, it is necessary to state that they do not appear to be at all dependent upon the size of the electrodes, or their distance from each other in the acid, except that when a current *can pass*, changes in these facilitate or retard its passage. For on repeating the experiment with one intervening and one pair of exciting plates (747), fig. 52, and in place of the interposed plate P using some-

times a mere wire, and sometimes very large plates (744), and also changing the terminal exciting plates Z and P, so that they were sometimes wires only and at others of great size, still the results were the same as those already obtained.

761. In illustration of the effect of distance, an experiment like that described with two exciting pairs and one intervening plate (748), fig. 53, was arranged so that the distance between the plates in the third cell could be increased to six or eight inches, or diminished to the thickness of a piece of intervening bibulous paper. Still the result was the same in both cases, the effect not being sensibly greater, when the plates were merely separated by the paper, than when a great way apart; so that the principal opposition to the current in this case does not depend upon the *quantity* of intervening electrolytic conductor, but on the *relation of its elements to the intensity of the current,* or to the chemical nature of the electrodes and the surrounding fluids.

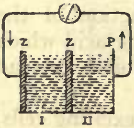

Fig. 60.

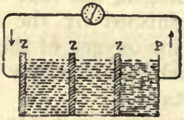

Fig. 61.

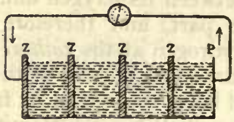

Fig. 62.

762. When the acid was sulphuric acid, *increasing its strength* in any of the cells caused no change in the effects; it did not produce a more intense current in the exciting cells (643), or cause the current produced to traverse the decomposing cells more freely. But if to very weak sulphuric acid a few drops of nitric acid were added, then either one or other of those effects could be produced; and, as might be expected in a case like this, where the exciting or conducting action bore a *direct* reference to the acid itself, increasing the strength of this (the nitric acid) also increased its powers.

763. The *nature of the interposed plate* was now varied to show its relation to the phenomena either of excitation or retardation, and amalgamated zinc was first substituted for platina. On employing one voltaic pair and one interposed zinc plate, fig. 60, there was as powerful a current, apparently, as if the interposed zinc plate was away. Hydrogen was evolved against P in cell II, and against the side of the second zinc in cell I; but no gas appeared against the side of the zinc in cell II, nor against the zinc in cell I.

764. On interposing two amalgamated zinc plates, fig. 61, instead of one, there was still a powerful current, but interference had taken place. On using three intermediate zinc plates, fig. 62, there was still further retardation, though a good current of electricity passed.

765. Considering the retardation as due to the inaction of the amalgamated zinc upon the dilute acid, in consequence of the slight though general effect of diminished chemical power produced by the mercury on the surface, and viewing this inaction as the circumstance which rendered it necessary that each plate should have its tendency to decompose water assisted slightly by the electric current, it was expected that plates of the metal in the unamalgamated state would probably not require such assistance, and would offer no sensible impediment to the passing of the current. This expectation was fully realised in the use of two and three interposed unamalgamated plates. The electric current passed through them as freely as if there had been no such plates in the way. They offered no obstacle, because they could decompose water without the current; and the latter had only to give direction to a part of the forces, which would have been active whether it had passed or not.

766. Interposed plates of copper were then employed. These seemed at first to occasion no obstruction, but after a few minutes the current almost entirely ceased. This effect appears due to the surfaces taking up that peculiar condition (776) by which they tend to produce a reverse current; for when one or more of the plates were turned round, which could easily be effected with the *couronne des tasses* form of experiment, fig. 50, then the current was powerfully renewed for a few moments, and then again ceased. Plates of platina and copper, arranged as a voltaic pile with dilute sulphuric acid, could not form a voltaic trough competent to act for more than a few minutes, because of this peculiar counteracting effect.

767. All these effects of retardation, exhibited by decomposition against surfaces for which the evolved elements have more or less affinity, or are altogether deficient in attraction, show generally, though beautifully, the chemical relations and source of the current, and also the balanced state of the affinities at the places of excitation and decomposition. In this way they add to the mass of evidence in favour of the identity of the two; for they demonstrate, as it were, the antagonism of the *chemical powers* at the electromotive part with the *chemical powers* at the interposed parts; they show that the first are *producing*

electric effects, and the second *opposing* them; they bring the two into direct relation; they prove that either can determine the other, thus making what appears to be cause and effect convertible, and thereby demonstrating that both chemical and electrical action are merely two exhibitions of one single agent or power (651, etc.).

768. It is quite evident, that as water and other electrolytes can conduct electricity without suffering decomposition (721), when the electricity is of sufficiently low intensity, it may not be asserted as absolutely true in all cases, that whenever electricity passes through an electrolyte, it produces a definite effect of decomposition. But the quantity of electricity which can pass in a given time through an electrolyte without causing decomposition is so small as to bear no comparison to that required in a case of very moderate decomposition, and with electricity above the intensity required for electrolysation, I have found no sensible departure as yet from the law of *definite electrolytic action* developed in the preceding parts of these Researches (518, etc.).

769. I cannot dismiss this division of the present paper without making a reference to the important experiments of M. Aug. de la Rive on the effects of interposed plates.[1] As I have had occasion to consider such plates merely as giving rise to new decompositions, and in that way only causing obstruction to the passage of the electric current, I was freed from the necessity of considering the peculiar effects described by that philosopher. I was the more willing to avoid for the present touching upon these, as I must at the same time have entered into the views of Sir Humphry Davy upon the same subject,[2] and also those of Marianini[3] and Ritter,[4] which are connected with it.

¶ v. *General Remarks on the active Voltaic Battery*

770. When the ordinary voltaic battery is brought into action, its very activity produces certain effects, which react upon it, and cause serious deterioration of its power. These render it an exceedingly inconstant instrument as to the *quantity* of effect which it is capable of producing. They are already,

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[1] *Annales de Chimie*, tom. xxviii. p. 190; and *Mémoires de Genéve.*

[2] *Philosophical Transactions*, 1826, p. 413.

[3] *Annales de Chimie*, tom. xxxiii. pp. 117, 119, etc.

[4] *Journal de Physique*, tom. lvii. pp. 349, 350.

in part, known and understood; but as their importance, and that of certain other coincident results, will be more evident by reference to the principles and experiments already stated and described, I have thought it would be useful, in this investigation of the voltaic pile, to notice them briefly here.

771. When the battery is in action, it causes such substances to be formed and arranged in contact with the plates as very much weaken its power, or even tend to produce a counter current. They are considered by Sir Humphry Davy as sufficient to account for the phenomena of Ritter's secondary piles, and also for the effects observed by M. A. de la Rive with interposed platina plates.[1]

772. I have already referred to this consequence (739) as capable, in some cases, of lowering the force of the current to one-eighth or one-tenth of what it was at the first moment, and have met with instances in which its interference was very great. In an experiment in which one voltaic pair and one interposed platina plate were used with dilute sulphuric acid in the cells, fig. 63, the wires of communication were so arranged that the end of that marked 3 could be placed at pleasure upon paper moistened in the solution of iodide of potassium at *x*, or directly upon the platina plate there. If, after an interval during which the circuit had not been complete, the wire 3 were placed upon the paper, there was evidence of a current, decomposition ensued, and the galvanometer was affected. If the wire 3 were made to touch the metal of *p*, a comparatively strong sudden current was produced, affecting the galvanometer, but lasting only for a moment; the effect at the galvanometer ceased, and if the wire 3 were placed on the paper at *x*, no signs of decomposition occurred. On raising the wire 3, and breaking the circuit altogether for a while, the apparatus resumed its first power, requiring, however, from five to ten minutes for this purpose; and then, as before, on making contact between 3 and *p*, there was again a momentary current, and immediately all the effects apparently ceased.

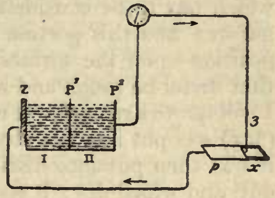

Fig. 63.

773. This effect I was ultimately able to refer to the state of the film of fluid in contact with the zinc plate in cell I. The acid of that film is instantly neutralised by the oxide formed;

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[1] *Philosophical Transactions*, 1826, p. 413.

the oxidation of the zinc cannot, of course, go on with the same facility as before; and the chemical action being thus interrupted, the voltaic action diminishes with it. The time of the rest was required for the diffusion of the liquid, and its replacement by other acid. From the serious influence of this cause in experiments with single pairs of plates of different metals, in which I was at one time engaged, and the extreme care required to avoid it, I cannot help feeling a strong suspicion that it interferes more frequently and extensively than experimenters are aware of, and therefore direct their attention to it.

774. In considering the effect in delicate experiments of this source of irregularity of action in the voltaic apparatus, it must be remembered that it is only that very small portion of matter which is directly in contact with the oxidisable metal which has to be considered with reference to the change of its nature; and this portion is not very readily displaced from its position upon the surface of the metal (328, 341), especially if that metal be rough and irregular. In illustration of this effect, I will quote a remarkable experiment. A burnished platina plate (305) was put into hot strong sulphuric acid for an instant only: it was then put into distilled water, moved about in it, taken out, and wiped dry: it was put into a second portion of distilled water, moved about in it, and again wiped: it was put into a third portion of distilled water, in which it was moved about for nearly eight seconds; it was then, without wiping, put into a fourth portion of distilled water, where it was allowed to remain five minutes. The two latter portions of water were then tested for sulphuric acid; the third gave no sensible appearance of that substance, but the fourth gave indications which were not merely evident, but abundant for the circumstances under which it had been introduced. The result sufficiently shows with what difficulty that portion of the substance which is in *contact* with the metal leaves it; and as the contact of the fluid formed against the plate in the voltaic circuit must be as intimate and as perfect as possible, it is easy to see how quickly and greatly it must vary from the general fluid in the cells, and how influential in diminishing the force of the battery this effect must be.

775. In the ordinary voltaic pile, the influence of this effect will occur in all variety of degrees. The extremities of a trough of twenty pairs of plates of Wollaston's construction were connected with the volta-electrometer, fig. 26 (446), of the fifth

part of these Researches, and after five minutes the number of bubbles of gas issuing from the extremity of the tube, in consequence of the decomposition of the water, noted. Without moving the plates, the acid between the copper and zinc was agitated by the introduction of a feather. The bubbles were immediately evolved more rapidly, about twice the number being produced in the same portion of time as before. In this instance it is very evident that agitation by a feather must have been a very imperfect mode of restoring the acid in the cells against the plates towards its first equal condition; and yet imperfect as the means were, they more than doubled the power of the battery. The *first effect* of a battery which is known to be so superior to the degree of action which the battery can sustain, is almost entirely due to the favourable condition of the acid in contact with the plates.

776. A *second* cause of diminution in the force of the voltaic battery, consequent upon its own action, is that extraordinary state of the surfaces of the metals (704) which was first described, I believe, by Ritter,[1] to which he refers the powers of his secondary piles, and which has been so well experimented upon by Marianini, and also by A. de la Rive. If the apparatus, fig. 63 (772), be left in action for an hour or two, with the wire 3 in contact with the plate *p*, so as to allow a free passage for the current, then, though the contact be broken for ten or twelve minutes, still, upon its renewal, only a feeble current will pass, not at all equal in force to what might be expected. Further, if P^1 and P^2 be connected by a metal wire, a powerful momentary current will pass from P^2 to P^1 through the acid, and therefore in the reverse direction to that produced by the action of the zinc in the arrangement; and after this has happened, the general current can pass through the whole of the system as at first, but by its passage again restores the plates P^2 and P^1 into the former opposing condition. This, generally, is the fact described by Ritter, Marianini, and De la Rive. It has great opposing influence on the action of a pile, especially if the latter consist of but a small number of alternations, and has to pass its current through many interpositions. It varies with the solution in which the interposed plates are immersed, with the intensity of the current, the strength of the pile, the time of action, and especially with accidental discharges of the plates by inadvertent contacts or reversions of the plates during experiments, and must be carefully watched

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[1] *Journal de Physique*, lvii. p. 349.

in every endeavour to trace the source, strength, and variations of the voltaic current. Its effect was avoided in the experiments already described (772, etc.), by making contact between the plates P^1 and P^2 before the effect dependent upon the state of the solution in contact with the zinc plate was observed, and by other precautions.

777. When an apparatus like fig. 58 (753) with several platina plates was used, being connected with a battery able to force a current through them, the power which they acquired, of producing a reverse current, was very considerable.

778. *Weak and exhausted charges* should never be used at the same time with *strong and fresh ones* in the different cells of a trough, or the different troughs of a battery: the fluid in all the cells should be alike, else the plates in the weaker cells, in place of assisting, retard the passage of the electricity generated in, and transmitted across, the stronger cells. Each zinc plate so circumstanced has to be assisted in decomposing power before the whole current can pass between it and the liquid. So that, if in a battery of fifty pairs of plates, ten of the cells contain a weaker charge than the others, it is as if ten decomposing plates were opposed to the transit of the current of forty pairs of generating plates (767). Hence a serious loss of force, and hence the reason why, if the ten pairs of plates were removed, the remaining forty pairs would be much more powerful than the whole fifty.

779. Five similar troughs, of ten pairs of plates each, were prepared, four of them with a good uniform charge of acid, and the fifth with the partially neutralised acid of a used battery. Being arranged in right order, and connected with a volta-electrometer (446), the whole fifty pairs of plates yielded 1.1 cubic inch of oxygen and hydrogen in one minute: but on moving one of the connecting wires so that only the four well-charged troughs should be included in the circuit, they produced with the same volta-electrometer 8.4 cubical inches of gas in the same time. Nearly seven-eighths of the power of the four troughs had been lost, therefore, by their association with the fifth trough.

780. The same battery of fifty pairs of plates, after being thus used, was connected with a volta-electrometer (446), so that by quickly shifting the wires of communication, the current of the whole of the battery, or of any portion of it, could be made to pass through the instrument for given portions of time in succession. The whole of the battery evolved 0.9 of a cubic inch of oxygen and hydrogen in half a minute; the forty

plates evolved 4.6 cubic inches in the same time; the whole then evolved 1 cubic inch in the half minute; the ten weakly charged evolved 0.4 of a cubic inch in the time given: and finally the whole evolved 1.15 cubic inch in the standard time. The order of the observations was that given: the results sufficiently show the extremely injurious effect produced by the mixture of strong and weak charges in the same battery.[1]

781. In the same manner associations of *strong and weak* pairs of plates should be carefully avoided. A pair of copper and platina plates arranged in *accordance* with a pair of zinc and platina plates in dilute sulphuric acid, were found to stop the action of the latter, or even of two pairs of the latter, as effectually almost as an interposed plate of platina (747), or as if the copper itself had been platina. It, in fact, became an interposed decomposing plate, and therefore a retarding instead of an assisting pair.

782. The *reversal*, by accident or otherwise, of the plates in a battery has an exceedingly injurious effect. It is not merely the counteraction of the current which the reversed plates can produce, but their effect also in retarding even as indifferent plates, and requiring decomposition to be effected upon their surface, in *accordance* with the course of the current, before the latter can pass. They oppose the current, therefore, in the first place, as interposed platina plates would do (747–754); and to this they add a force of opposition as counter-voltaic plates. I find that, in a series of four pairs of zinc and platina plates in dilute sulphuric acid, if one pair be reversed, it very nearly neutralises the power of the whole.

783. There are many other causes of reaction, retardation, and irregularity in the voltaic battery. Amongst them is the not unusual one of precipitation of copper upon the zinc in the cells, the injurious effect of which has before been adverted to (742). But their interest is not perhaps sufficient to justify any increase of the length of this paper, which is rather intended to be an investigation of the theory of the voltaic pile than a particular account of its practical application.

Note.—Many of the views and experiments in this part of my *Experimental Researches* will be seen at once to be corrections and extensions of the theory of electro-chemical decom-

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[1] The gradual increase in the action of the whole fifty pairs of plates was due to the elevation of temperature in the weakly charged trough by the passage of the current, in consequence of which the exciting energies of the fluid within were increased.

position, given in the third and fifth parts of these Researches. The expressions I would now alter are those which concern the independence of the evolved elements in relation to the poles or electrodes, and the reference of their evolution to powers entirely internal (260, 273, 397). The present paper fully shows my present views; and I would refer to paragraphs 626, 639, 645, 652, 653, 682, 698, 743, 767, etc., as stating what they are. I hope this note will be considered as sufficient in the way of correction at present; for I would rather defer revising the whole theory of electro-chemical decomposition until I can obtain clearer views of the way in which the power under consideration can appear at one time as associated with particles giving them their chemical attraction, and at another as free electricity (229, 692).—M. F.

March 31, 1834.

VII[1]

§ 9. ON THE SOURCE OF POWER IN THE VOLTAIC PILE. ¶ i. EXCITING ELECTROLYTES, ETC., BEING CONDUCTORS OF THERMO AND FEEBLE CURRENTS. ¶ ii. INACTIVE CONDUCTING CIRCLES CONTAINING AN ELECTROLYTIC FLUID. ¶ iii. ACTIVE CIRCLES EXCITED BY SOLUTION OF SULPHURET OF POTASSIUM, ETC.

§ 9. *On the Source of Power in the Voltaic Pile*

784. WHAT is the source of power in a voltaic pile? This question is at present of the utmost importance in the theory and to the development of electrical science. The opinions held respecting it are various; but by far the most important are the two which respectively find the source of power in contact, and in chemical force. The question between them touches the first principles of electrical action; for the opinions are in such contrast, that two men respectively adopting them are thenceforward constrained to differ, in every point, respecting the probable and intimate nature of the agent or force on which all the phenomena of the voltaic pile depend.

785. The theory of contact is the theory of Volta, the great discoverer of the voltaic pile itself, and it has been sustained since his day by a host of philosophers, amongst whom, in

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[1] Sixteenth Series, original edition, vol. ii. p. 18.

recent times, rank such men as Pfaff, Marianini, Fechner, Zamboni, Matteucci, Karsten, Bouchardat, and as to the excitement of the power, even Davy; all bright stars in the exalted regions of science. The theory of chemical action was first advanced by Fabroni,[1] Wollaston,[2] and Parrot,[3] and has been more or less developed since by Œrsted, Becquerel, De la Rive, Ritchie, Pouillet, Schœnbein, and many others, amongst whom Becquerel ought to be distinguished as having contributed, from the first, a continually increasing mass of the strongest experimental evidence in proof that chemical action always evolves electricity;[4] and De la Rive should be named as most clear and constant in his views, and most zealous in his production of facts and arguments, from the year 1827 to the present time.[5]

786. Examining this question by the results of definite electro-chemical action, I felt constrained to take part with those who believed the origin of voltaic power to consist in chemical action alone (610, 700), and ventured a paper on it in April, 1834[6] (610, etc.), which obtained the especial notice of Marianini.[7] The rank of this philosopher, the observation of Fechner,[8] and the consciousness that over the greater part of Italy and Germany the contact theory still prevailed, have induced me to re-examine the question most carefully. I wished not merely to escape from error, but was anxious to convince myself of the truth of the contact theory; for it was evident that if contact electromotive force had any existence, it must be a power not merely unlike every other natural power as to the phenomena it could produce, but also in the far higher points of limitation, definite force, and finite production (1053).

787. I venture to hope that the experimental results and arguments which have been thus gathered may be useful to science. I fear the detail will be tedious, but that is a necessary consequence of the state of the subject. The contact

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[1] A.D. 1792, 1799. Becquerel's *Traité de l'Electricité*, i. pp. 81-91, and Nicholson's *Quarto Journal*, iii. 308, iv. 120, or *Journal de Physique*, vi. 348.

[2] A.D. 1801. *Philosophical Transactions*, 1801, p. 427.

[3] A.D. 1801. *Annales de Chimie*, 1829, xlii. 45; 1831, xlvi. 361.

[4] A.D. 1824, etc. *Annales de Chimie*, 1824, xxv. 405; 1827, xxxv. 113; 1831, xlvi. 265, 276, 337; xlvii. 113; xlix. 131.

[5] *Ibid.* 1828, xxxvii. 225; xxxix. 297; 1836, lxii. 147: or *Mémoires de Genève*, 1829, iv. 285; 1832, vi. 149; 1835, vii.

[6] *Philosophical Transactions*, 1834, p. 425.

[7] *Memorie della Società Italiana in Modena*, 1837, xxi. p. 205.

[8] *Philosophical Magazine*, 1838, xiii. 205; or Poggendorf's *Annalen*, xlii. p. 481. Fechner refers also to Pfaff's reply to my paper. I never cease to regret that the German is a sealed language to me.

theory has long had possession of men's minds, is sustained by a great weight of authority, and for years had almost undisputed sway in some parts of Europe. If it be an error, it can only be rooted out by a great amount of forcible experimental evidence; a fact sufficiently clear to my mind by the circumstance, that De la Rive's papers have not already convinced the workers upon this subject. Hence the reason why I have thought it needful to add my further testimony to his and that of others, entering into detail and multiplying facts in a proportion far beyond any which would have been required for the proof and promulgation of a new scientific truth (1005). In so doing I may occasionally be only enlarging, yet then I hope strengthening, what others, and especially De la Rive, have done.

788. It will tend to clear the question, if the various views of contact are first stated. Volta's theory is, that the simple contact of conducting bodies causes electricity to be developed at the point of contact without any change in nature of the bodies themselves; and that though such conductors as water and aqueous fluids have this property, yet the degree in which they possess it is unworthy of consideration in comparison with the degree to which it rises amongst the metals.[1] The present views of the Italian and German contact philosophers are, I believe, generally the same, except that occasionally more importance is attached to the contact of the imperfect conductors with the metals. Thus Zamboni (in 1837) considers the metallic contact as the most powerful source of electricity, and not that of the metals with the fluids;[2] but Karsten, holding the contact theory, transfers the electromotive force to the contact of the fluids with the solid conductors.[3] Marianini holds the same view of the principle of contact, with this addition, that actual contact is not required to the exertion of the exciting force, but that the two approximated dissimiliar conductors may affect each other's state, when separated by sensible intervals of the $\frac{1}{10000}$dth of a line and more, air intervening.[4]

789. De la Rive, on the contrary, contends for simple and strict chemical action, and, as far as I am aware, admits of no current in the voltaic pile that is not conjoined with and dependent upon a complete chemical effect. That admirable electrician Becquerel, though expressing himself with great caution,

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[1] *Annales de Chimie*, 1802, xl. p. 225.
[2] *Bibliothèque Universelle*, 1836, v. 387; 1837, viii. 189.
[3] *L'Institut*, No. 150.
[4] *Mem. della Soc. Ital. in Modena*, 1837, xxi. 232-237.

seems to admit the possibility of chemical attractions being able to produce electrical currents when they are not strong enough to overcome the force of cohesion, and so terminate in combination.[1] Schœnbein states that a current may be produced by a tendency to chemical action, *i.e.* that substances which have a tendency to unite chemically may produce a current, though that tendency is not followed up by the actual combination of the substances.[2] In these cases the assigned force becomes the same as the contact of Volta, inasmuch as the acting matters are not altered whilst producing the current. Davy's opinion was, that contact like that of Volta excited the current or was the cause of it, but that chemical changes supplied the current. For myself I am at present of the opinion which De la Rive holds, and do not think that, in the voltaic pile, mere contact does anything in the excitation of the current, except as it is preparatory to, and ends in, complete chemical action.

790. Thus the views of contact vary, and it may be said that they pass gradually from one to another, even to the extent of including chemical action: but the two extremes appear to me irreconcilable in principle under any shape; they are as follows. The contact theory assumes that when two different bodies being conductors of electricity are in contact, there is a force at the point of contact by which one of the bodies gives a part of its natural portion of electricity to the other body, which the latter takes in addition to its own natural portion; that, though the touching points have thus respectively given and taken electricity, they cannot retain the charge which their contact has caused, but discharge their electricities to the masses respectively behind them (1055): that the force which, at the point of contact, induces the particles to assume a new state, cannot enable them to keep that state (1057): that all this happens without any permanent alteration of the parts that are in contact, and has no reference to their chemical forces (1053, 1057).

791. The chemical theory assumes that at the place of action the particles which are in contact act chemically upon each other and are able, under the circumstances, to throw more or less of the acting force into a dynamic form (682, 732): that in the most favourable circumstances, the whole is con-

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[1] *Annales de Chimie*, 1835, lx. 171; and *Traité de l'Electricité*, i. pp. 253, 258.

[2] *Philosophical Magazine*, 1838, xii. 227, 311, 314; also *Bibliothèque Universelle*, 1838, xiv. 155, 395.

verted into dynamic force (736): that then the amount of current force produced is an exact equivalent of the original chemical force employed; and that in no case (in the voltaic pile) can any electric current be produced, without the active exertion and consumption of an equal amount of chemical force, ending in a given amount of chemical change.

792. Marianini's paper[1] was to me a great motive for re-examining the subject; but the course I have taken was not so much for the purpose of answering particular objections, as for the procuring evidence, whether relating to controverted points or not, which should be satisfactory to my own mind, open to receive either one theory or the other. This paper, therefore, is not controversial, but contains further facts and proofs of the truth of De la Rive's views. The cases Marianini puts are of extreme interest, and all his objections must, one day, be answered, when numerical results, both as to intensity and quantity of force, are obtained; but they are all debatable, and, to my mind, depend upon variations of quantity which do not affect seriously the general question. Thus, when that philosopher quotes the numerical results obtained by considering two metals with fluids at their opposite extremities which tend to form counter currents, the difference which he puts down to the effect of metallic contact, either made or interrupted, I think accountable for, on the facts partly known respecting opposed currents; and with me differences quite as great, and greater, have arisen, and are given in former papers (782), when metallic contacts were in the circuit. So at page 213 of his memoir, I cannot admit that *e* should give an effect equal to the difference of *b* and *d*; for in *b* and *d* the opposition presented to the excited currents is merely that of a bad conductor, but in the case of *e* the opposition arises from the power of an opposed acting source of a current.

793. As to the part of his memoir respecting the action of sulphuretted solutions,[2] I hope to be allowed to refer to the investigations made further on. I do not find, as the Italian philosopher, that iron with gold or platina, in solution of the sulphuret of potassa, is positive to them,[3] but, on the contrary, powerfully negative, and for reasons given in the sequel (1037).

794. With respect to the discussion of the cause of the spark before contact,[4] Marianini admits the spark, but I give it up

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[1] *Memorie della Società Italiana in Modena*, 1827, xxi. p. 205.

[2] *Ibid.* p. 217.

[3] *Ibid.* p. 217.

[4] *Ibid.* p. 225.

altogether. Jacobi's paper[1] convinces me I was in error as to *that proof* of the existence of a state of tension in the metals before contact (650, 691). I need not therefore do more at present than withdraw my own observations.

795. I now proceed to address myself to the general argument, rather than to particular controversy, or to the discussion of cases feeble in power and doubtful in nature; for I have been impressed from the first with the feeling that it is no weak influence or feeble phenomenon that we have to account for, but such as indicates a force of extreme power, requiring, therefore, that the cause assigned should bear some proportion, both in intensity and quantity, to the effects produced.

796. The investigations have all been made by aid of currents and the galvanometer, for it seemed that such an instrument and such a course were best suited to an examination of the electricity of the voltaic pile. The electrometer is no doubt a most important instrument, but the philosophers who do use it are not of accord in respect to the safety and delicacy of its results. And even if the few indications as yet given by the electrometer be accepted as correct, they are far too general to settle the question of, whether contact or chemical action is the exciting force in the voltaic battery. To apply that instrument closely and render it of any force in supplying affirmative arguments to either theory, it would be necessary to construct a table of contacts, or the effects of contacts, of the different metals and fluids concerned in the construction of the voltaic pile, taken in pairs (856), expressing in such table both the *direction* and the *amount* of the contact force.

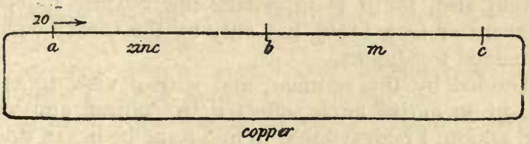

Fig. 64.

797. It is assumed by the supporters of the contact theory, that though the metals exert strong electromotive forces at their points of contact with each other, yet these are so balanced in a metallic circuit that no current is ever produced whatever their arrangement may be. So in fig. 64, if the contact force of copper and zinc is 10 ⟶, and a third metal be introduced at *m*, the effect of its contacts, whatever that metal may be, with the zinc

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[1] *Philosophical Magazine*, 1838, xiii. 401.

and copper at *b* and *c*, will be an amount of force in the opposite direction=10. Thus, if it were potassium, its contact force at *b* might be 5 →, but then its contact force at *c* would be ←15: or if it were gold, its contact force at *b* might be ←19, but then its contact force at *c* would be 9 →. This is a very large assumption, and that the theory may agree with the facts is necessary: still it is, I believe, only an assumption, for I am not aware of any data, independent of the theory in question, which prove its truth.

798. On the other hand, it is assumed that fluid conductors, and such bodies as contain water, or, in a word, those which I have called electrolytes (400, 558, 656), either exert no contact force at their place of contact with the metals, or if they do exert such a power, then it is with this most important difference, that the forces are not subject to the same law of compensation or neutralisation in the complete circuit, as holds with the metals (797). But this, I think I am justified in saying, is an assumption also, for it is supported not by any independent measurement or facts (796), but only by the theory which it is itself intended to support.

799. Guided by this opinion, and with a view to ascertain what is, in an active circle, effected by contact and what by chemical action, I endeavoured to find some bodies in this latter class (798), which should be without chemical action on the metals employed, so as to exclude that cause of a current, and yet such good conductors of electricity as to show any currents due to the contact of these metals with each other or with the fluid: concluding that any electrolyte which would conduct the thermo current of a single pair of bismuth and antimony plates would serve the required purpose, I sought for such, and fortunately soon found them.

¶ i. *Exciting Electrolytes, etc., being Conductors of Thermo and Feeble Currents*

800. *Sulphuret of potassium.*—This substance and its solution were prepared as follows. Equal weights of caustic potash (potassa fusa) and sulphur were mixed with and heated gradually in a Florence flask, till the whole had fused and united, and the sulphur in excess began to sublime. It was then cooled and dissolved in water, so as to form a strong solution, which by standing became quite clear.

801. A portion of this solution was included in a circuit containing a galvanometer and a pair of antimony and bismuth

plates; the connection with the electrolyte was made by two platinum plates, each about two inches long and half an inch wide: nearly the whole of each was immersed, and they were about half an inch apart. When the circuit was completed, and all at the same temperature, there was no current; but the moment the junction of the antimony and bismuth was either heated or cooled, the corresponding thermo current was produced, causing the galvanometer-needle to be permanently deflected, occasionally as much as 80°. Even the small difference of temperature occasioned by touching the Seebeck element with the finger, produced a very sensible current through the electrolyte. When in place of the antimony-bismuth combination mere wires of *copper and platinum*, or *iron and platinum* were used, the application of the spirit-lamp to the junction of these metals produced a thermo current which instantly travelled round the circuit.

802. Thus this electrolyte will, as to high conducting power, fully answer the condition required (799). It is so excellent in this respect, that I was able to send the thermo current of a single Seebeck's element across five successive portions connected with each other by platinum plates.

803. *Nitrous acid.*—Yellow anhydrous nitrous acid, made by distilling dry nitrate of lead, being put into a glass tube and included in a circuit with the antimony-bismuth arrangement and the galvanometer, gave no indication of the passage of the thermo current, though the immersed electrodes consisted each of about four inches in length of moderately thick platinum wire, and were not above a quarter of an inch apart.

804. A portion of this acid was mixed with nearly its volume of pure water; the resulting action caused depression of temperature, the evolution of some nitrous gas, the formation of some nitric acid, and a dark green fluid was produced. This was now such an excellent conductor of electricity that almost the feeblest current could pass it. That produced by Seebeck's circle was sensible when only one-eighth of an inch in length of the platinum wires dipped in the acid. When a couple of inches of each electrode was in the fluid, the conduction was so good that it made very little difference at the galvanometer whether the platinum wires touched each other in the fluid or were a quarter of an inch apart.[1]

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[1] De la Rive has pointed out the facility with which an electric current passes between platinum and nitrous acid.—*Annales de Chimie*, 1828, xxxvii. 278.

805. *Nitric acid.*—Some pure nitric acid was boiled to drive off all the nitrous acid, and then cooled. Being included in the circuit by platinum plates (801), it was found to conduct so badly that the effect of the antimony-bismuth pair, when the difference of temperature was at the greatest, was scarcely perceptible at the galvanometer.

806. On using a pale yellow acid, otherwise pure, it was found to possess rather more conducting power than the former. On employing a red nitric acid, it was found to conduct the thermo current very well. On adding some of the green nitrous acid (804) to the colourless nitric acid, the mixture acquired high conducting powers. Hence it is evident that nitric acid is not a good conductor when pure, but that the presence of nitrous acid in it (conjointly probably with water) gives it this power in a very high degree amongst electrolytes.[1] A very red strong nitric acid, and a weak green acid (consisting of one volume strong nitric acid and two volumes of water, which had been rendered green by the action of the negative platinum electrode of a voltaic battery), were both such excellent conductors that the thermo current could pass across five separate portions of them connected by platinum plates, with so little retardation, that I believe twenty interruptions would not have stopped this feeble current.

807. *Sulphuric acid.*—Strong oil of vitriol, when between platinum electrodes (801), conducted the antimony-bismuth thermo current sensibly, but feebly. A mixture of two volumes acid and one volume water conducted much better, but not nearly so well as the two former electrolytes (802, 804). A mixture of one volume of oil of vitriol and two volumes saturated solution of sulphate of copper conducted this feeble current very fairly.

Potassa.—A strong solution of caustic potassa, between platinum plates, conducted the thermo current sensibly, but very feebly.

808. I will take the liberty of describing here, as the most convenient place, other results relating to the conducting power of bodies, which will be required hereafter in these investigations. Galena, yellow sulphuret of iron, arsenical pyrites, native sulphuret of copper and iron, native grey artificial sulphuret of

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[1] Schœnbein's experiments on a compound of nitric and nitrous acids will probably bear upon and illustrate this subject.—*Bibliothèque Universelle*, 1817, x. 406.

copper, sulphurets of bismuth, iron, and copper, globules of oxide of burnt iron, oxide of iron by heat or scale oxide, conducted the thermo current very well. Native peroxide of manganese and peroxide of lead conducted it moderately well.

809. The following are bodies, in some respect analogous in nature and composition, which did not sensibly conduct this weak current when the contact surfaces were small:—artificial grey sulphuret of tin, blende, cinnabar, hæmatite, Elba iron-ore, native magnetic oxide of iron, native peroxide of tin or tinstone, wolfram, fused and cooled protoxide of copper, peroxide of mercury.

810. Some of the foregoing substances are very remarkable in their conducting power. This is the case with the solution of sulphuret of potassium (801) and the nitrous acid (804), for the great amount of this power. The peroxide of manganese and lead are still more remarkable for possessing this power, because the *protoxides* of these metals do not conduct either the feeble thermo current or a far more powerful one from a voltaic battery. This circumstance made me especially anxious to verify the point with the peroxide of lead. I therefore prepared some from red-lead by the action of successive portions of nitric acid, then boiled the brown oxide, so obtained, in several portions of distilled water, for days together, until every trace of nitric acid and nitrate of lead had been removed; after which it was well and perfectly dried. Still, when a heap of it in powder, and consequently in very imperfect contact throughout its own mass, was pressed between two plates of platinum and so brought into the thermo-electric circuit (801), the current was found to pass readily.

¶ ii. *Inactive Conducting Circles containing a Fluid or Electrolyte*

811. De la Rive has already quoted the case of potash, iron and platina,[1] to show that where there was no chemical action there was no current. My object is to increase the number of such cases; to use other fluids than potash, and such as have good conducting power for weak currents; to use also strong and weak solutions; and thus to accumulate the conjoint experimental and argumentative evidence by which the great question must finally be decided.

812. I first used the sulphuret of potassium as an electrolyte of good conducting power, but chemically inactive (799) when

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[1] *Philosophical Magazine*, 1837, xi. 275.

associated with iron and platinum in a circuit. The arrangement is given in fig. 65, where D, E represent two test-glasses containing the strong solution of sulphuret of potassium (800); and also four metallic plates, about 0.5 of an inch wide and two inches long in the immersed part, of which the three marked P, P, P were platinum, and that marked I, of clean iron: these were connected by iron and platinum wires, as in fig. 65, a galvanometer being introduced at G. In this arrangement there were three metallic contacts of platinum and iron, *a*, *b*, and *x*: the first two, being opposed to each other, may be considered as neutralising each other's forces; but the third, being unopposed by any other metallic contact, can be compared with either the difference of *a* and *b* when one is warmer than the other, or with itself when in a heated or cooled state (818), or with the force of chemical action when any body capable of such action is introduced there (819).

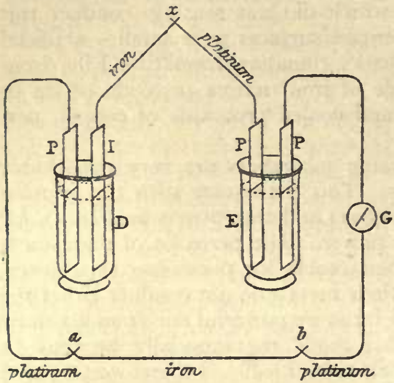

Fig. 65.

813. When this arrangement is completed and in order, there is absolutely no current circulating through it, and the galvanometer-needle rests at 0°; yet is the whole circuit open to a very feeble current, for a difference of temperature at any one of the junctions *a*, *b*, or *x*, causes a corresponding thermo current, which is instantly detected by the galvanometer, the needle standing permanently at 30° or 40°, or even 50°.

814. But to obtain this proper and normal state, it is necessary that certain precautions be attended to. In the first place, if the circuit be complete in every part except for the immersion of the iron and platinum plates into the cup D, then, upon their introduction, a current will be produced directed from the platinum (which appears to be positive) through the solution to the iron; this will continue perhaps five or ten minutes, or if the iron has been carelessly cleaned, for several hours; it is due to an action of the sulphuretted solution on

oxide of iron, and not to any effect on the metallic iron; and when it has ceased, the disturbing cause may be considered as exhausted. The experimental proofs of the truth of this explanation I will quote hereafter (1037).

815. Another precaution relates to the effect of accidental movements of the plates in the solution. If two platinum plates be put into a solution of this sulphuret of potassium, and the circuit be then completed, including a galvanometer, the arrangement, if perfect, will show no current; but if one of the plates be lifted up into the air for a few seconds and then replaced, it will be negative to the other, and produce a current lasting for a short time.[1] If the two plates be iron and platinum, or of any other metal or substance not acted on by the sulphuret, the same effect will be produced. In these cases, the current is due to the change wrought by the air on the film of sulphuretted solution adhering to the removed plate;[2] but a far less cause than this will produce a current, for if one of the platinum plates be removed, washed well, dried, and even heated, it will, on its re-introduction, almost certainly exhibit the negative state for a second or two.

816. These or other disturbing causes appear the greater in these experiments in consequence of the excellent conducting power of the solution used; but they do not occur if care be taken to avoid any disturbance of the plates or the solution, and then, as before said, the whole acquires a normal and perfectly inactive state.

817. Here then is an arrangement in which the contact of platinum and iron at x is at liberty to produce any effect which such a contact may have the power of producing; and yet what is the consequence? absolutely nothing. This is not because the electrolyte is so bad a conductor that a current of contact cannot pass, for currents far feebler than this is assumed to be pass readily (801); and the electrolyte employed is vastly superior in conducting power to those which are commonly used in voltaic batteries or circles, in which the current is still assumed to be dependent upon contact. The simple conclusion to which the experiment should lead is, in my opinion, that the contact of iron and platinum is absolutely without any electromotive force (823, 847, 877).

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[1] Marianini observed effects of this kind produced by exposure to the air, of one of two plates dipped in nitric acid.—*Annales de Chimie,* 1830, xlv. p. 42.

[2] Becquerel long since referred to the effect of such exposure of a plate, dipped in certain solutions, to the air. Generally the plate so exposed became positive on reimmersion.—*Annales de Chimie,* 1824, xxv. 405.

818. If the contact be made really active and effective, according to the beautiful discovery of Seebeck, by making its temperature different to that of the other parts of the circuit, then its power of generating a current is shown (812). This enables us to compare the supposed power of the mere contact with that of a thermo contact; and we find that the latter comes out as infinitely greater than the former, for the former is nothing. The same comparison of mere contact and thermo contact may be made by contrasting the effect of the contact *c* at common temperatures, with either the contact at *a* or at *b*, either heated or cooled. Very moderate changes of temperature at these places produce instantly the corresponding current, but the mere contact at *x* does nothing.

819. So also I believe that a true and philosophic and even rigid comparison may be made at *x*, between the assumed effect of mere contact and that of chemical action. For if the metals at *x* be separated, and a piece of paper moistened in dilute acid, or a solution of salt, or if only the tongue or a wet finger be applied there, then a current is caused, stronger by far than the thermo currents before produced (818), passing from the iron through the introduced acid or other active fluid to the platinum. This is a case of current from chemical action without any metallic contact in the circuit on which the effect can for a moment be supposed to depend (614); it is even a case where metallic contact is changed for chemical action, with the result that where contact is found to be quite ineffectual, chemical action is very energetic in producing a current.

820. It is of course quite unnecessary to say that the same experimental comparisons may be made at either of the other contacts, *a* or *b*.

821. Admitting for the moment that the arrangement proves that the contact of platinum and iron at *x* has no electromotive force (823, 847), then it follows also that the contact of either platinum or iron with any other metal has no such force. For if another metal, as zinc, be interposed between the iron and platinum at *x*, fig. 65, no current is produced; and yet the test application of a little heat at *a* or *b* will show by the corresponding current that the circuit being complete will conduct any current that may tend to pass. Now that the contacts of zinc with iron and with platinum are of equal electromotive force is not for a moment admitted by those who support the theory of contact activity; we ought therefore to have a resulting action equal to the differences of the two forces, producing

a certain current. No such current is produced, and I conceive, with the admission above, that such a result proves that the contacts *iron-zinc* and *platinum-zinc* are entirely without electromotive force.

822. Gold, silver, potassium, and copper were introduced at x with the like negative effect; and so no doubt might every other metal, even according to the relation admitted amongst the metals by the supporters of the contact theory (797). The same negative result followed upon the introduction of many other conducting bodies at the same place; as, for instance, those already mentioned as easily conducting the thermo current (808); and the effect proves, I think, that the contact of any of these with either iron or platinum is utterly ineffective as a source of electromotive force.

823. The only answer which, as it appears to me, the contact theory can set up in opposition to the foregoing facts and conclusions is to say that the solution of sulphuret of potassium in the cup D, fig. 65, acts as a metal would do (797), and so the effects of all the contacts in the circuit are exactly balanced. I will not stop at this moment to show that the departure with respect to electrolytes, or the fluid bodies in the voltaic pile, *from the law* which is supposed to hold good with the metals and solid conductors, though only an assumption, is still essential to the contact theory of the voltaic pile (798, 849);[1] nor to prove that the electrolyte is no otherwise like the metals than in having no contact electromotive force whatever. But believing that this will be very evident shortly, I will go on with the experimental results, and resume these points hereafter (847, 877).

824. The experiment was now repeated with the substitution of a bar of *nickel* for that of iron, fig. 65 (812), all other things remaining the same.[2] The circuit was again found to be a good conductor of a feeble thermo current, but utterly inefficient as a voltaic circuit when all was at the same temperature, and due precautions taken (1039). The introduction of metals at the

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[1] See Fechner's words.—*Philosophical Magazine*, 1838, xiii. 377.

[2] There is another form of this experiment which I sometimes adopted, in which the cup E, fig. 65, with its contents, was dismissed, and the platinum plates in it connected together. The arrangement may then be considered as presenting three contacts of iron and platinum, two acting in one direction, and one in the other. The arrangement and the results are virtually the same as those already given. A still simpler but equally conclusive arrangement for many of the arguments, is to dismiss the iron between a and b altogether, and so have but one contact, that at x, to consider.

contact x was as ineffective as before (822); the introduction of chemical action at x was as striking in its influence as in the former case (819); all the results were, in fact, parallel to those already obtained; and if the reasoning then urged was good, it will now follow that the contact of platinum and nickel with each other, or of either with any of the different metals or solid conductors introduced at x, is entirely without electromotive force.[1]

825. Many other pairs of metals were compared together in the same manner; the solution of sulphuret of potassium connecting them together at one place, and their mutual contact doing that office at another. The following are cases of this kind: iron and gold; iron and palladium; nickel and gold; nickel and palladium; platina and gold; platina and palladium. In all these cases the results were the same as those already given with the combinations of platinum and iron.

826. It is necessary that due precaution be taken to have the arrangements in an unexceptionable state. It often happened that the first immersion of the plates gave deflections; it is, in fact, almost impossible to put two plates of the *same metal* into the solution without causing a deflection; but this generally goes off very quickly, and then the arrangement may be used for the investigation (814). Sometimes there is a feeble but rather permanent deflection of the needle; thus when platinum and palladium were the metals, the first effect fell and left a current able to deflect the galvanometer-needle 3°, indicating the platinum to be positive to the palladium. This effect of 3°, however, is almost nothing compared to what a mere thermo current can cause, the latter producing a deflection of 60° or more; besides which, even supposing it an essential effect of the arrangement, it is in the wrong direction for the contact theory. I rather incline to refer it to that power which platinum and other substances have of effecting combination and decomposition without themselves entering into union; and I have occasionally found that when a platinum plate has been left for some hours in a strong solution of sulphuret of potassium (800) a small quantity of sulphur has been deposited upon it. Whatever the cause of the final feeble current may be, the effect is

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[1] One specimen of nickel was, on its immersion, positive to platinum for seven or eight minutes, and then became neutral. On taking it out it seemed to have a yellowish tint on it, as if invested by a coat of sulphuret; and I suspected this piece had acted like lead (873) and bismuth (883). It is difficult to get pure and also perfectly compact nickel; and if porous, then the matter retained in the pores produces currents.

too small to be of any service in support of the contact theory; while, on the other hand, it affords delicate, and, therefore, strong indications in favour of the chemical theory.

827. A change was made in the form and arrangement of the cup D, fig. 65, so as to allow of experiments with other bodies than the metals. The solution of sulphuret of potassium was placed in a shallow vessel, the platinum plate was bent so that the immersed extremity corresponded to the bottom of the vessel; on this a piece of loosely folded cloth was laid in the solution, and on that again the mineral or other substance to be compared with the platinum; the fluid being of such depth that only part of that substance was in it, the rest being clean and dry; on this portion the platinum wire, which completed the circuit, rested. The arrangement of this part of the circuit is given in section at fig. 66, where H represents a piece of galena to be compared with the platinum P.

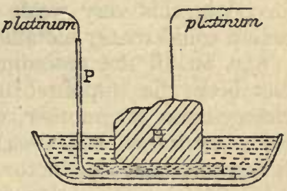

Fig. 66.

828. In this way galena, compact yellow copper pyrites, yellow iron pyrites, and globules of oxide of burnt iron, were compared with platinum (the solution of sulphuret of potassium being the electrolyte used in the circuit), and with the same results as were before obtained with metals (817, 821).

829. Experiments hereafter to be described gave arrangements in which, with the same electrolyte, sulphuret of lead was compared with gold, palladium, iron, nickel, and bismuth (873, 874); also sulphuret of bismuth with platinum, gold, palladium, iron, nickel, lead, and sulphuret of lead (882), and always with the same result. Where no chemical action occurred there no current was formed; although the circuit remained an excellent conductor, and the contact existed by which, it is assumed in the contact theory, such a current should be produced.

830. Instead of the strong solution, a dilute solution of the yellow sulphuret of potassium, consisting of one volume of strong solution (800) and ten volumes of water, was used. Plates of platinum and iron were arranged in this fluid as before (812): at first the iron was negative (1037), but in ten minutes it was neutral, and the needle at 0. Then a weak chemical current excited at *x* (819) easily passed: and even a thermo current (818) was able to show its effects at the needle. Thus

a strong or weak solution of this electrolyte showed the same phenomena.[1] By diluting the solution still further, a fluid could be obtained in which the iron was, after the first effect, permanently but feebly positive. On allowing time, however, it was found that in all such cases black sulphuret formed here and there on the iron. Rusted iron was negative to platinum (1037) in this very weak solution, which by direct chemical action could render metallic iron positive.

831. In all the preceding experiments the electrolyte used has been the sulphuret of potassium solution; but I now changed this for another, very different in its nature, namely, the *green nitrous acid* (804), which has already been shown to be an excellent conductor of electricity. Iron and platinum were the metals employed, both being in the form of wires. The vessel in which they were immersed was a tube like that formerly described (803); in other respects the arrangement was the same in principle as those already used (812, 824). The first effect was the production of a current, the iron being positive in the acid to the platina; but this *quickly ceased*, and the galvanometer-needle came to 0°. In this state, however, the circuit could not in all things be compared with the one having the solution of sulphuret of potassium for its electrolyte (812); for although it could conduct the thermo current of antimony and bismuth in a certain degree, yet that degree was very small compared to the power possessed by the former arrangement, or to that of a circle in which the nitrous acid was between two platinum plates (804). This remarkable retardation is consequent upon the assumption by the iron of that peculiar state which Schœnbein has so well described and illustrated by his numerous experiments and investigations. But though it must be admitted that the iron in contact with the acid is in a peculiar state (939, 989, 1021), yet it is also evident that a circuit consisting of platinum, iron, peculiar iron, and nitrous acid, does not cause a current though it have sufficient conducting power to carry a thermo current.

832. But if the contact of platinum and iron has an electromotive force, why does it not produce a current? The application of heat (818), or of a little chemical action (819) at the place of contact, does produce a current, and in the latter case

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[1] Care was taken in these and the former similar cases to discharge the platinum surface of any reacting force it might acquire from the action of the previous current, by separating it from the other metals, and touching it in the liquid for an instant with another platinum plate.

a strong one. Of if any other of the contacts in the arrangement can produce a current, why is not that shown by some corresponding effect? The only answers are, to say, that the peculiar iron has the same electromotive properties and relations as platinum, or that the nitrous acid is included under the same law with the metals (797, 823); and so the sum of the effects of all the contacts in the circuit is nought, or an exact balance of forces. That the iron is like the platinum in having no electromotive force at its contacts without chemical action, I believe; but that it is unlike it in its electrical relations, is evident from the difference between the two in strong nitric acid, as well as in weak acid; from their difference in the power of transmitting electric currents to either nitric acid or sulphuret of potassium, which is very great; and also by other differences. That the nitrous acid is, as to the power of its contacts, to be separated from other electrolytes and classed with the metals in what is, with them, only an assumption, is a gratuitous mode of explaining the difficulty, which will come into consideration, with the case of sulphuret of potassium, hereafter (823, 847, 877, 1048).

833. To the electro-chemical philosopher, the case is only another of the many strong instances, showing that where chemical action is absent in the voltaic circuit, there no current can be formed; and that whether solution of sulphuret of potassium or nitrous acid be the electrolyte or connecting fluid used, still the results are the same, and contact is shown to be inefficacious as an active electromotive condition.

834. I need not say that the introduction of different metals between the iron and platinum at their point of contact, produced no difference in the results (821, 822) and caused no current; and I have said that heat and chemical action applied there produced their corresponding effects. But these parallels in action and non-action show the identity in nature of this circuit (notwithstanding the production on the surface of peculiar iron on that metal), and that with solution of sulphuret of potassium: so that all the conclusions drawn from it apply here; and if that case ultimately stand firm as a proof against the theory of contact force, this will stand also.

835. I now used oxide of iron and platinum as the extremes of the solid part of the circuit, and the nitrous acid as the fluid; *i.e.* I heated the iron wire in the flame of a spirit-lamp, covering it with a coat of oxide in the manner recommended by Schœnbein in his investigations, and then used it instead of

the clean iron (831). The oxide of iron was at first in the least degree positive, and then immediately neutral. This circuit, then, like the former, gave no current at common temperatures; but it differed much from it in conducting power, being a very excellent conductor of a thermo current, the oxide of iron not offering that obstruction to the passage of the current which the peculiar iron did (831, 832). Hence scale oxide of iron and platinum produce no current by contact, the third substance in the proof circuit being nitrous acid; and so the result agrees with that obtained in the former case, where that third substance was solution of sulphuret of potassium.

836. In using nitrous acid it is necessary that certain precautions be taken, founded on the following effect. If a circuit be made with the green nitrous acid, platinum wires, and a galvanometer, in a few seconds all traces of a current due to first disturbances will disappear; but if one wire be raised into the air and instantly returned to its first position, a current is formed, and that wire is negative, across the electrolyte, to the other. If one wire be dipped only a small distance into the acid, as for instance one-fourth of an inch, then the raising that wire not more than one-eighth of an inch and instantly restoring it, will produce the same effect as before. The effect is due to the evaporation of the nitrous acid from the exposed wire (925). I may perhaps return to it hereafter, but wish at present only to give notice of the precaution that is required in consequence, namely, to retain the immersed wires undisturbed during the experiment.

837. Proceeding on the facts made known by Schœnbein respecting the relation of iron and nitric acid, I used that acid as the fluid in a voltaic current formed with iron and platinum. Pure nitric acid is so deficient in conducting power (805) that it may be supposed capable of stopping any current due to the effect of contact between the platinum and iron; and it is further objectionable in these experiments, because, acting feebly on the iron, it produces a chemically excited current, which may be considered as mingling its effect with that of contact: whereas the object at present is, by excluding such chemical action, to lay bare the influence of contact alone. Still the results with it are consistent with the more perfect ones already described; for in a circuit of iron, platinum, and nitric acid, the joint effects of the chemical action on the iron and the contact of iron and platinum, being to produce a current

of a certain constant force indicated by the galvanometer, a little chemical action, brought into play where the iron and platinum were in contact as before (819), produced a current far stronger than that previously existing. If then, from the weaker current, the part of the effect due to chemical action be abstracted, how little room is there to suppose that any effect is due to the contact of the metals!

838. But a *red nitric acid* with platinum plates conducts a thermo current well, and will do so even when considerably diluted (806). When such red acid is used between iron and platinum, the conducting power is such, that one half of the permanent current can be overcome by a counter thermo current of bismuth and antimony. Thus a sort of comparison is established between a thermo current on the one hand, and a current due to the joint effects of chemical action on iron and contact of iron and platinum on the other. Now considering the admitted weakness of a thermo current, it may be judged what the strength of that part of the second current due to contact can at the utmost be; and how little it is able to account for the strong currents produced by ordinary voltaic combinations.

839. If for a clean iron wire one oxidised in the flame of a spirit-lamp be used, being associated with platinum in pure strong nitric acid, there is a feeble current, the oxide of iron being positive to the platinum, and the facts mainly as with iron. But the further advantage is obtained of comparing the contact of strong and weak acid with this oxidised wire. If one volume of the strong acid and four volumes of water be mixed, this solution may be used, and there is even less deflection than with the strong acid: the iron side is now not sensibly active, except the most delicate means be used to observe the current. Yet in both cases if a chemical action be introduced in place of the contact, the resulting current passes well, and even a thermo current can be made to show itself as more powerful than any due to contact.

840. In these cases it is safest to put the whole of the oxidised iron under the surface and connect it in the circle by touching it with a platinum wire; for if the oxidised iron be continued through from the acid to the air, it is almost certain to suffer from the joint action of the acid and air at their surface of contact.

841. I proceeded to use a fluid differing from any of the

former: this was solution of *potassa*, which has already been employed by De la Rive (811) with iron and platina, and which when strong has been found to be a substance conducting so well, that even a thermo current could pass it (807), and therefore fully sufficient to show a contact current, if any such exists.

842. Yet when a strong solution of this substance was arranged with silver and platinum (bodies differing sufficiently from each other when connected by nitric or muriatic acid), as in the former cases, a very feeble current was produced, and the galvanometer-needle stood nearly at zero. The contact of these metals therefore did not appear to produce a sensible current; and, as I fully believe, because no electromotive power exists in such contact. When that contact was exchanged for a very feeble chemical action, namely, that produced by interposing a little piece of paper moistened in dilute nitric acid (819), a current was the result. So here, as in the many former cases, the arrangement with a little chemical action and no metallic contact produces a current, but that without the chemical action and with the metallic contact produces none.

843. Iron or nickel associated with platinum in this strong solution of potassa was positive. The force of the produced current soon fell, and after an hour or so was very small. Then annulling the metallic contact at *x*, fig. 65, and substituting a feeble chemical action there, as of dilute nitric acid, the current established by the latter would pass and show itself. Thus the cases are parallel to those before mentioned (837, etc.), and show how little contact alone could do, since the effect of the conjoint contact of iron and platinum and chemical action of potash and iron were very small as compared with the contrasted chemical action of the dilute nitric acid.

844. Instead of a strong solution of potassa, a much weaker one consisting of one volume of strong solution and six volumes of water was used, but the results with the silver and platinum were the same: no current was produced by the metallic contact as long as that only was left for exciting cause, but on substituting a little chemical action in its place (819), the current was immediately produced.

845. Iron and nickel with platinum in the weak solution also produced similar results, except that the positive state of these metals was rather more permanent than with the strong solution. Still it was so small as to be out of all proportion to what was to be expected according to the contact theory.

846. Thus these different contacts of metals and other well-conducting solid bodies prove utterly inefficient in producing a current, as well when solution of potassa is the third or fluid body in the circuit, as when that third body is either solution of sulphuret of potassium, or hydrated nitrous acid, or nitric acid, or mixed nitric and nitrous acids. Further, all the arguments respecting the inefficacy of the contacts of bodies interposed at the junction of the two principal solid substances, which were advanced in the case of the sulphuret of potassium solution (821), apply here with potassa; as they do indeed in every case of a conducting circuit where the interposed fluid is without chemical action and no current is produced. If a case could be brought forward in which the interposed fluid is without action, is yet a sufficiently good conductor, and a current *is* produced; then, indeed, the theory of contact would find evidence in its favour, which, as far as I can perceive, could not be overcome. I have most anxiously sought for such a case, but cannot find one (786).

847. The argument is now in a fit state for the resumption of that important point before adverted to (823, 832), which, if truly advanced by an advocate for the contact theory, would utterly annihilate the force of the previous experimental results, though it would not enable that theory to give a reason for the activity of, and the existence of a current in, the pile; but which, if in error, would leave the contact theory utterly defenceless and without foundation.

848. A supporter of the contact theory may say that the various conducting electrolytes used in the previous experiments are like the metals; *i.e.* that they have an electromotive force at their points of contact with the metals and other solid conductors employed to complete the circuit; but that this is of such consistent strength at each place of contact, that, in a complete circle, the sum of the forces is 0 (797). The actions at the contacts are tense electromotive actions, but balanced, and so no current is produced. But what experiment is there to support this statement? where are the measured electromotive results proving it (796)? I believe there are none.

849. The contact theory, after assuming that mere contacts of dissimilar substances have electromotive powers, further assumes a difference between metals and liquid conductors (798) without which it is impossible that the theory can explain the current in the voltaic pile: for whilst the contact effects in a

metallic circuit are assumed to be always perfectly balanced, it is also assumed that the contact effects of the electrolytes or interposed fluid with the metals are not balanced, but are so far removed from anything like an equilibrium, as to produce most powerful currents, even the strongest that a voltaic pile can produce. If so, then why should the solution of sulphuret of potassium be an exception? it is quite unlike the metals: it does not appear to conduct without decomposition; it is an excellent electrolyte, and an excellent *exciting* electrolyte in proper cases (868), producing most powerful currents when it acts chemically; it is in all these points quite unlike the metals, and, in its action, like any of the acid or saline exciting electrolytes commonly used. How then can it be allowed that, without a single direct experiment, and solely for the purpose of avoiding the force of those which are placed in opposition, we should suppose it to leave its own station amongst the electrolytes, and class with the metals; and that too, in a point of character, which, even with them, is as yet a mere assumption (797)?

850. But it is not with the sulphuret of potassium alone that this freedom must be allowed; it must be extended to the nitrous acid (831, 835), to the nitric acid (837, etc.), and even to the solution of potash (842); all these being of the class of electrolytes, and yet exhibiting no current in circuits where they do not occasion chemical action. Further, this exception must be made for *weak solutions* of sulphuret of potassium (830) and of potassa (844), for they exhibit the same phenomena as the stronger solutions. And if the contact theorists claim it for these weak solutions, then how will they meet the case of weak nitric acid which is not similar in its action on iron to strong nitric acid (965), but can produce a powerful current?

851. The chemical philosopher is embarrassed by none of these difficulties; for he first, by a simple direct experiment, ascertains whether any of the two given substances in the circuit are active chemically on each other. If they are, he expects and finds the corresponding current; if they are not, he expects and he finds no current, though the circuit be a good conductor and he look carefully for it (817).

852. Again; taking the case of iron, platina, and solution of sulphuret of potassium, there is no current; but for iron substitute zinc, and there is a powerful current. I might for zinc substitute copper, silver, tin, cadmium, bismuth, lead, and other metals; but I take zinc, because its sulphuret dissolves

and is carried off by the solution, and so leaves the case in a very simple state; the fact, however, is as strong with any of the other metals. Now if the contact theory be true, and if the iron, platina, and solution of sulphuret of potassium give contacts which are in perfect equilibrium as to their electromotive force, then why does changing the iron for zinc destroy the equilibrium? Changing one metal for another in a metallic circuit causes no alteration of this kind: nor does changing one substance for another among the great number of bodies which, as solid conductors, may be used to form conducting (but chemically inactive) circuits (855, etc.). If the solution of sulphuret of potassium is to be classed with the metals as to its action in the experiments I have quoted (813, etc.), then, how comes it to act quite unlike them, and with a power equal to the *best* of the other class, in the new case; of zinc, copper, silver, etc. (870, 873, etc.)?

853. This difficulty, as I conceive, must be met, on the part of the contact theorists, by a new assumption, namely, that this fluid sometimes acts as the best of the metals, or first class of conductors, and sometimes as the best of the electrolytes or second class. But surely this would be far too loose a method of philosophising in an experimental science (857); and further, it is most unfortunate for such an assumption, that this second condition or relation of it never comes on by itself, so as to give us a pure case of a current from contact alone; it never comes on *without* that chemical action to which the chemist so simply refers all the current which is then produced.

854. It is unnecessary for me to say that the same argument applies with equal force to the cases where nitrous acid, nitric acid, and solution of potash are used; and it is supported with equal strength by the results which they have given (831, 837, 841).

855. It may be thought that it was quite unnecessary, but in my desire to establish contact electromotive force, to do which I was at one time very anxious, I made many circuits of three substances, including a galvanometer, all being conductors, with the hope of finding an arrangement, which, without chemical action, should produce a current. The number and variety of these experiments may be understood from the following summary; in which metals, plumbago, sulphurets and oxides, all being conductors even of a thermo current, were thus combined in various ways:

1. Platinum.
2. Iron.
3. Zinc.
4. Copper.
5. Plumbago.
6. Scale oxide of iron.
7. Native peroxide of manganese.
8. Native grey sulphuret of copper.
9. Native iron pyrites.
10. Native copper pyrites.
11. Galena.
12. Artificial sulphuret of copper.
13. Artificial sulphuret of iron.
14. Artificial sulphuret of bismuth.

1 and 2 with 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, in turn.
1 and 3 with 5, 6, 7, 8, 9, 10, 11, 12, 13, 14.
1 and 5 with 6, 7, 8, 9, 10, 11, 12, 13, 14.
3 and 6 with 7, 8, 9, 10, 11, 12, 13, 14.
4 and 5 with 6, 7, 8, 9, 10, 11, 12, 13, 14.
4 and 6 with 7, 8, 9, 10, 11, 12, 13, 14.
4 and 7 with 8, 9, 10, 11, 12, 13, 14.
4 and 8 with 9, 10, 11, 12, 13, 14.
4 and 9 with 10, 11, 12, 13, 14.
4 and 10 with 11, 12, 13, 14.
4 and 11 with 12, 13, 14.
4 and 12 with 13, 14.
4 and 13 with 14.
1 and 4 with 12.

856. Marianini states from experiment that copper is positive to sulphuret of copper;[1] with the Voltaists, according to the same philosopher, sulphuret of copper is positive to iron (866), and with them also iron is positive to copper. These three bodies therefore ought to give a most powerful circle: but on the contrary, whatever sulphuret of copper I have used, I have found not the slightest effect from such an arrangement.

857. As peroxide of lead is a body causing a powerful current in solution of sulphuret of potassium, and indeed in every case of a circuit where it can give up part of its oxygen, I thought it reasonable to expect that its contact with metals would produce a current, if contact ever could. A part of that which had been prepared (810), was therefore well dried, which is

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[1] *Memorie della Società Italiana in Modena*, 1827, xxi. 224.

quite essential in these cases, and formed into the following combinations:

Platinum.	Zinc.	Peroxide of lead.
Platinum.	Lead.	Peroxide of lead.
Platinum.	Cadmium.	Peroxide of lead.
Platinum.	Iron.	Peroxide of lead.

Of these varied combinations, not one gave the least signs of a current, provided differences of temperature were excluded; though in every case the circle formed was, as to conducting power, perfect for the purpose, *i.e.* able to conduct even a very weak thermo current.

858. In the contact theory it is not therefore the metals alone that must be assumed to have their contact forces so balanced as to produce, in any circle of them, an effect amounting to nothing (797); but all solid bodies that are able to conduct, whether they be forms of carbon, or oxides, or sulphurets, must be included in the same category. So also must the electrolytes already referred to, namely, the solutions of sulphuret of potassium and potash, and nitrous and nitric acids, in every case where they do not act chemically. In fact *all conductors* that do not act chemically in the circuit must be assumed, by the contact theory, to be in this condition, until a case of voltaic current without chemical action is produced (846).

859. Then, even admitting that the results obtained by Volta and his followers with the electrometer prove that mere contact has an electromotive force and can produce an effect, surely all experience with contact alone goes to show that the electromotive forces in a circuit are always balanced. How else is it likely that the above-named most varied substances should be found to agree in this respect? unless indeed it be, as I believe, that all substances agree in this, of having no such power at all. If so, then where is the source of power which can account by the theory of contact for the current in the voltaic pile? If they are not balanced, then where is the sufficient case of contact alone producing a current? or where are the numerical data which indicate that such a case can be (796, 856)? The contact philosophers are bound to produce, not a case where the current is infinitesimally small, for such cannot account for the current of the voltaic pile, and will always come within the debatable ground which De la Rive has so well defended, but a case and data of such distinctness and importance as may be

worthy of opposition to the numerous cases produced by the chemical philosopher (880); for without them the contact theory as applied to the pile appears to me to have *no* support, and, as it asserts contact electromotive force even *with* the balanced condition, to be almost without foundation.

860. To avoid these and similar conclusions, the contact theory must bend about in the most particular and irregular way. Thus the contact of solution of sulphuret of potassium with iron must be considered as balanced by the joint force of its contact with platinum, and the contact of iron and platinum with each other; but changing the iron for lead, then the contact of the sulphuret with the latter metal is no longer balanced by the other two contacts, it has all of a sudden changed its relation: after a few seconds, when a film of sulphuret has been formed by the chemical action, then the current ceases, though the circuit be a good conductor (873); and now it must be assumed that the solution has acquired its first relation to the metals and to the sulphuret of lead, and gives an equilibrium condition of the contacts in the circle.

861. So also with this sulphuretted solution and with potassa, dilution must, by the theory, be admitted as producing *no change* in the character of the contact force; but with nitric acid, it, on the contrary, must be allowed to change the character of the force greatly (965). So again acids and alkalies (as potassa) in the cases where the currents are produced by them, as with zinc and platinum for instance, must be assumed as giving the preponderance of electromotive force on the same side, though these are bodies which might have been expected to give opposite currents, since they differ so much in their nature.

862. Every case of a current is obliged to be met, on the part of the contact advocates, by assuming powers at the points of contact, in *the particular case,* of such proportionate strengths as will consist with the results obtained, and the theory is made to bend about, having no general relation for the acids or alkalies, or other electrolytic solution used. The result therefore comes to this: The theory can predict nothing regarding the results; it is accompanied by no case of a voltaic current produced without chemical action, and in those associated with chemical action it bends about to suit the real results, these contortions being exactly parallel to the variations which the pure chemical force, by experiment, indicates.

863. In the midst of all this, how simply does the chemical

theory meet, include, combine, and even predict, the numerous experimental results! When there is a current there is also chemical action; when the action ceases, the current stops (870, 873, 882); the action is determined either at the anode or the cathode, according to circumstances (1027, 1029), and the direction of the current is invariably associated with the direction in which the active chemical forces oblige the anions and cations to move in the circle (697, 1040).

864. Now when in conjunction with these circumstances it is considered, that the many arrangements without chemical action (813, etc.) produce no current; that those with chemical action almost always produce a current; that hundreds occur in which chemical action without contact produces a current (1005, etc.); and that as many with contact but without chemical action (855) are known and are inactive; how can we resist the conclusion, that the powers of the voltaic battery originate in the exertion of chemical force?

¶ iii. *Active Circles excited by Solution of Sulphuret of Potassium*

865. In 1812 Davy gave an experiment to show, that of two different metals, copper and iron, that having the strongest attraction for oxygen was positive in oxidising solutions, and that having the strongest attraction for sulphur was positive in sulphuretting solutions.[1] In 1827 De la Rive quoted several such inversions of the states of two metals, produced by using different solutions, and reasoned from them, that the mere contact of the metals could not be the cause of their respective states, but that the chemical action of the liquid produced these states.[2]

866. In a former paper I quoted Sir Humphry Davy's experiment (678), and gave its result as a proof that the contact of the iron and copper could not originate the current produced; since when a dilute acid was used in place of the sulphuret, the current was reverse in direction, and yet the contact of the metals remained the same. M. Marianini[3] adds, that copper will produce the same effect with tin, lead, and even zinc; and also that silver will produce the same results as copper. In the case of copper he accounts for the effect by

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[1] *Elements of Chemical Philosophy*, p. 148.

[2] *Annales de Chimie*, 1828, xxxvii. 231-237; xxxix. 299.

[3] *Memorie della Società Italiana in Modena*, 1837, xxi. p. 224.

referring it to the relation of the iron and the new body formed on the copper, the latter being, according to Volta, positive to the former.[1] By his own experiment the same substance was negative to the iron across the same solution.[2]

867. I desire at present to resume the class of cases where a solution of sulphuret of potassium is the liquid in a voltaic circuit; for I think they give most powerful proof that the current in the voltaic battery cannot be produced by contact, but is due altogether to chemical action.

868. The solution of sulphuret of potassium (800) is a most excellent conductor of electricity (802). When subjected between platinum electrodes to the decomposing power of a small voltaic battery, it readily gave pure sulphur at the anode, and a little gas, which was probably hydrogen, at the cathode. When arranged with platinum surfaces so as to form a Ritter's secondary pile, the passage of a feeble primary current, for a few seconds only, makes this secondary battery effective in causing a counter current; so that, in accordance with electrolytic conduction (658), it probably does not conduct without decomposition, or if at all, its point of electrolytic intensity (701, 718) must be very low. Its exciting action (speaking on the chemical theory) is either the giving an anion (sulphur) to such metallic and other bodies as it can act upon, or, in some cases, as with the peroxides of lead and manganese, and the protoxide of iron (1034), the abstraction of an anion *from* the body in contact with it, the current produced being in the one or the other direction accordingly. Its chemical affinities are such, that in many cases its anion goes to that metal, of a pair of metals, which is left untouched when the usual exciting electrolytes are employed; and so a beautiful inversion of the current in relation to the metals is obtained; thus, when copper and nickel are used with it, the anion goes to the copper; but when the same metals are used with the ordinary electrolytic fluids, the anion goes to the nickel. Its excellent conducting power renders the currents it can excite very evident and strong; and it should be remembered that the strength of the resulting currents, as indicated by the galvanometer, depends jointly upon the energy (not the mere quantity) of the exciting action called into play, and the conductive ability of the circuit through which the current has to run. The value of this exciting electrolyte is increased for the present

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[1] *Memorie della Società Italiana in Modena*, 1837, xxi. p. 219.

[2] *Ibid.* p. 224.

investigation, by the circumstance of its giving, by its action on the metals, resulting compounds, some of which are insoluble, whilst others are soluble; and, of the insoluble results, some are excellent conductors, whilst others have no conducting power at all.

869. The experiments to be described were made generally in the following manner. Wires of platinum, gold, palladium, iron, lead, tin, and the other malleable metals, about one-twentieth of an inch in diameter and six inches long, were prepared. Two of these being connected with the ends of the galvanometer-wires, were plunged at the same instant into the solution of sulphuret of potassium in a test-glass, and kept there without agitation (907), the effects at the same time being observed. The wires were in every case carefully cleansed with fresh fine sand-paper and a clean cloth; and were sometimes even burnished by a glass rod, to give them a smooth surface. Precautions were taken to avoid any difference of temperature at the junctions of the different metals with the galvanometer wires.

870. *Tin and platinum.*—When tin was associated with platinum, gold, or, I may say, any other metal which is chemically inactive in the solution of the sulphuret, a strong electric current was produced, the tin being positive to the platinum through the solution, or, in other words, the current being from the tin through the solution to the platinum. In a very short time this current fell greatly in power, and in ten minutes the galvanometer-needle was nearly at 0°. On then endeavouring to transmit the antimony-bismuth thermo current (813) through the circuit, it was found that it could not pass, the circle having lost its conducting power. This was the consequence of the formation on the tin of an insoluble, investing, non-conducting sulphuret of that metal; the non-conducting power of the body formed is not only evident from the present result, but also from a former experiment (809).

871. Marianini thinks it is possible that (in the case of copper, at least (866), and, so I presume, for all similar cases, for surely one law or principle should govern them), the current is due to the contact force of the sulphuret formed. But that application is here entirely excluded; for how can a *non-conducting* body form a current, either by contact or in any other way? No such case has ever been shown, nor is it in the nature of things; so that it cannot be the contact of the sulphuret that here causes the current; and if not in the present, why in any

case? for nothing happens here that does not happen in any other instance of a current produced by the same exciting electrolyte.

872. On the other hand, how beautiful a proof the result gives in confirmation of the chemical theory! Tin can take sulphur from the electrolyte to form a sulphuret; and whilst it is doing so, and in proportion to the degree in which it is doing so, it produces a current; but when the sulphuret which is formed, by investing the metal, shuts off the fluid and prevents further chemical action, then the current ceases also. Nor is it *necessary* that it should be a non-conductor for this purpose, for conducting sulphurets will perform the same office (873, 882), and bring about the same result. What, then, can be more clear, than that whilst the sulphuret is *being formed* a current is produced, but that when formed its mere contact can do nothing towards such an effect?

873. *Lead.*—This metal presents a fine result in the solution of sulphuret of potassium. Lead and platinum being the metals used, the lead was at first highly positive, but in a few seconds the current fell, and in two minutes the galvanometer-needle was at 0°. Still the arrangement conducted a feeble thermo current extremely well, the conducting power not having disappeared, as in the case of tin; for the investing sulphuret of lead is a conductor (808). Nevertheless, though a conductor, it could stop the further chemical action; and that ceasing, the current ceased also.

874. Lead and gold produced the same effect. Lead and palladium the same. Lead and iron the same, except that the circumstances respecting the tendency of the latter metal under common circumstances to produce a current from the electrolyte to itself, have to be considered and guarded against (814, 1037). Lead and nickel also the same. In all these cases, when the lead was taken out and washed, it was found beautifully invested with a thin polished pellicle of sulphuret of lead.

875. With lead, then, we have a *conducting* sulphuret formed, but still there is no sign that its contact can produce a current, any more than in the case of the *non-conducting* sulphuret of tin (870). There is no new or additional action produced by this *conducting* body; there was no deficiency of action with the former *non-conducting* product; both are alike in their results, being, in fact, essentially alike in their relation to that on which the current really depends, namely, an active chemical

force. A piece of lead put *alone* into the solution of sulphuret of potassium, has its surface converted into sulphuret of lead, the proof thus being obtained, even when the current cannot be formed, that there is a force (chemical) present and active under such circumstances; and such force can produce a current of chemical force when the circuit form is given to the arrangement. The force at the place of excitement shows itself, both by the formation of sulphuret of lead and the production of a current. In proportion as the formation of the one decreases the production of the other diminishes, though all the bodies produced are conductors, and contact still remains to perform any work or cause any effect to which it is competent.

876. It may perhaps be said that the current is due to the contact between the solution of sulphuret and the lead (or tin, as the case may be), which occurs at the beginning of the experiment; and that when the action ceases, it is because a new body, the sulphuret of lead, is introduced into the circuit, the various contacts being then balanced in their force. This would be to fall back upon the assumption before resisted, namely, that the solution may class with metals and such like bodies, giving balanced effects of contact in relation to *some* of these bodies, as in this case, to the sulphuret of lead produced, but not with *others*, as the lead itself; both the lead and its sulphuret being in the same category as the metals generally (797, 858).

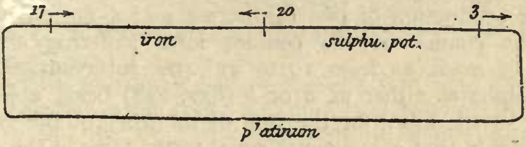

Fig. 67.

877. The utter improbability of this as a natural effect, and the absence of all experimental proof in support of it, have been already stated (849, 859), but one or two additional reasons against it now arise. The state of thing may perhaps be made clearer by a diagram or two, in which assumed contact forces may be assigned, in the absence of all experimental expression, without injury to the reasoning. Let fig. 67 represent the electromotive forces of a circle of platinum, iron, and solution of sulphuret of potassium; or platinum, nickel, and solution of sulphuret; cases in which the forces are, according to the

contact theory, balanced (848). Then fig. 68 may represent the circle of platinum, lead, and solution of sulphuret, which does produce a current, and, as I have assumed, with a resulting force of 11 ⟶. This in a few minutes becomes quiescent, *i.e.* the current ceases, and fig. 69 may represent this new case according to the contact theory. Now is it at all likely that by the intervention of sulphuret of lead at the contact *c*, fig. 68, and the production of two contacts *d* and *e*, fig. 69, such an enormous change of the contact force suffering alteration should be made as from 10 to 21? the intervention of the same sulphuret either at *a* or *b* (822, 828) being able to do nothing of the kind, for the sum of the force of the two new contacts is in that case exactly equal to the force of the contact which they replace, as is proved by such interposition making no change in the effects of the circle (855, 828). If therefore the intervention of this body between *lead* and platinum at *a*, or between solution of *sulphuret of potassium* and platinum at *b* (fig. 68) causes no change, these cases including its contact with both lead and the solution of sulphuret, is it at all probable that its intervention between these two bodies at *c* should make a difference equal to double the amount of force previously existing, or indeed any difference at all?

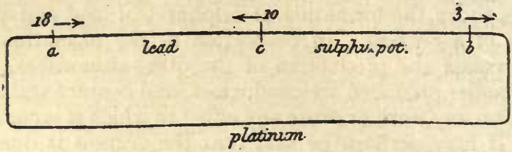

Fig. 68.

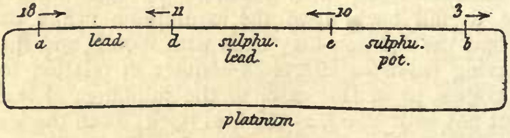

Fig. 69.

878. Such an alteration as this in the sum assigned as the amount of the forces belonging to the sulphuret of lead by virtue of its two places of contact, is equivalent I think to saying that it partakes of the anomalous character already supposed

to belong to certain fluids, namely, of sometimes giving balanced forces in circles of good conductors, and at other times not (853).

879. Even the metals themselves must in fact be forced into this constrained condition; for the effect at a point of contact, if there be *any at all,* must be the result of the *joint* and *mutual actions* of the bodies in contact. If therefore in the circuit, fig. 68, the contact forces are not balanced, it must be because of the deficient *joint* action of the lead and solution at *c*.[1] If the metal and fluid were to act in their proper character, and as iron or nickel would do in the place of the lead, then the force there would be ⟵ 21, whereas it is less, or according to the assumed numbers only ⟵ 10. Now as there is no reason why the lead should have any superiority assigned to it over the solution, since the latter can give a balanced condition amongst good conductors in its proper situation as well as the former; how can this be, unless lead possess that strange character of sometimes giving equipoised contacts, and at other times not (853)?

880. If that be true of lead, it must be true of all the metals which, with this sulphuretted electrolyte, give circles producing currents; and this would include bismuth, copper, antimony, silver, cadmium, zinc, tin, etc., etc. With other electrolytic fluids iron and nickel would be included, and even gold, platinum, palladium; in fact all the bodies that can be made to yield in any way active voltaic circuits. Then is it possible that this can be true, and yet not a single combination of this extensive class of bodies be producible that can give the current without chemical action (855), considered not as a result, but as a known and pre-existing force?

881. I will endeavour to avoid further statement of the arguments, but think myself bound to produce (787) a small proportion of the enormous body of facts which appear to me to bear evidence all in one direction.

882. *Bismuth.*—This metal, when associated with platinum, gold, or palladium in solution of the sulphuret of potassium, gives active circles, the bismuth being positive. In the course of less than half an hour the current ceases; but the circuit is still an excellent conductor of thermo currents. Bismuth with iron or nickel produces the same final result with the reservation before made (814). Bismuth and lead give an active

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[1] My numbers are assumed, and if other numbers were taken, the reasoning might be removed to contact *b*, or even to contact *a*, but the end of the argument would in every case be the same.

circle; at first the bismuth is positive; in a minute or two the current ceases, but the circuit still conducts the thermo current well.

883. Thus whilst sulphuret of bismuth is in the act of formation the current is produced; when the chemical action ceases the current ceases also; though contact continues and the sulphuret be a good conductor. In the case of bismuth and lead the chemical action occurs at both sides, but is most energetic at the bismuth, and the current is determined accordingly. Even in that instance the cessation of chemical action causes the cessation of the current.

884. In these experiments with *lead* and *bismuth* I have given their associations with platinum, gold, palladium, iron, and nickel; because, believing in the first place that the results prove all current to depend on chemical action, then, the quiescent state of the resulting or final circles shows that the contacts of these metals in their respective pairs are *without force* (817): and upon that again follows the passive condition of all those contacts which can be produced by interposing other conducting bodies between them (821); an argument that need not again be urged.

885. *Copper.*—This substance being associated with platinum, gold, iron, or any metal chemically inactive in the solution of sulphuret, gives an active circle, in which the copper is positive through the electrolyte to the other metal. The action, though it falls, does not come to a close as in the former cases, and for these simple reasons; that the sulphuret formed is not compact but porous, and does not adhere to the copper, but separates from it in scales. Hence results a continued renewal of the chemical action between the metal and electrolyte, and a continuance of the current. If after a while the copper plate be taken out and washed and dried, even the wiping will remove part of the sulphuret in scales, and the nail separates the rest with facility. Or if a copper plate be left in abundance of the solution of sulphuret, the chemical action *continues*, and the coat of sulphuret of copper becomes thicker and thicker.

886. If, as Marianini has shown,[1] a copper plate which has been dipped in the solution of sulphuret, be removed before the coat formed is so thick as to break up from the metal beneath, and be washed and dried, and then replaced, in association with platinum or iron, in the solution, it will at first be neutral, or, as is often the case, negative (815, 826) to the

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[1] *Memorie della Società Italiana in Modena*, 1837, xxi. 224.

other metal, a result quite in opposition to the idea, that the mere presence of the sulphuret on it could have caused the former powerful current and positive state of the copper (885, 866). A further proof that it is not the mere *presence*, but the *formation*, of the sulphuret which causes the current, is, that if the plate be left long enough for the solution to penetrate the investing crust of sulphuret of copper and come into activity on the metal beneath, then the plate becomes active, and a current is produced.

887. I made some sulphuret of copper, by igniting thick copper wire in a Florence flask or crucible in abundance of vapour of sulphur. The body produced is in an excellent form for these experiments, and a good conductor; but it is not without action on the sulphuretted solution, from which it can take more sulphur, and the consequence is, that it is positive to platinum or iron in such a solution. If such sulphuret of copper be left long in the solution and then be washed and dried, it will generally acquire the final state of sulphuration, either in parts or altogether, and also be inactive, as the sulphuret formed on the copper was before (886); *i.e.* when its chemical action is exhausted, it ceases to produce a current.

888. *Native grey sulphuret of copper* has the same relation to the electrolyte: it takes sulphur from it and is raised to a higher state of combination; and, as it is also a conductor (808), it produces a current, being itself positive so long as the action continues.

889. But when the copper is *fully sulphuretted*, then all these actions cease; though the sulphuret be a conductor, the contacts still remain, and the circle can carry with facility a feeble thermo current. This is not only shown by the quiescent cases just mentioned (886), but also by the utter inactivity of platinum and *compact yellow copper pyrites*, when conjoined by this electrolyte, as shown in a former part of this paper (828).

890. *Antimony.*—This metal, being put alone into a solution of sulphuret of potassium, is acted on, and a sulphuret of antimony formed which does not adhere strongly to the metal, but wipes off. Accordingly, if a circle be formed of antimony, platinum, and the solution, the antimony is positive in the electrolyte, and a powerful current is formed, which continues. Here then is another beautiful variation of the conditions under which the chemical theory can so easily account for the effects, whilst the theory of contacts cannot. The sulphuret produced

in this case is a non-conductor whilst in the solid state (138); it cannot therefore be that any contact of this sulphuret can produce the current; in that respect it is like the sulphuret of tin (870). But that circumstance does not stop the occurrence of the chemical current; for, as the sulphuret forms a porous instead of a continuous crust, the electrolyte has access to the metal and the action goes on.

891. *Silver.*—This metal, associated with platinum, iron, or other metals inactive in this electrolyte, is strongly positive, and gives a powerful continuous current. Accordingly, if a plate of silver, coated with sulphuret by the simple action of the solution, be examined, it will be found that the crust is brittle and broken, and separates almost spontaneously from the metal. In this respect, therefore, silver and copper are alike, and the action consequently continues in both cases, but they differ in the sulphuret of silver being a non-conductor (170) for these feeble currents, and, in that respect, this metal is analogous to antimony (890).

892. *Cadmium.*—Cadmium with platinum, gold, iron, etc., gives a powerful current in the solution of sulphuret, and the cadmium is positive. On several occasions this current continued for two or three hours or more; and at such times, the cadmium being taken out, washed, and wiped, the sulphuret was found to separate easily in scales on the cloth used.

893. Sometimes the current would soon cease; and then the circle was found not to conduct the thermo current (801). In these cases, also, on examining the cadmium, the coat of sulphuret was strongly adherent, and this was more especially the case when prior to the experiment the cadmium, after having been cleaned, was burnished by a glass rod (869). Hence it appears that the sulphuret of this metal is a non-conductor, and that its contact could not have caused the current (871) in the manner Marianini supposes. All the results it supplies are in perfect harmony with the chemical theory and adverse to contact theory.

894. *Zinc.*—This metal, with platinum, gold, iron, etc., and the solution of sulphuret, produces a very powerful current, and is positive through the solution to the other metal. The current was permanent. Here another beautiful change in the circumstances of the general experiment occurs. Sulphuret of zinc is a non-conductor of electricity (809), like the sulphurets of tin, cadmium, and antimony; but then it is soluble in the solution of sulphuret of potassium; a property

easily ascertainable by putting a drop of solution of zinc into a portion of the electrolytic solution, and first stirring them a little, by which abundance of sulphuret of zinc will be formed; and then stirring the whole well together, when it will be redissolved. The consequence of this solubility is, that the zinc when taken out of the solution is perfectly free from investing sulphuret of zinc. Hence, therefore, a very sufficient reason, on the chemical theory, why the action should go on. But how can the theory of contact refer the current to any contact of the metallic sulphuret, when that sulphuret is, in the first place, a non-conductor, and, in the next, is dissolved and carried off into the solution at the moment of its formation?

895. Thus all the phenomena with this admirable electrolyte (868), whether they be those which are related to it as an active (867) or as a passive (813, etc.) body, confirm the chemical theory, and oppose that of contact. With tin and cadmium it gives an impermeable non-conducting body; with lead and bismuth it gives an impermeable conducting body; with antimony and silver it produces a permeable non-conducting body; with copper a permeable conducting body; and with zinc a soluble non-conducting body. The chemical action and its resulting current are perfectly consistent with all these variations. But try to explain them by the theory of contact, and, as far as I can perceive, that can only be done by twisting the theory about and making it still more tortuous than before; special assumptions being necessary to account for the effects which, under it, become so many special cases.

896. *Solution of protosulphuret of potassium, or bihydrosulphuret of potassa.*—I used a solution of this kind as the electrolyte in a few cases. The results generally were in accordance with those already given, but I did not think it necessary to pursue them at length. The solution was made by passing sulphuretted hydrogen gas for twenty-four hours through a strong solution of pure caustic potassa.

897. Iron and platinum with this solution formed a circle in which the iron was first negative, then gradually became neutral, and finally acquired a positive state. The solution first acted as the yellow sulphuret in reducing the investing oxide (1037), and then, apparently, directly on the iron, dissolving the sulphuret formed. Nickel was positive to platinum from the first, and continued so though producing only a weak current. When weak chemical action was substituted for metallic contact at *x*, fig. 65 (819), a powerful current passed.

Copper was highly positive to iron and nickel; as also to platinum, gold, and the other metals which were unacted upon by the solution. Silver was positive to iron, nickel, and even lead; as well as to platinum, gold, etc. Lead is positive to platinum, then the current falls, but does not cease. Bismuth is also positive at first, but after a while the current almost entirely ceases, as with the yellow sulphuret of potassium (882).

898. Native grey sulphuret of copper and artificial sulphuret of copper (887) were positive to platinum and the inactive metals: but yellow copper pyrites, yellow iron pyrites, and galena, were inactive with these metals in this solution; as before they had been with the solution of yellow or bisulphuret of potassium. This solution, as might be expected from its composition, has more of alkaline characters in it than the yellow sulphuret of potassium.

899. Before concluding this account of results with the sulphuretted solutions, as exciting electrolytes, I will mention the varying and beautiful phenomena which occur when copper and silver, or two pieces of copper, or two pieces of silver, form a circle with the yellow solution. If the metals be copper and silver, the copper is at first positive and the silver remains untarnished; in a short time this action ceases, and the silver becomes positive; at the same instant it begins to combine with sulphur and becomes covered with sulphuret of silver; in the course of a few moments the copper again becomes positive; and thus the action will change from side to side several times, and the current with it, according as the circumstances become in turn more favourable at one side or the other.

900. But how can it be thought that the current first produced is due in any way to the *contact* of the sulphuret of copper formed, since its presence there becomes at last the reason why that first current diminishes, and enables the silver, which is originally the weaker in exciting force, and has no sulphuret as yet formed on it, to assume for a time the predominance, and produce a current which can overcome that excited at the copper (899)? What can account for these changes, but chemical action? which, as it appears to me, accounts, as far as we have yet gone, with the utmost simplicity, for *all* the effects produced, however varied the mode of action and their circumstances may be.

December 12, 1839.

VIII[1]

§ 9. ON THE SOURCE OF POWER IN THE VOLTAIC PILE—*Continued.* ¶ iv. THE EXCITING CHEMICAL FORCE AFFECTED BY TEMPERATURE. ¶ v. THE EXCITING CHEMICAL FORCE AFFECTED BY DILUTION. ¶ vi. DIFFERENCES IN THE ORDER OF THE METALLIC ELEMENTS OF VOLTAIC CIRCLES. ¶ vii. ACTIVE VOLTAIC CIRCLES AND BATTERIES WITHOUT METALLIC CONTACT. ¶ viii. CONSIDERATIONS OF THE SUFFICIENCY OF CHEMICAL ACTION. ¶ ix. THERMO-ELECTRIC EVIDENCE. ¶ x. IMPROBABLE NATURE OF THE ASSUMED CONTACT FORCE

¶ iv. *The Exciting Chemical Force affected by Temperature*

901. On the view that chemical force is the origin of the electric current in the voltaic circuit, it is important that we have the power of causing by ordinary chemical means, a variation of that force within certain limits, without involving any alteration of the metallic or even the other contacts in the circuit. Such variations should produce corresponding voltaic effects, and it appeared not improbable that these differences alone might be made effective enough to produce currents without any metallic contact at all.

902. De la Rive has shown that the increased action of a pair of metals, when put into hot fluid instead of cold, is in a great measure due to the exaltation of the chemical affinity on that metal which was acted upon.[2] My object was to add to the argument by using but one metal and one fluid, so that the fluid might be alike at both contacts, but to exalt the chemical force at one only of the contacts by the action of heat. If such difference produced a current with circles which either did not generate a thermo current themselves, or could not onduct that of an antimony and bismuth element, it seemed probable that the effect would prove to be a result of pure chemical force, contact doing nothing.

903. The apparatus used was a glass tube (fig. 70), about five inches long and 0.4 of an inch internal diameter, open at both

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[1] Seventeenth Series, original edition, vol. ii. p. 59.

[2] *Annales de Chimie*, 1828, xxxvii. p. 242.

ends, bent and supported on a retort-stand. In this the liquid was placed, and the portion in the upper part of one limb could then easily be heated and retained so, whilst that in the other limb was cold. In the experiments I will call the left-hand side A, and the right-hand side B, taking care to make no change of these designations. C and D are the wires of metal (869) to be compared; they were formed into a circuit by means of the galvanometer, and, often also, a Seebeck's thermo-element of antimony and bismuth; both these, of course, caused no disturbing effect so long as the temperature of their various junctions was alike. The wires were carefully prepared, and when two of the same metal were used, they consisted of the successive portions of the same piece of wire.

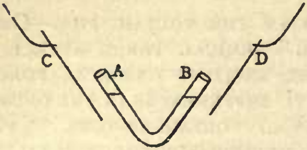

Fig. 70.

904. The precautions which are necessary for the elimination of a correct result are rather numerous, but simple in their nature.

905. *Effect of first immersion.*—It is hardly possible to have the two wires of the same metal, even platinum, so exactly alike that they shall not produce a current in consequence of their difference; hence it is necessary to alternate the wires and repeat the experiment several times, until an undoubted result independent of such disturbing influences is obtained.

906. *Effect of the investing fluid or substance.*—The fluid produced by the action of the liquid upon the metal exerts, as is well known, a most important influence on the production of a current. Thus when two wires of cadmium were used with the apparatus, fig. 70 (903), containing dilute sulphuric acid, hot on one side and cold on the other, the hot cadmium was at first positive, producing a deflection of about 10°; but in a short time this effect disappeared, and a current in the reverse direction equal to 10° or more would appear, the hot cadmium being now negative. This I refer to the quicker exhaustion of the chemical forces of the film of acid on the heated metallic surface, and the consequent final superiority of the colder side at which the action was thus necessarily more powerful. Marianini has described many cases of the effects of investing solutions, showing that if two pieces of the same metal (iron, tin, lead, zinc, etc.) be used, the one first immersed is negative

to the other, and has given his views of the cause.[1] The precaution against this effect was not to put the metals into the acid until the proper temperature had been given to both parts of it, and then to observe the *first effect* produced, accounting that as the true indication, but repeating the experiment until the result was certain.

907. *Effect of motion.*—This investing fluid (906) made it necessary to guard against the effect of successive rest and motion of the metal in the fluid. As an illustration, if two tin wires (869) be put into dilute nitric acid, there will probably be a little motion at the galvanometer, and then the needle will settle at 0°. If either wire be then moved, the other remaining quiet, that in motion will become positive. Again, tin and cadmium in dilute sulphuric acid gave a strong current, the cadmium being positive, and the needle was deflected 80°. When left, the force of the current fell to 35°. If the cadmium were then moved it produced very little alteration; but if the tin were moved it produced a great change, not showing, as before, an increase of its force, but the reverse, for it became more negative, and the current force rose up again to 80°.[2] The precaution adopted to avoid the interference of these actions, was not only to observe the first effect of the introduced wires, but to keep them moving from the moment of the introduction.

908. The above effect was another reason for heating the acids, etc. (906) before the wires were immersed; for in the experiment just described, if the cadmium side were heated to boiling, the moment the fluid was agitated on the tin side by the boiling on the cadmium side, there was more effect by far produced by the motion than the heat: for the heat at the cadmium alone did little or nothing, but the jumping of the acid over the tin made a difference in the current of 20° or 30°.

909. *Effect of air.*—Two platinum wires were put into cold

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[1] *Annales de Chimie*, 1830, xlv. p. 40.

[2] Tin has some remarkable actions in this respect. If two tins be immersed in succession into dilute nitric acid, the one last in is positive to the other at the moment: if, both being in, one be moved, that is for the time positive to the other. But if dilute sulphuric acid be employed, the last tin is always negative: if one be taken out, cleaned, and re-immersed, it is negative: if, both being in and neutral, one be moved, it becomes negative to the other. The effects with muriatic acid are the same in kind as those with sulphuric acid, but not so strong. This effect perhaps depends upon the compound of tin first produced in the sulphuric and muriatic acids tending to acquire some other and more advanced state, either in relation to the oxygen, chlorine or acid concerned, and so adding a force to that which at the first moment, when only metallic tin and acid are present, tends to determine a current.

strong solution of sulphuret of potassium (800), fig. 70; and the galvanometer was soon at 0°. On heating and boiling the fluid on the side A (903) the platinum in it became negative; cooling that side, by pouring a little water over it from a jug, and heating the side B, the platinum there in turn became negative; and, though the action was irregular, the same general result occurred however the temperatures of the parts were altered. This was not due to the chemical effect of the electrolyte on the heated platinum. Nor do I believe it was a true thermo current (921); but if it were the latter, then the heated platinum was *negative* through the electrolyte to the cold platinum. I believe it was altogether the increased effect of the air upon the electrolyte at the heated side; and it is evident that the application of the heat, by causing currents in the fluid and also in the air, facilitates their mutual action at that place. It has been already shown, that lifting up a platinum wire in this solution, so as to expose it for a moment to the air (815), renders it negative when reimmersed, an effect which is in perfect accordance with the assumed action of the heated air and fluid in the present case. The interference of this effect is obviated by raising the temperature of the electrolyte quietly before the wires are immersed (906), and observing only the first effect.

910. *Effect of heat.*—In certain cases where two different metals are used, there is a very remarkable effect produced on heating the negative metal. This will require too much detail to be described fully here; but I will briefly point it out and illustrate it by an example or two.

911. When two platinum wires were compared in hot and cold dilute sulphuric acid (923), they gave scarcely a sensible trace of any electric current. If any real effect of heat occurred, it was that the hot metal was the least degree positive. When silver and silver were compared, hot and cold, there was also no sensible effect. But when platinum and silver were compared in the same acid, different effects occurred. Both being cold, the silver in the A side, fig. 70 (903), was positive about 4°, by the galvanometer; moving the platina on the other side B did not alter this effect, but on heating the acid and platinum there, the current became very powerful, deflecting the needle 30°, and the silver was positive. Whilst the heat continued, the effect continued; but on cooling the acid and platinum it went down to the first degree. No such effect took place at the silver; for on heating that side, instead of becoming

negative, it became more positive, but only to the degree of deflecting the needle 16°. Then, *motion* of the platinum (907) facilitated the passing of the current and the deflection increased, but *heating* the platinum side did far more.

912. *Silver and copper* in dilute sulphuric acid produced very little effect; the copper was positive about 1° by the galvanometer; moving the copper or the silver did nothing; heating the copper side caused no change; but on heating the silver side it became negative 20°. On cooling the silver side this effect went down, and then, either moving the silver or copper, or heating the copper side, caused very little change: but heating the silver side made it negative as before.

913. All this revolves itself into an effect of the following kind; that where two metals are in the relation of positive and negative to each other in such an electrolyte as dilute acids (and perhaps others), heating the negative metal at its contact with the electrolyte enables the current, which tends to form, to pass with such facility, as to give a result sometimes tenfold more powerful than would occur without it. It is not displacement of the investing fluid, for motion will in these cases do nothing: it is not chemical action, for the effect occurs at that electrode where the chemical action is not active; it is not a thermo-electric phenomenon of the ordinary kind, because it depends upon a voltaic relation; *i.e.* the metal showing the effect must be negative to the other metal in the electrolyte; so silver heated does nothing with silver cold, though it shows a great effect with copper either hot or cold (912); and platinum hot is as nothing to platina cold, but much to silver either hot or cold.

914. Whatever may be the intimate action of heat in these cases, there is no doubt that it is dependent on the current which tends to pass round the circuit. It is essential to remember that the increased effect on the galvanometer is not due to any increase in the electromotive force, but solely to the removal of obstruction to the current by an increase probably of discharge. M. de la Rive has described an effect of heat, on the passage of the electric current, through dilute acid placed in the circuit, by platinum electrodes. Heat applied to the negative electrode increased the deflection of a galvanometer needle in the circuit, from 12° to 30° or 45°; whilst heat applied to the positive electrode caused no change.[1] I have not been able to obtain this nullity of effect at the positive electrode

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[1] *Bibliothèque Universelle*, 1837, vii. 388.

when a voltaic battery was used; but I have no doubt the present phenomena will prove to be virtually the same as those which that philosopher has described.

915. The effect interferes frequently in the ensuing experiments when *two* metals, hot and cold, are compared with each other; and the more so as the negative metal approximates in inactivity of character to platinum or rhodium. Thus in the comparison of cold copper, with hot silver, gold, or platinum, in dilute nitric acid, this effect tends to make the copper appear more positive than it otherwise would do.

916. *Place of the wire terminations.*—It is requisite that the *end* of the wire on the hot side should be *in* the heated fluid. Two copper wires were put into diluted solution of sulphuret of potassium, fig. 71, that portion of the liquid extending from C to D was heated, but the part between D and E remained cold. Whilst both ends of the wires were in the cold fluid, as in the figure, there were irregular movements of the galvanometer, small in degree, leaving the B wire positive. Moving the wires about, but retaining them as in the figure, made no difference; but on raising the wire in A, so that its termination should be in the hot fluid between C and D, then it became positive and continued so. On lowering the end into the cold part, the former state recurred; on raising it into the hot part, the wire again became positive. The same is the case with two silver wires in dilute nitric acid; and though it appears very curious that the current should increase in strength as the extent of bad conductor increases, yet such is often the case under these circumstances. There can be no reason to doubt that the part of the wire which is in the hot fluid at the A side, is at all times equally positive or nearly so; but at one time the whole of the current it produces is passing through the entire circuit by the wire in B, and at another, a part, or the whole, of it is circulating to the cold end of its own wire, only by the fluid in tube A.

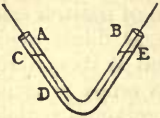

Fig. 71.

917. *Cleaning the wires.*—That this should be carefully done has been already mentioned (869); but it is especially necessary to attend to the very extremities of the wires, for if these circular spaces, which occur in the most effective part of the circle, be left covered with the body produced on them in a preceding trial, an experimental result will often be very much deranged, or even entirely falsified.

918. Thus the best mode of experimenting (903) is to heat the liquid in the limb A or B, fig. 71, first; and, having the wires well cleaned and connected, to plunge both in at once, and, retaining the *end* of the heated wire in the hot part of the fluid, to keep both wires in motion, and observe, especially, the first effects: then to take out the wires, reclean them, change them side for side and repeat the experiment, doing this so often as to obtain from the several results a decided and satisfactory conclusion.

919. It next becomes necessary to ascertain whether any true thermo current can be produced by electrolytes and metals, which can interfere with any electro-chemical effects dependent upon the action of heat. For this purpose different combinations of electrolytes and metals not acted on chemically by them, were tried, with the following results.

920. Platinum and a very *strong solution of potassa* gave, as the result of many experiments, the hot platinum positive across the electrolyte to the cold platinum, producing a current that could deflect the galvanometer needle about 5°, when the temperatures at the two junctures were 60° and 240°. Gold and the same solution gave a similar result. Silver and a moderately strong solution, of specific gravity 1070, like that used in the ensuing experiments (936) gave the hot silver positive, but now the deflection was scarcely sensible, and not more than 1°. Iron was tried in the same solution, and there was a constant current and deflection of 50° or more, but there was also chemical action (936).

921. I then used *solution of the sulphuret of potassium* (800). As already said, hot platinum is negative in it to the cold metal (909); but I do not think the action was thermo-electric. Palladium with a weaker solution gave no indication of a current.

922. Employing dilute nitric acid, consisting of one volume strong acid and fifty volumes water, platinum gave no certain indication: the hot metal was sometimes in the least degree positive, and at others an equally small degree negative. Gold in the same acid gave a scarcely sensible result; the hot metal was negative. Palladium was as gold.

923. With dilute sulphuric acid, consisting of one by weight of oil of vitriol and eighty of water, neither platinum nor gold produced any sensible current to my galvanometer by the mere action of heat.

924. *Muriatic acid* and platinum being conjoined, and heated

as before, the hot platinum was very slightly negative in strong acid: in dilute acid there was no sensible current.

925. *Strong nitric acid* at first seemed to give decided results. Platinum and pure strong nitric acid being heated at one of the junctions, the hot platinum became constantly negative across the electrolyte to the cold metal, the deflection being about 2°. When a yellow acid was used, the deflection was greater; and when a very orange-coloured acid was employed, the galvanometer needle stood at 70°, the hot platinum being still negative. This effect, however, is not a pure thermo current, but a peculiar result due to the presence of nitrous acid (836). It disappears almost entirely when a dilute acid is used (922); and what effect does remain indicates that the hot metal is negative to the cold.

926. Thus the *potash solution* seems to be the fluid giving the most probable indications of a thermo current. Yet there the deflection is only 5°, though the fluid, being very strong, is a good conductor (807). When the fluid was diluted, and of specific gravity 1070, like that before used (920), the effect was only 1°, and cannot therefore be confounded with the results I have to quote.

927. The dilute *sulphuric* (923) and *nitric* acids used (922) gave only doubtful indications in some cases of a thermo current. On trial it was found that the thermo current of an antimony-bismuth pair could not pass these solutions, as arranged in these and other experiments (937, 938); that, therefore, if the little current obtained in the experiments be of a thermo-electric nature, this combination of platinum and acid is far more powerful than the antimony-bismuth pair of Seebeck; and yet that (with the interposed acid) it is scarcely sensible by this delicate galvanometer. Further, when there is a current, the hot metal is generally negative to the cold, and it is therefore impossible to confound these results with those to be described where the current has a contrary direction.

928. In strong nitric acid, again, the hot metal is negative.

929. If, after I show that heat applied to metals in acids or electrolytes which *can act on them* produces considerable currents, it be then said that though the metals which are inactive in the acids produce no thermo currents, those which, like copper, silver, etc., act chemically, may; then, I say, that such would be a mere supposition, and a supposition at variance with what we know of thermo-electricity; for amongst the solid conductors, metallic or non-metallic (855), there are none, I

believe, which are able to produce thermo currents with some of the metals, and not with others. Further, these metals, copper, silver, etc., do not always show effects which can be mistaken or pass for thermo-electric, for silver in hot dilute nitric acid is scarcely different from silver in the same acid cold (938); and in other cases, again, the hot metals become negative instead of positive (941).

Cases of one Metal and one Electrolyte; one Junction being heated

930. The cases I have to adduce are far too numerous to be given in detail; I will therefore describe one or two, and sum up the rest as briefly as possible.

931. *Iron in diluted sulphuret of potassium.*—The hot iron is well positive to the cold metal. The negative and cold wire continues quite clean, but from the hot iron a dark sulphuret separates, which becoming diffused through the solution discolours it. When the cold iron is taken out, washed and wiped, it leaves the cloth clean; but that which has been heated leaves a black sulphuret upon the cloth when similarly treated.

932. *Copper and the sulphuretted solution.*—The hot copper is well positive to the cold on the first immersion, but the effect quickly falls, from the general causes already referred to (906).

933. *Tin and solution of potassa.*—The hot tin is strongly and constantly positive to the cold.

934. *Iron and dilute sulphuric acid* (923).—The hot iron was constantly positive to the cold, 60° or more. *Iron and diluted nitric acid gave* even a still more striking result.

I must now enumerate merely, not that the cases to be mentioned are less decided than those already given, but to economise time.

935. *Dilute solution of yellow sulphuret of potassium,* consisting of one volume of the strong solution (800), and eighteen volumes of water.—Iron, silver, and copper, with this solution, gave good results. The hot metal was positive to the cold.

936. *Dilute solution of caustic potassa* (920).—Iron, copper, tin, zinc, and cadmium gave striking results in this electrolyte. The hot metal was always positive to the cold. Lead produced the same effect, but there was a momentary jerk at the galvanometer at the instant of immersion, as if the hot lead was negative at that moment. In the case of iron it was necessary to continue the application of heat. and then the formation of oxide at it

could easily be observed; the alkali gradually became turbid, for the protoxide first formed was dissolved, and becoming peroxide by degrees, was deposited, and rendered the liquid dull and yellow.

937. *Dilute sulphuric acid* (923).—Iron, tin, lead, and zinc, in this electrolyte, showed the power of heat to produce a current by exalting the chemical affinity, for the hot side was in each case positive.

938. *Dilute nitric acid* is remarkable for presenting only one case of a metal hot and cold exhibiting a striking difference, and that metal is iron. With silver, copper, and zinc, the hot side is at the first moment positive to the cold, but only in the smallest degree.

939. *Strong nitric acid.*—Hot iron is positive to cold. Both in the hot and cold acid the iron is in its peculiar state (832, 989).

940. *Dilute muriatic acid:* 1 *volume strong muriatic acid, and* 29 *volumes water.*—This acid was as remarkable for the number of cases it supplied as the dilute nitric acid was for the contrary (938). Iron, copper, tin, lead, zinc, and cadmium gave active circles with it, the hot metal being positive to the cold; all the results were very striking in the strength and permanency of the electric current produced.

941. Several cases occur in which the hot metal becomes *negative* instead of positive, as above; and the principal cause of such an effect I have already adverted to (906). Thus with the solution of the *sulphuret of potassium* and zinc, on the first immersion of the wires into the hot and cold solution there was a pause, *i.e.* the galvanometer needle did not move at once, as in the former cases; afterwards a current gradually came into existence, rising in strength until the needle was deflected 70° or 80°, the hot metal being *negative* through the electrolyte to the cold metal. *Cadmium* in the same solution gave also the first pause and then a current, the hot metal being negative; but the effect was very small. Lead, hot, was negative, producing also only a feeble current. Tin gave the same result, but the current was scarcely sensible.

942. *In dilute sulphuric acid.*—Copper and zinc, after having produced a first positive effect at the hot metal, had that reversed, and a feeble current was produced, the hot metal being negative. Cadmium gave the same phenomena, but stronger (906).

943. *In dilute nitric acid.*—Lead produced no effect at the first moment; but afterwards an electric current, gradually increasing in strength, appeared, which was able to deflect the needle 20° or more, the hot metal being negative. Cadmium gave the same results as lead. Tin gave an uncertain result: at first the hot metal appeared to be a very little negative, it then became positive, and then again the current diminished, and went down almost entirely.

944. I cannot but view in these results of the action of heat, the strongest proofs of the dependence of the electric current in voltaic circuits on the chemical action of the substances constituting these circuits: the results perfectly accord with the known influence of heat on chemical action. On the other hand, I cannot see how the theory of contact can take cognisance of them, except by adding new assumptions to those already composing it (862). How, for instance, can it explain the powerful effects of iron in sulphuret of potassium, or in potassa, or in dilute nitric acid; or of tin in potassa or sulphuric acid; or of iron, copper, tin, etc., in muriatic acid; or indeed of any of the effects quoted? That they cannot be due to thermo contact has been already shown by the results with inactive metals (919, 929); and to these may now be added those of the active metals, silver and copper in dilute nitric acid, for heat produces scarcely a sensible effect in these cases. It seems to me that no other cause than chemical force (a very sufficient one), remains, or is needed to account for them.

945. If it be said that, on the theory of chemical excitement, the experiments prove either too much or not enough, that, in fact, heat ought to produce the same effect with *all* the metals that are acted on by the electrolytes used, then, I say, that that does not follow. The force and other circumstances of chemical affinity vary almost infinitely with the bodies exhibiting its action, and the added effect of heat upon the chemical affinity would, necessarily, partake of these variations. Chemical action often goes on without any current being produced; and it is well known that, in almost every voltaic circuit, the chemical force has to be considered as divided into that which is local and that which is current. Now heat frequently assists the local action much, and, sometimes, without appearing to be accompanied by any great increase in the *intensity* of chemical affinity; whilst at other times we are sure, from the chemical phenomena, that it does affect the intensity of the force. The

electric current, however, is not determined by the amount of action which takes place, but by the intensity of the affinities concerned; and so cases may easily be produced, in which that metal exerting the least amount of action is nevertheless the positive metal in a voltaic circuit; as with copper in weak nitric acid associated with other copper in strong acid (963), or iron or silver in the same weak acid against copper in the strong acid (984). Many of those instances where the hot side ultimately becomes negative, as of zinc in dilute solution of sulphuret of potassium (941), or cadmium and lead in dilute nitric acid (943), are of this nature; and yet the conditions and result are in perfect agreement with the chemical theory of voltaic excitement (906).

946. The distinction between currents founded upon that difference of intensity which is due to the difference in force of the chemical action which is their exciting cause, is, I think, a necessary consequence of the chemical theory, and in 1834 I adopted that opinion.[1] De la Rive in 1836 gave a still more precise enunciation of such a principle,[2] by saying, that the intensity of currents is exactly proportional to the degree of affinity which reigns between the particles, the combination or separation of which produces the currents.

947. I look upon the question of the origin of the power in the voltaic battery as abundantly decided by the experimental results not connected with the action of heat. I further view the results with heat as adding very strong confirmatory evidence to the chemical theory; and the numerous questions which arise as to the varied results produced, only tend to show how important the voltaic circuit is as a means of investigation into the nature and principles of chemical affinity (955). This truth has already been most strikingly illustrated by the researches of De la Rive made by means of the galvanometer, and the investigations of my friend Professor Daniell into the real nature of acid and other compound electrolytes.[3]

Cases of two Metals and one Electrolyte; one Junction being heated

948. Since heat produced such striking results with single metals, I thought it probable that it might be able to affect the

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[1] *Philosophical Transactions*, 1834, p. 428.

[2] *Annales de Chimie*, 1836, lxi. p. 44, etc.

[3] *Philosophical Transactions*, 1839, p. 97.

mutual relation of the metals in some cases, and even invert their order: on making circuits with two metals and electrolytes, I found the following cases.

949. In the solution of *sulphuret of potassium*, hot tin is well positive to cold silver: cold tin is very slightly positive to hot silver, and the silver then rapidly tarnishes.

950. In the solution of *potassa*, cold tin is fairly positive to hot lead, but hot tin is much more positive to cold lead. Also cold cadmium is positive to hot lead, but hot cadmium is far more positive to cold lead. In these cases, therefore, there are great differences produced by heat, but the metals still keep their order.

951. In *dilute sulphuric acid*, hot iron is *well positive* to cold tin, but hot tin is *still more positive* to cold iron. Hot iron is a little positive to cold lead, and hot lead is very positive to cold iron. These are cases of the actual inversion of order; and tin and lead may have their states reversed exactly in the same manner.

952. *In dilute nitric acid*, tin and iron, and iron and lead may have their states reversed, whichever is the hot metal being rendered positive to the other. If, when the iron is to be plunged into the heated side (918) the acid is only moderately warm, it seems at first as if the tin would almost overpower the iron, so beautifully can the forces be either balanced or rendered predominant on either side at pleasure. Lead is positive to tin in both cases; but far more so when hot than when cold.

953. These effects show beautifully that in many cases, when two different metals are taken, either can be made positive to the other at pleasure, by acting on their chemical affinities; though the contacts of the metals with each other (supposed to be an electromotive cause) remain *entirely unchanged*. They show the effect of heat in reversing or strengthening the natural differences of the metals, according as its action is made to oppose or combine with their natural chemical forces, and thus add further confirmation to the mass of evidence already adduced.

954. There are here, as in the cases of one metal, some instances where the heat renders the metal more negative than it would be if cold. They occur, principally, in the solution of sulphuret of potassium. Thus, with zinc and cadmium, or zinc and tin, the coldest metal is positive. With lead and tin, the hot tin is a little positive, cold tin very positive. With lead and

zinc, hot zinc is a little positive, cold zinc much more so. With silver and lead, the hot silver is a little positive to the lead, the cold silver is more, and well positive. In these cases the current is preceded by a moment of quiescence (941), during which the chemical action at the hot metal reduces the efficacy of the electrolyte against it more than at the cold metal, and the latter afterwards shows its advantage.

955. Before concluding these observations on the effects of heat, and in reference to the probable utility of the voltaic circuit in investigations of the intimate nature of chemical affinity (947), I will describe a result which, if confirmed, may lead to very important investigations. Tin and lead were conjoined and plunged into cold dilute sulphuric acid; the tin was positive a little. The same acid was heated, and the tin and lead, having been perfectly cleaned, were reintroduced, then the lead was a little positive to the tin. So that a difference of temperature not limited to one contact, for the two electrolytic contacts were always at the same temperature, caused a difference in the relation of these metals the one to the other. Tin and iron in dilute sulphuric acid appeared to give a similar result; *i.e.* in the cold acid the tin was always positive, but with hot acid the iron was sometimes positive. The effects were but small, and I had not time to enter further into the investigation.

956. I trust it is understood that, in every case, the precautions as to very careful cleansing of the wires, the places of the ends, simultaneous immersion, observation of the first effects, etc., were attended to.

¶ v. *The Exciting Chemical Force affected by Dilution*

957. Another mode of affecting the chemical affinity of these elements of voltaic circuits, the metals and acids, and also applicable to the cases of such circuits, is to vary the proportion of water present. Such variation is known, by the simplest chemical experiments, to affect very importantly the resulting action, and, upon the chemical theory, it was natural to expect that it would also produce some corresponding change in the voltaic pile. The effects observed by Avogadro and Œrsted in 1823 are in accordance with such an expectation, for they found that when the same pair of metals was plunged in succession into a strong and a dilute acid, in certain cases an in-

version of the current took place.[1] In 1828 De la Rive carried these and similar cases much further, especially in voltaic combinations of copper and iron with lead.[2] In 1827 Becquerel[3] experimented with one metal, copper, plunged at its two extremities into a solution of the same substance (salt) of *different strengths;* and in 1828 De la Rive[4] made many such experiments with one metal and a fluid in different states of dilution, which I think of very great importance.

958. The argument derivable from effects of this kind appeared to me so strong that I worked out the facts to some extent, and think the general results well worthy of statement. Dilution is the circumstance which most generally exalts the existing action, but how such a circumstance should increase the electromotive force of *mere contact* did not seem evident to me, without *assuming*, as before (862), exactly those influences at the points of contact in the various cases which the prior results, ascertained by experiments, would require.

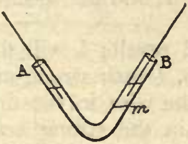

Fig. 72.

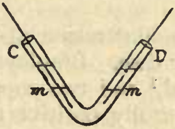

Fig 73.

959. The form of apparatus used was the bent tube already described (903), fig. 70. The precautions before directed with the wires, tube, etc., were here likewise needful. But there were others also requisite, consequent upon the current produced by combination of water with acid, an effect which has been described long since by Becquerel,[5] but whose influence in the present researches requires explanation.

960. Figs. 72 and 73 represent the two arrangements of fluids used, the part below *m* in the tubes being strong acid, and that above diluted. If the fluid was nitric acid and the platinum wires as in the figures, drawing the end of the wire D upwards above *m*, or depressing it from above *m* downwards, caused great changes at the galvanometer; but if they were preserved quiet at any place, then the electro-current ceased, or very nearly so. Whenever the current existed it was from the weak to the strong acid through the liquid.

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[1] *Annales de Chimie*, 1823, xxii. p. 361.

[2] *Ibid.* 1828, xxxvii. p. 234.

[3] *Ibid.* 1827, xxxv. p. 120.

[4] *Ibid.* 1828, xxxvii. pp. 240, 241.

[5] *Traité de l'Electricité*, ii. p. 81.

961. When the tube was arranged, as in fig. 72, with water or dilute acid on one side only, and the wires were immersed not more than one-third of an inch, the effects were greatly diminished; and more especially if, by a little motion with a platinum wire, the acids had been mixed at *m*, so that the transition from weak to strong was gradual instead of sudden. In such cases, even when the wires were moved, horizontally, in the acid, the effect was so small as to be scarcely sensible, and not likely to be confounded with the chemical effects to be described hereafter. Still more surely to avoid such interference, an acid moderately diluted was used instead of water. The precaution was taken of emptying, washing, and rearranging the tubes with fresh acid after each experiment, lest any of the metal dissolved in one experiment should interfere with the results of the next.

962. I occasionally used the tube with dilute acid on one side only, fig. 72, and sometimes that with dilute acid on both sides, fig. 73. I will call the first No. 1, and the second No. 2.

963. In illustration of the general results I will describe a particular case. Employing tube No. 1 with strong and dilute nitric acid,[1] and two copper wires, the wire in the dilute acid was powerfully positive to the one in the strong acid at the first moment, and continued so. By using tube No. 2, the galvanometer-needle could be held stiffly in either direction, simply by simultaneously raising one wire and depressing the other, so that the first should be in weak and the second in strong acid; the former was always the positive piece of metal.

964. On repeating the experiments with the substitution of platinum, gold, or even palladium for the copper, scarcely a sensible effect was produced (961).

965. *Strong and dilute nitric acid.*[1]—The following single metals being compared with themselves in these acids, gave most powerful results of the kind just described with copper (963); silver, iron, lead, tin, cadmium, zinc. The metal in the weaker acid was positive to that in the stronger. Silver is very changeable, and after some time the current is often suddenly reversed, the metal in the strong acid becoming positive: this again will change back, the metal in the weaker acid returning to its positive state. With tin, cadmium, and zinc, violent action in the acid quickly supervenes and mixes all

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[1] The dilute acid consisted of three volumes of strong nitric acid and two volumes of water.

up together. Iron and lead show the alternations of state in the tube No. 2 as beautifully as copper (963).

966. *Strong and dilute sulphuric acid.*—I prepared an acid of 49 by weight, strong oil of vitriol, and 9 of water, giving a sulphuric acid with two proportions of water, and arranged the tube No. 1 (962) with this and the strongest acid. But as this degree of dilution produced very little effect with the iron, as compared with what a much greater dilution effected, I adopted the plan of putting strong acid into the tube, and then adding a little water at the top at one of the sides, with the precaution of stirring and cooling it previous to the experiment (961).

967. With *iron*, the part of the metal in the weaker acid was powerfully positive to that in the stronger acid. With copper, the same result, as to direction of the current, was produced; but the amount of the effect was small. With silver, cadmium, and zinc, the difference was either very small or unsteady, or nothing; so that, in comparison with the former cases, the electromotive action of the strong and weak acid appeared balanced. With lead and tin, the part of the metal in the *strong* acid was *positive* to that in the weak acid; so that they present an effect the reverse of that produced by iron or copper.

968. *Strong and dilute muriatic acid.*—I used the strongest pure muriatic acid in tube No. 1, and added water on the top of one side for the dilute extremity (961), stirring it a little as before. With silver, copper, lead, tin, cadmium, and zinc, the metal in the *strongest acid* was positive, and the current in most cases powerful. With iron, the end in the strongest acid was first positive: but shortly after the weak acid side became positive and continued so. With palladium, gold, and platinum, nearly insensible effects were the results.

969. *Strong and dilute solution of caustic potassa.*—With iron, copper, lead, tin, cadmium, and zinc, the metal in the strong solution was positive: in the case of iron slightly, in the case of copper more powerfully, deflecting the needle 30° or 38°, and in the cases of the other metals very strongly. Silver, palladium, gold, and platinum gave the merest indications (961).

Thus potash and muriatic acid are, in several respects, contrasted with nitric and sulphuric acids. As respects muriatic acid, however, and perhaps even the potash, it may be admitted that, even in their strongest states, they are not fairly comparable to the very strong nitric and sulphuric acids, but rather to those acids when somewhat diluted (973).

970. I know it may be said in reference to the numerous changes with strong and dilute acids, that the results are the consequence of corresponding alterations in the contact force; but this is to change about the theory with the phenomena and with chemical force (862, 944, 973, 994, 1002, 1051); or it may be alleged that it is the contact force of the solutions produced at the metallic surfaces which, differing, causes difference of effect; but this is to put the effect before the cause in the order of *time*. If the liberty of shifting the point of efficacy from metals to fluids, or from one place to another, be claimed, it is at all events quite time that some definite statement and data respecting the active points (796) should be given. At present it is difficult to lay hold of the contact theory by any argument derived from experiment, because of these uncertainties or variations, and it is in that respect in singular contrast with the definite expression as to the place of action which the chemical theory supplies.

971. All the variations which have been given are consistent with the extreme variety which chemical action under different circumstances possesses, but, as it still appears to me, are utterly incompatible with, what should be, the simplicity of mere contact action; further they admit of even greater variation, which renders the reasons for the one view and against the other still more conclusive.

972. Thus if a contact philosopher say that it is only the very strongest acids that can render the part of the metals in it negative, and therefore the effect does not happen with muriatic acid or potash (968, 969), though it does with nitric and sulphuric acids (965, 966); then the following result is an answer to such an assumption. Iron in *dilute nitric acid*, consisting of one volume of strong acid and twenty of water, is positive to iron in strong acid, or in a mixture of one volume of strong acid with one of water, or with three, or even with five volumes of water. Silver also, in the weakest of these acids, is positive to silver in any of the other four states of it.

973. Or if, modifying the statement upon these results, it should be said that diluting the acid at one contact *always* tends to give it a certain *proportionate* electromotive force, and therefore diluting one side more than the other will still allow this force to come into play; then, how is it that with muriatic acid and potassa the effect of dilution is the reverse of that which has been quoted in the cases with nitric acid and iron or silver (965, 972)? Or if, to avoid *difficulty*, it be assumed that each

electrolyte must be considered apart, the nitric acid by itself, and the muriatic acid by itself, for that one may differ from another in the *direction* of the change induced by dilution, then how can the following results with a single acid be accounted for?

974. I prepared four nitric acids:

A was very strong pure nitric acid;
B was one volume of A and one volume of water;
C was one volume of A and three volumes of water;
D was one volume of A and twenty volumes of water.

Experimenting with these acids and a metal, I found that copper in C acid was positive to copper in A or D acid. Nor was it the *first* addition of water to the strong acid that brought about this curious relation, for copper in the B acid was positive to copper in the strong acid A, but negative to the copper in the weak acid D: the negative effect of the stronger nitric acid with this metal does not therefore depend upon a very high degree of concentration.

975. Lead presents the same beautiful phenomena. In the C acid it is positive to lead either in A or D acid: in B acid it is positive to lead in the strongest, and negative to lead in the weakest acid.

976. I prepared also three sulphuric acids:

E was strong oil of vitriol;
F one volume of E and two volumes of water;
G one volume of E and twenty volumes of water.

Lead in F was well *negative* to lead either in E or G. Copper in F was also negative to copper in E or G, but in a smaller degree. So here are two cases in which metals in an acid of a certain strength are *negative* to the same metals in the same acid, either stronger or weaker. I used platinum wires ultimately in all these cases with the same acids to check the interference of the combination of acid and water (961); but the results were then almost nothing, and showed that the phenomena could not be so accounted for.

977. To render this complexity for the contact theory still more complicated, we have further variations, in which, with the same acid strong and diluted, some metals are positive in the strong acid and others in the weak. Thus, tin in the strongest sulphuric acid E (976) was positive to tin in the moderate or weak acids F and G; and tin in the moderate acid F was positive to the same metal in G. Iron, on the contrary,

being in the strong acid E was negative to the weaker acids F and G; and iron in the medium acid F was negative to the same metal in G.

978. For the purpose of understanding more distinctly what the contact theory has to do here, I will illustrate the case by a diagram. Let fig. 74 represent a circle of metal and sulphuric acid. If A be an arc of iron or copper, and B C strong oil of vitriol, there will be no determinate current: or if B C be weak acid, there will be no such current: but let it be strong acid at B, and diluted at C, and an electric current will run round A C B. If the metal A be silver, it is equally indifferent with the strong and also with the weak acid, as iron has been found to be as to the production of a current; but, besides that, it is indifferent with the strong acid at B and the weak acid at C. Now if the dilution of the electrolyte at one part, as C, had so far increased the contact electromotive force there, when iron or copper was present, as to produce the current found by experiment; surely it ought (consistently with any reasonable limitations of the assumptions in the contact theory) to have produced the same effect with silver: but there was none. Making the metal A lead or tin, the difficulty becomes far greater; for though with the strong or the weak acid alone any effect of a determinate current is nothing, yet one occurs upon dilution at C, but now dilution must be supposed to *weaken* instead of *strengthen* the contact force, for the current is in the reverse direction.

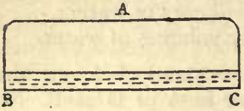

Fig. 74.

979. Neither can these successive changes be referred to a gradual progression in the effect of dilution, dependent upon the *order of the metals*. For supposing dilution more favourable to the electromotive force of the contact of an acid and a metal, *in proportion* as the metals were in a certain order, as for instance that of their efficacy in the voltaic battery; though such an assumption might seem to account for the gradual diminution of effect from iron to copper, and from copper to silver, one would not expect the reverse effects, or those on the other side of zero, to appear by a return back to such metals as lead and tin (967, 977), but rather look for them in platinum or gold, which, however, produce no results of the kind (964, 976). To increase still further this complexity, it appears, from what has been before stated, that on changing the *acids* the

order must again be changed (969); nay, more, that with the same acid, and merely by changing the proportion of dilution, such alteration of the order must take place (974, 976).

980. Thus it appears, as before remarked (970), that to apply the theory of contact electromotive force to the facts, that theory must twist and bend about with every variation of chemical action; and after all, with every variety of contact, active and inactive, in no case presents phenomena independent of the active exertion of chemical force.

981. As the influence of dilution and concentration was so strong in affecting the relation of different parts of the same metal to an acid, making one part either positive or negative to another, I thought it probable that, by mere variation in the strength of the interposed electrolyte, the order of metals when in acids or other solutions of uniform strength might be changed. I therefore proceeded to experiment on that point, by combining together two metals, tin and lead, through the galvanometer (903); arranging the electrolytic solution in tube No. 1, strong on one side and weak on the other: immersing the wires simultaneously, tin into the strong, and lead into the weak solution, and after observing the effect, re-cleaning the wires, rearranging the fluid, and reimmersing the wires, the tin into the weak, and the lead into the strong portion. De la Rive has already stated[1] that inversions take place when dilute and strong sulphuric acid is used; these I could not obtain when care was taken to avoid the effect of the investing fluid (906): the general statement is correct, however, when applied to another acid, and I think the evidence very important to the consideration of the great question of contact or chemical action.

982. *Two metals in strong and weak solution of potash.*—Zinc was positive to tin, cadmium, or lead, whether in the weak or strong solution. Tin was positive to cadmium, either in weak or strong alkali. Cadmium was positive to lead both ways, but most when in the strong alkali. Thus, though there were *differences in degree* dependent on the strength of the solution, there was *no inversion* of the order of the metals.

983. *Two metals in strong and weak sulphuric acid.*—Cadmium was positive to iron and tin both ways: tin was also positive to iron, copper, and silver; and iron was positive to copper and silver, whichever side the respective metals were in. Thus none of the metals tried could be made to pass the others, and so take a different order from that which they have in acid uniform

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[1] *Annales de Chimie*, 1828, xxxvii. p. 240.

in strength. Still there were great variations in degree; thus iron in strong acid was only a little positive to silver in weak acid, but iron in weak acid was very positive to silver in strong acid. Generally the metal, usually called positive, was most positive in the weak acid; but that was not the case with lead, tin, and zinc.

984. *Two metals in strong and weak nitric acid.*—Here the degree of change produced by difference in the strength of the acid was so great as to cause not merely difference in degree, but inversions of the order of the metals, of the most striking nature. Thus iron and silver being in tube No. 2 (962), whichever metal was in the weak acid was positive to the other in the strong acid. It was merely requisite to raise the one and lower the other metal to make either positive at pleasure (963). Copper in weak acid was positive to silver, lead, or tin in strong acid. Iron in weak acid was positive to silver, copper, lead, zinc, or tin in strong acid. Lead in weak acid was positive to copper, silver, tin, cadmium, zinc, and iron in strong acid. Silver in weak acid was positive to iron, lead, copper, and, though slightly, even to tin in strong acid. Tin in weak acid was positive to copper, lead, iron, zinc, and silver, and either neutral or a little positive to cadmium in strong acid. Cadmium in weak acid is very positive, as might be expected, to silver, copper, lead, iron, and tin, and, moderately so, to zinc in the strong acid. When cadmium is in the strong acid it is slightly positive to silver, copper, and iron in weak acid. Zinc in weak acid is very positive to silver, copper, lead, iron, tin, and cadmium in strong acid: when in the strong acid it is a little positive to silver and copper in weak acid.

985. Thus wonderful changes occur amongst the metals in circuits containing this acid, merely by the effect of dilution; so that of the five metals, silver, copper, iron, lead, and tin, any one of them can be made either positive or negative to any other, with the exception of silver positive to copper. The order of these five metals only may therefore be varied about one hundred different ways in the same acid, merely by the effect of dilution.

986. So also zinc, tin, cadmium, and lead; and likewise zinc, tin, iron, and lead, being groups each of four metals; any one of these metals may be made either positive or negative to any other metal of the same group, by dilution of this acid.

987. But the case of variation by dilution may, as regards the

opposed theories, be made even still stronger than any yet stated; for the *same metals* in the *same acid* of the *same strength at the two sides* may be made to change their order, as the chemical action of the acid on each particular metal is affected, by dilution, in a smaller or greater degree.

988. A voltaic association of iron and silver was dipped, both metals at once, into the same strong nitric acid; for the first instant, the iron was positive; the moment after, the silver became positive, and continued so. A similar association of iron and silver was put into weak nitric acid, and the iron was immediately positive, and continued so. With iron and copper the same results were obtained.

989. These, therefore, are *finally* cases of such an inversion (987), but as the iron in the strong nitric acid acquires a state the moment after its immersion which is probably not assumed by it in the weak acid (831, 939, 1021), and as the action on the iron in its *ordinary* state may be said to be to render it positive to the silver or copper, both in the strong or weak acid, we will not endeavour to force the fact, but look to other metals.

990. *Silver and nickel* being associated in weak nitric acid, the nickel was positive; being associated in strong nitric acid, the nickel was still positive at the first moment, but the silver was finally positive. The nickel lost its superiority through the influence of an investing film (906); and though the effect might easily pass unobserved, the case cannot be allowed to stand, as fulfilling the statement made (987).

991. *Copper and nickel* were put into strong nitric acid; the copper was positive from the first moment. Copper and nickel being in dilute nitric acid, the nickel was slightly but clearly positive to the copper. Again, *zinc and cadmium* in strong nitric acid; the cadmium was positive strongly to the zinc; the same metals being in dilute nitric acid, the zinc was very positive to the cadmium. These I consider beautiful and unexceptionable cases (987).

992. Thus the nitric acid furnishes a most wonderful variety of effects when used as the electrolytic conductor in voltaic circles; and its difference from sulphuric acid (983) or from potassa (982) in the phenomena consequent upon dilution, tend, in conjunction with many preceding facts and arguments, to show that the electromotive force in a circle is not the consequence of any power in bodies generally, belonging to them in classes rather than as individuals, and having that simplicity

of character which contact force has been assumed to have; but one that has all the variations which chemical force is *known* to exhibit.

993. The changes occurring where any one of four or five metals, differing from each other as far as silver and tin, can be made positive or negative to the others (985, 986), appears to me to shut out the probability that the contact of these metals with each other can produce the smallest portion of the effect in these voltaic arrangements; and then, if not there, neither can they be effective in any other arrangements; so that what has been deduced in that respect from former experiments (817, 821) is confirmed by the present.

994. Or if the scene be shifted, and it be said that it is the *contact* of the acids or solutions which, by dilution at one side, produce these varied changes (862, 970, 979, 1002, 1048), then how *utterly unlike* such contact must be to that of the numerous class of conducting solid bodies (797, 855)! and where, to give the assumption any show of support, is the case of such contact (apart from chemical action) producing such currents?

995. That it cannot be an alteration of contact force by mere dilution at one side (994) is also shown by making such a change, but using metals that are chemically inactive in the electrolyte employed. Thus when nitric or sulphuric acids were diluted at one side, and then the strong and the weak parts connected by platinum or gold (964), there was no sensible current, or only one so small as to be unimportant.

996. A still stronger proof is afforded by the following result. I arranged the tube, fig. 72 (960), with strong solution of yellow sulphuret of potassium (800) from A to *m*, and a solution consisting of one volume of the strong solution, with six of water from *m* to B. The extremities were then connected by platinum and iron in various ways; and when the first effect of immersion was guarded against, including the first brief negative state of the iron (1037), the effects were as follows. Platinum being in A and in B, that in A, or the strong solution, was very slightly positive, causing a permanent deflection of 2°. Iron being in A and in B, the same result was obtained. Iron being in A and platinum in B, the iron was positive about 2° to the platinum. Platinum being in A and iron in B, the platinum was now positive to the iron by about 2°. So that not only the contact of the iron and platinum passes for nothing, but the contact of strong and weak solution of this electrolyte with either iron or platinum is ineffectual in producing a

current. The current which is constant is very feeble, and evidently related to the mutual position of the strong and weak solutions, and is probably due to their gradual mixture.

997. The results obtained by dilution of an electrolyte capable of acting on the metals employed to form with it a voltaic circuit may in some cases depend on making the acid a better electrolyte. It would appear, and would be expected from the chemical theory, that whatever circumstance tends to make the fluid a more powerful chemical agent and a better electrolyte (the latter being a relation purely chemical and not one of contact), favours the production of a determinate current. Whatever the cause of the effect of dilution may be, the results still tend to show how valuable the voltaic circle will become as an investigator of the nature of chemical affinity (947).

¶ vi. *Differences in the Order of the Metallic Elements of Voltaic Circles*

998. Another class of experimental arguments, bearing upon the great question of the origin of force in the voltaic battery, is supplied by a consideration of the different order in which the metals appear as electromotors when associated with different exciting electrolytes. The metals are usually arranged in a certain order; and it has been the habit to say that a metal in the list so arranged is negative to any one above it, and positive to any one beneath it, as if (and indeed upon the conviction that) they possessed a certain direct power one with another. But in 1812 Davy showed inversions of this order in the case of iron and copper[1] (678); and in 1828 De la Rive showed many inversions in different cases[2] (865); gave a strong contrast in the order of certain metals in strong and dilute nitric acid;[3] and in objecting to Marianini's result most clearly says that any order must be considered in relation only to that liquid employed in the experiments from which the order is derived.[4]

999. I have pursued this subject in relation to several solutions, taking the precautions before referred to (905, etc.), and find that no such single order as that just referred to can be maintained. Thus nickel is negative to antimony and bismuth in strong nitric acid; it is positive to antimony and bismuth in

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[1] *Elements of Chemical Philosophy*, p. 149.

[2] *Annales de Chimie*, 1828, xxxvii. p. 232.

[3] *Ibid.* p. 235.

[4] *Ibid.* p. 243.

dilute nitric acid; it is positive to antimony and negative to bismuth in strong muriatic acid; it is positive to antimony and bismuth in dilute sulphuric acid; it is negative to bismuth and antimony in potash; and it is very negative to bismuth and antimony, either in the colourless or the yellow solution of sulphuret of potassium.

1000. In further illustration of this subject I will take ten metals, and give their order in seven different solutions, as on opposite page.

1001. The dilute nitric acid consisted of one volume strong acid and seven volumes of water; the dilute sulphuric acid, of one volume strong acid and thirteen of water; the muriatic acid, of one volume strong solution and one volume water. The strong nitric acid was pure, and of specific gravity 1.48. Both strong and weak solution of potassa gave the same order. The yellow sulphuret of potassium consisted of one volume of strong solution (800) and five volumes of water. The metals are numbered in the order which they presented in the dilute acids (the negative above), for the purpose of showing, by the comparison of these numbers in the other columns, the striking departures there from this, the most generally assumed order. Iron is included, but only in its ordinary state; its place in nitric acid being given as that which it possesses on its first immersion, not that which it afterwards acquires.

1002. The displacements appear to be most extraordinary, as extraordinary as those consequent on dilution (993); and thus show that there is no general ruling influence of fluid conductors, or even of acids, alkalies, etc., as distinct classes of such conductors, apart from their pure chemical relations. But how can the contact theory account for these results? To meet such facts it must be bent about in the most extraordinary manner, following all the contortions of the string of facts (862, 944, 980, 994, 1051), and yet never showing a case of the production of a current by contact alone, *i.e.* unaccompanied by chemical action.

1003. On the other hand, how simply does the chemical theory of excitement of the current represent the facts! as far as we can yet follow them they go hand in hand. Without chemical action, no current; with the changes of chemical action, changes of current; whilst the influence of the strongest cases of *contact*, as of silver and tin (985) with each other, pass for nothing in the result. In further confirmation, the exciting power does not rise, but fall, by the contact of the bodies pro-

Dilute nitric acid.	Dilute sulphuric acid.	Muriatic acid.	Strong nitric acid.	Solution of caustic potassa.	Colourless bihydrosulphuret of potassium.	Yellow hydrosulphuret of potassium.
1. Silver	1. Silver	3. Antimony	5. Nickel	1. Silver	6. Iron	6. Iron
2. Copper	2. Copper	1. Silver	1. Silver	5. Nickel	5. Nickel	5. Nickel
3. Antimony	3. Antimony	5. Nickel	3. Antimony	2. Copper	4. Bismuth	4. Bismuth
4. Bismuth	4. Bismuth	4. Bismuth	2. Copper	6. Iron	8. Lead	3. Antimony
5. Nickel	5. Nickel	2. Copper	4. Bismuth	4. Bismuth	1. Silver	8. Lead
6. Iron	6. Iron	6. Iron	6. Iron	8. Lead	3. Antimony	1. Silver
7. Tin	8. Lead	8. Lead	7. Tin	3. Antimony	7. Tin	7. Tin
8. Lead	7. Tin	7. Tin	8. Lead	9. Cadmium	2. Copper	9. Cadmium
9. Cadmium	9. Cadmium	9. Cadmium	10. Zinc	7. Tin	10. Zinc	2. Copper
10. Zinc	10. Zinc	10. Zinc	9. Cadmium	10. Zinc	9. Cadmium	10. Zinc

duced, as the chemical actions producing these decay or are exhausted; the consequent result being well seen in the effect of the investing fluids produced (906, 941, 954).

1004. Thus, as De la Rive has said, any list of metals in their order should be constructed in reference to the exciting fluid selected. Further, a zero point should be expressed in the series; for as the electromotive power may be either at the anode or cathode (1028, 1040), or jointly at both, that substance (if there be one) which is absolutely without any exciting action should form the zero point. The following may be given, by way of illustration, as the order of a few metals, and other substances in relation to muriatic acid:

Peroxide of lead,
Peroxide of manganese,
Oxide of iron,
PLUMBAGO,
Rhodium,
Platinum,
Gold,
Antimony,
Silver,
Copper,
Zinc:

in which plumbago is the neutral substance; those in italics are active at the cathode, and those in Roman characters at the anode. The upper are of course negative to the lower. To make such lists as complete as they will shortly require to be, numbers expressive of the relative exciting force, counting from the zero point, should be attached to each substance.

¶ vii. *Active Voltaic Circles and Batteries without Metallic Contact*

1005. There are cases in abundance of electric currents produced by pure chemical action, but not one undoubted instance of the production of a current by pure contact. As I conceive the great question must now be settled by the weight of evidence, rather than by simple philosophic conclusions (787), I propose adding a few observations and facts to show the number of these cases, and their force. In the sixth part of these Researches[1] (April 1834) I gave the first experiment, that I am aware of, in which chemical action was made to produce an electric current and chemical decomposition at a distance, in a

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[1] *Philosophical Transactions*, 1834, p. 426.

simple circuit, without any contact of metals (615, etc.). It was further shown that when a pair of zinc and platinum plates were excited at one end of the dilute nitro-sulphuric acid (615), or solution of potash (619), or even in some cases a solution of common salt (620), decompositions might be produced at the other end, of solutions of iodide of potassium (635), protochloride of tin (636), sulphate of soda, muriatic acid, and nitrate of silver (641); or of the following bodies in a state of fusion: nitre, chlorides of silver and lead, and iodide of lead (637, 641); no metallic contact being allowed in any of the experiments.

1006. I will proceed to mention new cases; and first, those already referred to, where the action of a little dilute acid produced a current passing through the solution of the sulphuret of potassium (819), or green nitrous acid (832), or the solution of potassa (842); for here no metallic contact was allowed, and chemical action was the evident and only cause of the currents produced.

1007. On the following page is a table of cases of similar excitement and voltaic action, produced by chemical action without metallic contact. Each horizontal line contains the four substances forming a circuit, and they are so arranged as to give the direction of the current, which was in all cases from left to right through the bodies as they now stand. All the combinations set down were able to effect decomposition, and they are but a few of those which occurred in the course of the investigation.

1008.—*See next page.*

1009. It appears to me probable that any one of the very numerous combinations which can be made out of the following table, by taking one substance from each column and arranging them in the order in which the columns stand, would produce a current without metallic contact, and that some of these currents would be very powerful.

Rhodium	Strong nitrous acid, or strong solution of sulphuret of potassium.	Iron	Dilute nitric acid
Gold			Dilute sulphuric acid
Platinum			Muriatic acid
Palladium			Solution of vegetable acids
Silver			Iodide of potassium
Nickel			Iodide of zinc
Copper			Solution of salt
Lead			Many metallic solutions
Tin			
Zinc			
Cadmium			

1008

Iron	Dilute nitric acid	Platinum	Sulph. of Potassium (1812)	Full current
Iron	Dilute nitric acid	Platinum	Red nitric acid	Full current
Iron	Dilute nitric acid	Platinum	Pale nitric acid, strong	Good
Iron	Dilute nitric acid	Platinum	Green nitrous acid	Very powerful
Iron	Dilute nitric acid	Platinum	Iodide of potassium	Full current
Iron	Dilute sulphuric acid	Platinum	Sulphuret of potassium	Full
Iron	Dilute sulphuric acid	Platinum	Red nitric acid	Good
Iron	Muriatic acid	Platinum	Green nitrous acid	Most powerful
Iron	Dilute muriatic acid	Platinum	Red nitric acid	Good
Iron	Dilute muriatic acid	Platinum	Sulphuret of potassium	Good
Iron	Solution of salt	Platinum	Green nitrous acid	Most powerful
Iron	Common water	Platinum	Green nitrous acid	Good
Zinc	Dilute nitric acid	Platinum	Iodide of potassium	Good
Zinc	Muriatic acid	Platinum	Iodide of potassium	Good
Cadmium	Dilute nitric acid	Platinum	Iodide of potassium	Good
Cadmium	Muriatic acid	Platinum	Iodide of potassium	Good
Lead	Dilute nitric acid	Platinum	Iodide of potassium	Good
Lead	Muriatic acid	Platinum	Iodide of potassium	Good
Copper	Dilute nitric acid	Platinum	Iodide of potassium	
Copper	Muriatic acid	Platinum	Iodide of potassium	
Lead	Strong sulphuric acid	Iron	Dilute sulphuric acid	Strong
Tin	Strong sulphuric acid	Iron	Dilute sulphuric acid	Strong
Copper	Sulphuret of potassium	Iron	Dilute nitric acid	Powerful
Copper	Sulphuret of potassium	Iron	Iodide of potassium	
Copper	Strong nitric acid	Iron	Dilute nitric acid	Very powerful
Copper	Strong nitric acid	Iron	Iodide of potassium	
Silver	Strong nitric acid	Iron	Dilute nitric acid	Strong
Silver	Strong nitric acid	Iron	Iodide of potassium	Good
Silver	Sulphuret of potassium	Iron	Dilute nitric acid	Strong
Tin	Strong sulphuric acid	Copper	Dilute sulphuric acid	

1010. To these cases must be added the many in which one metal in a uniform acid gave currents when one side was heated (930, etc.). Also those in which one metal with an acid strong and diluted gave a current (965, etc.).

1011. In the cases where by dilution of the acid one metal can be made either positive or negative to another (984, etc.), one half of the results should be added to the above, except that they are too strong; for instead of proving that chemical action can produce a current without contact, they go to the extent of showing a total disregard of it, and production of the current against the force of contact, as easily as with it.

1012. That it is easy to construct batteries without metallic contact was shown by Sir Humphry Davy in 1801,[1] when he described various effective arrangements including only one metal. At a later period Zamboni constructed a pile in which but one metal and one fluid was used,[2] the only difference being extent of contact at the two surfaces. The following forms, which are dependent upon the mere effect of dilution, may be added to these.

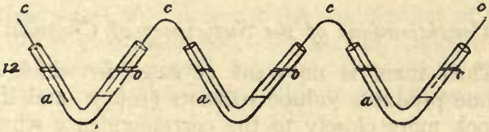

Fig. 75.

1013. Let *a b*, *a b*, *a b*, fig. 75, represent tubes or other vessels, the parts at *a* containing strong nitric or sulphuric acid, and the parts at *b* dilute acid of the same kind; then connect these by wires, rods, or plates of one metal only, being copper, iron, silver, tin, lead, or any of those metals which become positive and negative by difference of dilution in the acid (967, etc.). Such an arrangement will give an effective battery.

1014. If the acid used be the sulphuric, and the metal employed be iron, the current produced will be in one direction, thus ⟵, through the part figured; but if the metal be tin, the resulting current will be in the contrary direction, thus ⟶

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[1] *Philosophical Transactions*, 1801, p. 397. Also *Journals of the Royal Institution*, 1802, p. 51; and *Nicholson's Journal*, 8vo, 1802, vol. i. p. 144.

[2] *Quarterly Journal of Science*, viii. 177; or *Annales de Chimie*, 1819, xi. 190.

1015. Strong and weak solutions of potassa being employed in the tubes, then the single metals zinc, lead, copper, tin, and cadmium (969) will produce a similar battery.

1016. If the arrangements be as in fig. 76, in which the vessels 1, 3, 5, etc. contain strong sulphuric acid, and the vessels 2, 4, 6, etc. dilute sulphuric acid; and if the metals *a*, *a*, *a* are tin, and *b*, *b*, *b* are iron (967), a battery electric current will be produced in the direction of the arrow. If the metals be changed for each other, the acids remaining; or the acids be changed, the metals remaining; the direction of the current will be reversed.

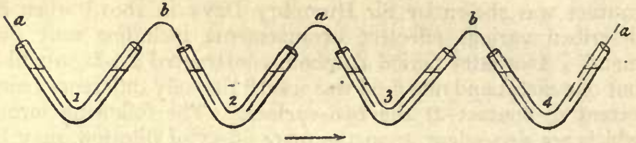

Fig. 76.

¶ viii. *Considerations of the Sufficiency of Chemical Action*

1017. Thus there is no want of cases in which chemical action alone produces voltaic currents (1005); and if we proceed to look more closely to the correspondence which ought to exist between the chemical action and the current produced, we find that the further we trace it the more exact it becomes; in illustration of which the following cases will suffice.

1018. *Chemical action does evolve electricity.*—This has been abundantly proved by Becquerel and De la Rive. Becquerel's beautiful voltaic arrangement of acid and alkali[1] is a most satisfactory proof that chemical action is abundantly sufficient to produce electric phenomena. A great number of the results described in the present papers prove the same statement.

1019. *Where chemical action has been, but diminishes or ceases, the electric current diminishes or ceases also.*—The cases of tin (870, 872), lead (873), bismuth (883), and cadmium (893), in the solution of sulphuret of potassium, are excellent instances of the truth of this proposition.

1020. If a piece of grain tin be put into strong nitric acid, it will generally exert no action, in consequence of the film of

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[1] *Annales de Chimie*, 1827, xxxv. p. 122. *Bibliothèque Universelle*, 1838, xiv. 129, 171.

oxide which is formed upon it by the heat employed in the process of breaking it up. Then two platinum wires, connected by a galvanometer, may be put into the acid, and one of them pressed against the piece of tin, yet without producing an electric current. If, whilst matters are in this position, the tin be scraped under the acid by a glass rod, or other non-conducting substance capable of breaking the surface, the acid acts on the metal newly exposed, and produces a current; but the action ceases in a moment or two from the formation of oxide of tin and an exhausted investing solution (906), and the current ceases with it. Each scratch upon the surface of the tin reproduces the series of phenomena.

1021. The case of iron in strong nitric acid, which acts and produces a current at the first moment (831, 939, 989), but is by that action deprived of so much of its activity, both chemical and electrical, is also a case in point.

1022. If lead and tin be associated in muriatic acid, the lead is positive at the first moment to the tin. The tin then becomes positive, and continues so. This change I attribute to the circumstance that the chloride of lead formed partly invests that metal, and prevents the continuance of the action there; but the chloride of tin, being far more soluble than that of lead, passes more readily into the solution; so that action goes on there, and the metal exhibits a permanent positive state.

1023. The effect of the investing fluid already referred to in the cases of tin (907) and cadmium (906), some of the results with two metals in hot and cold acid (954), and those cases where metal in a heated acid became negative to the same metal in cold acid (941, etc.), are of the same kind. The latter can be beautifully illustrated by two pieces of lead in dilute nitric acid: if left a short time, the needle stands nearly at 0°, but on heating either side, the metal there becomes negative 20° or more, and continues so as long as the heat is continued. On cooling that side and heating the other, that piece of lead which before was positive now becomes negative in turn, and so on for any number of times.

1024. *When the chemical action changes the current changes also.*—This is shown by the cases of two pieces of the same active metal in the same fluid. Thus if two pieces of silver be associated in strong muriatic acid, first the one will be positive and then the other; and the changes in the direction of the current will not be slow as if by a gradual action, but exceedingly sharp and sudden. So if silver and copper be associated in a dilute solution of sulphuret of potassium, the copper will be chemically active and positive, and the silver will remain clean; until of a sudden the copper will cease to act, the silver will become instantly covered with sulphuret, showing by that the commencement of chemical action there, and the needle of the galvanometer will jump through 180°. Two pieces of silver or of copper in solution of sulphuret of potassium produce the same effect.

1025. If metals be used which are inactive in the fluids employed, and the latter undergo no change during the time, from other circumstances, as heat, etc. (826, 925), then no currents, and of course no such alterations in direction, are produced.

1026. *Where no chemical action occurs no current is produced.*—This in regard to ordinary solid conductors is well known to be the case, as with metals and other bodies (855). It has also been shown to be true when fluid conductors (electrolytes) are used, in every case where they exert no chemical action, though such different substances as acid, alkalies and sulphurets have been employed (831, 841, 813, 817). These are very striking facts.

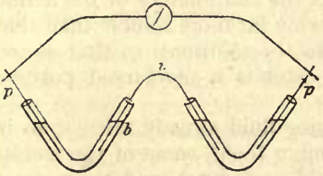

Fig. 77.

1027. *But a current will occur the moment chemical action commences.*—This proposition may be well illustrated by the following experiment. Make an arrangement like that in fig. 77: the two tubes being charged with the same pure, pale, strong nitric acid, the two platinum wires *p p* being connected by a galvanometer, and the wire *i*, of iron. The apparatus is only another form of the simple arrangement, fig. 78, where, in imitation of a former experiment (624), two plates of iron and platinum are placed parallel, but separated by a drop of strong nitric acid at each extremity. Whilst in this state no current is produced in either apparatus; but if a drop of water be added at *b*, fig. 78, chemical action commences, and a powerful current is produced, though without metallic or any additional contact. To observe this with the apparatus, fig. 77, a drop of water was put in at *b*. At first there was no chemical

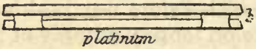

Fig. 78.

action and no electric current, though the water was there, so that contact with the water did nothing: the water and acid were moved and mixed together by means of the end of the wire *i;* in a few moments proper chemical action came on, the iron evolving nitrous gas at the place of its action, and at the same time acquiring a positive condition at that part, and producing a powerful electric current.

1028. *When the chemical action which either has or could have produced a current in one direction is reversed or undone, the current is reversed (or undone) also.*

1029. This is a principle or result which most strikingly confirms the chemical theory of voltaic excitement, and is illustrated by many important facts. Volta in the year 1802 [1] showed that crystallised *oxide of manganese* was highly negative to zinc and similar metals, giving, according to his theory, electricity to the zinc at the point of contact. Becquerel worked carefully at this subject in 1835,[2] and came to the conclusion, but reservedly expressed, that the facts were favourable to the theory of contact. In the following year De la Rive examined the subject,[3] and shows, to my satisfaction at least, that the peroxide is at the time undergoing chemical change and losing oxygen, a change perfectly in accordance with the direction of the current it produces.

1030. The peroxide associated with platinum in the green nitrous acid originates a current, and is negative to the platinum, at the same time giving up oxygen and converting the nitrous acid into nitric acid, a change easily shown by a common chemical experiment. In nitric acid the oxide is negative to platinum, but its negative state is much increased if a little alcohol be added to the acid, that body assisting in the reduction of the oxide. When associated with platinum in solution of potash, the addition of a little alcohol singularly favours the increase of the current for the same reason. When the peroxide and platinum are associated with solution of sulphuret of potassium, the peroxide, as might have been expected, is strongly negative.

1031. In 1835 M. Muncke [4] observed the striking power of peroxide of lead to produce phenomena like those of the peroxide of manganese, and these M. de la Rive in 1836 immediately referred to corresponding chemical changes.[5] M. Schœnbein

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[1] *Annales de Chimie*, 1802, xl. 224.

[2] *Ibid.* 1835, lx. 164, 171.

[3] *Ibid.* 1836, lxi. 40; and *Bibliothèque Universelle*, 1836, i. 152, 158.

[4] *Bibliothèque Universelle*, 1836, i. 160.

[5] *Ibid.* 1836, i., 154 162.

does not admit this inference, and bases his view of "currents of tendency" on the phenomena presented by this body and its non-action with nitric acid.[1] My own results confirm those of M. de la Rive, for by direct experiment I find that the peroxide is acted upon by such bodies as nitric acid. Potash and pure strong nitric acid boiled on peroxide of lead readily dissolved it, forming protonitrate of lead. A dilute nitric acid was made and divided into two portions; one was tested by a solution of sulphuretted hydrogen, and showed no signs of lead: the other was mingled with a little peroxide of lead (810) at common temperatures, and after an hour filtered and tested in the same manner, and found to contain plenty of lead.

1032. The peroxide of lead is negative to platinum in solutions of common salt and potash, bodies which might be supposed to exert no chemical action on it. But direct experiments show that they do exert sufficient action to produce all the effects. A circumstance in further proof that the current in the voltaic circuit formed by these bodies is chemical in its origin is the rapid depression in the force of the current produced, after the first moment of immersion.

1033. The most powerful arrangement with peroxide of lead, platinum, and one fluid, was obtained by using a solution of the yellow sulphuret of potassium as the connecting fluid. A convenient mode of making such experiments was to form the peroxide into a fine soft paste with a little distilled water, to cover the lower extremity of a platinum plate uniformly with this paste, using a glass rod for the purpose, and making the coat only thick enough to hide the platinum well, then to dry it well, and finally, to compare that plate with a clean platinum plate in the electrolyte employed. Unless the platinum plate were perfectly covered, local electrical currents took place which interfered with the result. In this way, the peroxide is easily shown to be negative to platinum either in the solution of the sulphuret of potassium or in nitric acid. Red lead gave the same results in both these fluids.

1034. But using this sulphuretted solution, the same kind of proof in support of the chemical theory could be obtained from protoxides as before from the peroxides. Thus, some pure protoxide of lead, obtained from the nitrate by heat and fusion, was applied on the platinum plate (1033), and found to be strongly negative to metallic platinum in the solution of

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[1] *Philosophical Magazine*, 1838, xii. 226, 311; and *Bibliothèque Universelle*, 1838, xiv. 155.

sulphuret of potassium. White lead applied in the same manner was also found to acquire the same state. Either of these bodies when compared with platinum in dilute nitric acid was, on the contrary, very positive.

1035. The same effect is well shown by the action of oxidised iron. If a plate of iron be oxidised by heat so as to give an oxide of such aggregation and condition as to be acted on scarcely or not at all by the solution of sulphuret, then there is little or no current, such an oxide being as platinum in the solution (828). But if it be oxidised by exposure to air, or by being wetted and dried; or by being moistened by a little dilute nitric or sulphuric acid and then washed, first in solution of ammonia or potassa, and afterwards in distilled water and dried; or if it be moistened in solution of potassa, heated in the air, and then washed well in distilled water and dried; such iron associated with platinum and put into a solution of the sulphuret will produce a powerful current until all the oxide is reduced, the iron during the whole time being negative.

1036. A piece of rusty iron in the same solution is powerfully negative. So also is a platinum plate with a coat of protoxide, or peroxide, or native carbonate of iron on it (1033).

1037. This result is one of those effects which has to be guarded against in the experiments formerly described (814, 874). If what appears to be a clean plate of iron is put into a dilute solution of the sulphuret of potassium, it is first negative to platinum, then neutral, and at last generally feebly positive; if it be put into a strong solution, it is first negative, and then becomes neutral, continuing so. It cannot be cleansed so perfectly with sand-paper but that when immersed it will be negative, but the more recently and well the plate has been cleansed, the shorter time does this state continue. This effect is due to the instantaneous oxidation of the surface of the iron during its momentary exposure to the atmosphere, and the after reduction of this oxide by the solution. Nor can this be considered an unnatural result to those who consider the characters of iron. Pure iron in the form of a sponge takes fire spontaneously in the air; and a plate recently cleansed, if dipped into water, or breathed upon, or only exposed to the atmosphere, produces an instant smell of hydrogen. The thin film of oxide which can form during a momentary exposure is, therefore, quite enough to account for the electric current produced.

1038. As a further proof of the truth of these explanations, I placed a plate of iron under the surface of a solution of the sulphuret of potassium, and rubbed it there with a piece of wood which had been soaking for some time in the same sulphuret. The iron was then neutral or very slightly positive to platinum connected with it. Whilst in connection with the platinum it was again rubbed with the wood so as to acquire a fresh surface of contact; it did not become negative, but continued in the least degree positive, showing that the former negative current was only a temporary result of the coat of oxide which the iron had acquired in the air.

1039. Nickel appears to be subject to the same action as iron, though in a much slighter degree. All the circumstances were parallel, and the proof applied to iron (1038) was applied to it also, with the same result.

1040. So all these phenomena with protoxides and peroxides agree in referring the current produced to chemical action; not merely by showing that the current depends upon the action, but also that the *direction* of the current depends upon the direction which the chemical affinity determines the exciting or electromotive anion to take. And it is, I think, a most striking circumstance, that these bodies, which when they can and do act chemically produce currents, have not the least power of the kind when *mere contact only* is allowed (857), though they are excellent conductors of electricity, and can readily carry the currents formed by other and more effectual means.

1041. With such a mass of evidence for the efficacy and sufficiency of chemical action as that which has been given (866, 1040); with so many current circuits without metallic contact (1005) and so many non-current circuits with (855); what reason can there be for referring the effect in the joint cases where both chemical action and contact occur, to contact, or to anything but the chemical force alone? Such a reference appears to me most unphilosophical: it is dismissing a proved and active cause to receive in its place one which is merely hypothetical.

¶ ix. *Thermo-electric Evidence*

1042. The phenomena presented by that most beautiful discovery of Seebeck, thermo-electricity, has occasionally and, also, recently been adduced in proof of the electromotive influence of contact amongst the metals, and such-like solid conductors[1] (797, 855). A very brief consideration is, I think, sufficient to show how little support these phenomena give to the theory in question.

1043. If the contact of metals exert any exciting influence in the voltaic circuit, then we can hardly doubt that thermo-electric currents are due to the same force; *i.e.* to disturbance, by local temperature, of the balanced forces of the different contacts in a metallic or similar circuit. Those who quote thermo effects as proofs of the effect of contact must, of course, admit this opinion.

1044. Admitting contact force, we may then assume that heat either increases or diminishes the electromotive force of contact. For if in fig. 79, A be antimony and B bismuth, heat applied at x causes a current to pass in the direction of the arrow; if it be assumed that bismuth in contact with antimony tends to become positive and the antimony negative, then heat diminishes the effect; but if it be supposed that the tendency of bismuth is to become negative, and of antimony positive, then heat increases the effect. How we are to decide which of these two views is the one to be adopted, does not seem to me clear; for nothing in the thermo-electric phenomena alone can settle the point by the galvanometer.

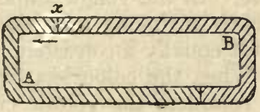

Fig. 79.

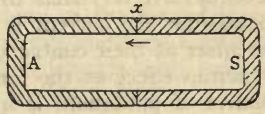

Fig. 80.

1045. If for that purpose we go to the voltaic circuit, there the situation of antimony and bismuth varies according as one or another fluid conductor is used (1000). Antimony, being negative to bismuth with the acids, is positive to it with an alkali or sulphuret of potassium; still we find they come *nearly together* in the midst of the metallic series. In the thermo series, on the contrary, their position is at the *extremes*, being as different or as much opposed to each other as they can be. This difference was long ago pointed out by Professor Cumming:[2] how is it consistent with the contact theory of the voltaic pile?

1046. Again, if silver and antimony form a thermo circle

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[1] See Fechner's words.—*Philosophical Magazine*, 1838, xiii. p. 206.

[2] *Annals of Philosophy*, 1823, vi. 177.

(fig. 80), and the junction *x* be heated, the current there is from the silver to the antimony. If silver and bismuth form a thermo series (fig. 81), and the junction *x* be heated, the current is from the bismuth to the silver; and assuming that heat increases the force of contact (1044), these results will give the direction of contact force between these metals, *antimony* ⟵ *silver*, and *bismuth* ⟶ *silver*. But in the voltaic series the current is *from the silver* to both the antimony and bismuth at their points of contact, whenever dilute sulphuric or nitric acid, or strong nitric acid, or solution of potassa (1000) are used; so that metallic contact, like that in the thermo circle, can at all events have *very little* to do here. In the yellow sulphuret of potassium the current is from both antimony and bismuth *to the silver* at their contacts, a result equally inconsistent with the thermo effect as the former. When the colourless hydrosulphuret of potassium is used to complete the voltaic circle, the current is from bismuth to silver, and from silver to antimony at their points of contact; whilst, with strong muriatic acid, precisely the reverse direction occurs, for it is from silver to bismuth, and from antimony to silver at the junctions.

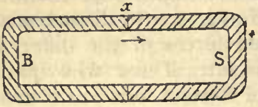

Fig. 81.

1047. Again;—by the heat series copper gives a current to gold; tin and lead give currents to copper, rhodium, or gold; zinc gives one to antimony, or iron, or even plumbago; and bismuth gives one to nickel, cobalt, mercury, silver, palladium, gold, platinum, rhodium, and plumbago; at the *point of contact* between the metals:—currents which are just the reverse of those produced by the same metals, when formed into voltaic circuits and excited by the ordinary acid solutions (1000).

1048. These, and a great number of other discrepancies, appear by a comparison, according to theory, of thermo contact and voltaic contact action, which can only be accounted for by assuming a specific effect of the contact of water, acids, alkalies, sulphurets, and other exciting electrolytes, for each metal; this assumed contact force being not only unlike thermometallic contact, in not possessing a balanced state in the complete circuit at uniform temperatures, but also having no relation to it as to the *order* of the metals employed. So bismuth and antimony, which are far apart in thermo-electric order, must have this extra character of acid contact very greatly developed in an opposite direction as to its result, to render them only a feeble voltaic combination with each other: and with respect to silver, which stands between tin and zinc thermo-electrically, not only must the same departure be required, but how great must the effect of this, its incongruous contact, be, to overcome so completely as it does, and even powerfully reverse the differences which the metals (according to the contact theory) tend to produce!

1049. In further contrast with such an assumption, it must be remembered that, though the series of thermo-electric bodies is different from the usual voltaic order (1000), it is perfectly consistent with itself, *i.e.* that if iron and antimony be weak with each other, and bismuth be strong with iron, it will also be strong with antimony. Also that if the electric current pass from bismuth to rhodium at the hot junction, and also from rhodium to antimony at the hot junction, it will pass far more powerfully from bismuth to antimony at the heated junction. To be at all consistent with this simple and true relation, sulphuric acid should not be strongly energetic with iron or tin and weakly so with silver, as it is in the voltaic circuit, since these metals are not far apart in the thermo series: nor should it be nearly alike to platinum and gold voltaically, since they are far apart in the thermo series.

1050. Finally, in the thermo circuit there is that relation to heat which shows that for every portion of electric force evolved there is a corresponding change in another force, or form of force, namely heat, able to account for it; this, the united experiments of Seebeck and Peltier have shown. But contact force is a force which has to produce something from nothing, a result of the contact theory which can be better stated a little further on (1057, 1059, 1061).

1051. What evidence then for mere contact excitement, derivable from the facts of thermo-electricity, remains, since the power must thus be referred to the acid or other electrolyte used (1048) and made, not only to vary uncertainly for each metal, but to vary also in direct conformity with the variation of chemical action (862, 944, 980, 994, 1002)?

1052. The contact theorist seems to consider that the advocate of the chemical theory is called upon to account for the phenomena of thermo-electricity. I cannot perceive that Seebeck's circle has any relation to the voltaic pile, and think that the researches of Becquerel[1] are quite sufficient to authorise that conclusion.

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[1] *Annales de Chimie*, 1829, xli. 355; xlvi. 275.

¶ x. *Improbable Nature of the Assumed Contact Force*

1053. I have thus given a certain body of experimental evidence and consequent conclusions, which seem to me fitted to assist in the elucidation of the disputed point, in addition to the statements and arguments of the great men who have already advanced their results and opinions in favour of the chemical theory of excitement in the voltaic pile, and against that of contact. I will conclude by adducing a further argument founded upon the, to me, unphilosophical nature of the force to which the phenomena are, by the contact theory, referred.

1054. It is assumed by the theory (790) that where two dissimilar metals (or rather bodies) touch, the dissimilar particles act on each other, and induce opposite states. I do not deny this, but on the contrary think that in many cases such an effect takes place between contiguous particles; as for instance, preparatory to action in common chemical phenomena, and also preparatory to that act of chemical combination which, in the voltaic circuit, causes the current (726, 731).

1055. But the contact theory assumes that these particles, which have thus by their mutual action acquired opposite electrical states, can discharge these states one to the other, and yet remain in the state they were first in, being *in every point* entirely unchanged by what has previously taken place. It assumes also that the particles, being by their mutual action rendered plus and minus, can, whilst under this inductive action, discharge to particles of like matter with themselves and so produce a current.

1056. This is in no respect consistent with known actions. If in relation to chemical phenomena we take two substances, as oxygen and hydrogen, we may conceive that two particles, one of each, being placed together and heat applied, they induce contrary states in their opposed surfaces, according, perhaps, to the view of Berzelius (727), and that these states becoming more and more exalted end at last in a mutual discharge of the forces, the particles being ultimately found combined, and unable to repeat the effect. Whilst they are under induction and before the final action comes on, they cannot spontaneously lose that state; but by removing the *cause* of the increased inductive effect, namely the heat, the effect itself can be lowered to its first condition. If the acting particles are involved in the constitution of an electrolyte, then they can produce current force (656, 659) proportionate to the amount of chemical force consumed (603).

1057. But the contact theory, which is obliged, according to the facts, to admit that the acting particles are not changed (790, 1055) (for otherwise it would be the chemical theory), is constrained to admit also that the force which is able to make two particles assume a certain state in respect to each other, is unable to make them *retain* that state; and so it virtually denies the great principle in natural philosophy, that cause and effect are equal (1059). If a particle of platinum by contact with a particle of zinc willingly gives of its own electricity to the zinc, because this by its presence tends to make the platinum assume a negative state, why should the particle of platinum take electricity from any other particle of platinum behind it, since that would only tend to destroy the very state which the zinc has just forced it into? Such is not the case in common induction (and Marianini admits that the effect of contact may take place through air and measurable distances [1]); for there a ball rendered negative by induction will not take electricity from surrounding bodies, however thoroughly we may uninsulate it; and if we force electricity into it, it will, as it were, be spurned back again with a power equivalent to that of the inducing body.

1058. Or if it be supposed rather, that the zinc particle, by its inductive action, tends to make the platinum particle positive, and the latter, being in connection with the earth by other platinum particles, calls upon them for electricity, and so acquires a positive state; why should it discharge that state to the zinc, the very substance which, making the platinum assume that condition, ought of course to be able to sustain it? Or again, if the zinc tends to make the platinum particle positive, why should not electricity go to the platinum *from the zinc*, which is as much in contact with it as its neighbouring platinum particles are? Or if the zinc particle in contact with the platinum tends to become positive, why does not electricity flow to it from the zinc particles behind, as well as from the platinum?[2]

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[1] *Memorie della Società Italiana in Modena*, 1837, xxi. 232, 233, etc.

[2] I have spoken, for simplicity of expression, as if one metal were active and the other passive in bringing about these induced states, and not, as the theory implies, as if each were mutually subject to the other. But this makes no difference in the force of the argument; whilst an endeavour to state fully the joint changes on both sides would rather have obscured the objections which arise, and which yet are equally strong in either view.

There is no sufficient probable or philosophic cause assigned for the assumed action; or reason given why one or other of the consequent effects above mentioned should not take place: and, as I have again and again said, I do not know of a single fact, or case of contact current, on which, in the absence of such probable cause, the theory can rest.

1059. The contact theory assumes, in fact, that a force which is able to overcome powerful resistance, as for instance that of the conductors, good or bad, through which the current passes, and that again of the electrolytic action where bodies are decomposed by it, can arise out of nothing; that, without any change in the acting matter or the consumption of any generating force, a current can be produced which shall go on for ever against a constant resistance, or only be stopped, as in the voltaic trough, by the ruins which its exertion has heaped up in its own course. This would indeed be *a creation of power*, and is like no other force in nature. We have many processes by which the form of the power may be so changed that an apparent *conversion* of one into another takes place. So we can change chemical force into the electric current, or the current into chemical force. The beautiful experiments of Seebeck and Peltier show the convertibility of heat and electricity; and others by Œrsted and myself show the convertibility of electricity and magnetism. But in no cases, not even those of the Gymnotus and Torpedo (778), is there a pure creation of force; a production of power without a corresponding exhaustion of something to supply it.[1]

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[1] (*Note*, March 29, 1840).—I regret that I was not before aware of most important evidence for this philosophical argument, consisting of the opinion of Dr. Roget, given in his treatise on Galvanism in the Library of Useful Knowledge, the date of which is January 1829. Dr. Roget is, upon the facts of the science, a supporter of the chemical theory of excitation; but the striking passage I desire now to refer to is the following, at § 113 of the article Galvanism. Speaking of the voltaic theory of contact, he says, "Were any further reasoning necessary to overthrow it, a forcible argument might be drawn from the following consideration. If there could exist a power having the property ascribed to it by the hypothesis, namely, that of giving continual impulse to a fluid in one constant direction, without being exhausted by its own action, it would differ essentially from all the other known powers in nature. All the powers and sources of motion, with the operation of which we are acquainted, when producing their peculiar effects, are expended in the same proportion as those effects are produced; and hence arises the impossibility of obtaining by their agency a perpetual effect; or, in other words, a perpetual motion. But the electromotive force ascribed by Volta to the metals when in contact is a force which, as long as a free course is allowed to the electricity it sets in motion, is never expended, and continues to be excited with undiminished power, in the production of a never-ceasing effect. Against the truth of such a supposition, the probabilities are all but infinite."—*Roget.*

1060. It should ever be remembered that the chemical theory sets out with a power the existence of which is pre-proved, and then follows its variations, rarely assuming anything which is not supported by some corresponding simple chemical fact. The contact theory sets out with an assumption, to which it adds others as the cases require, until at last the contact force, instead of being the firm unchangeable thing at first supposed by Volta, is as variable as chemical force itself.

1061. Were it otherwise than it is, and were the contact theory true, then, as it appears to me, the equality of cause and effect must be denied (1057). Then would the perpetual motion also be true; and it would not be at all difficult, upon the first given case of an electric current by contact alone, to produce an electro-magnetic arrangement, which, as to its principle, would go on producing mechanical effects for ever.

December 26, 1839.

NOTE

1062. In a former part (660, etc.) I have said that I do not think any part of the electricity of the voltaic pile is due to the combination of the oxide of zinc with the sulphuric acid used, and that I agreed so far with Sir Humphry Davy in thinking that acids and alkalies did not in combining evolve electricity in large quantity when they were not parts of electrolytes.

This I would correct; for I think that Becquerel's pile is a perfect proof that when acid and alkali combine an electric current is produced.[1]

I perceive that Dr. Mohr of Coblentz appears to have shown that it is only nitric acid which amongst acids can in combining with alkalies produce an electric current.[2]

For myself, I had made exception of the hydracids (664) on theoretical grounds. I had also admitted that oxyacids when in solution might in such cases produce small currents of electricity (663 and *note*); and Jacobi says that in Becquerel's improved acid and alkaline pile, it is not above a thirtieth part of the whole power which appears as current. But I now wish to say, that though in the voltaic battery, dependent for its power on the oxidisement of zinc, I do not think that the

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[1] *Bibliothèque Universelle*, 1838, xiv. 129, 171. *Comptes Rendus*, i. p. 455. *Annales de Chimie*, 1827, xxxv. 122.

[2] *Philosophical Magazine*, 1838, xiii. p. 382; or Poggendorf's *Annalen*, xlii. p. 76.

quantity of electricity is at all increased or affected by the combination of the oxide with the acid (668, 680), still the latter circumstance cannot go altogether for nothing. The researches of Mr. Daniell on the nature of compound electrolytes[1] ties together the electrolysation of a salt and the water in which it is dissolved, in such a manner as to make it almost certain that, in the corresponding cases of the *formation* of a salt at the place of excitement in the voltaic circuit, a similar connection between the water and the salt formed must exist: and I have little doubt that the joint action of water, acids, and bases, in Becquerel's battery, in Daniell's electrolysations, and at the zinc in the ordinary active pile, are, in principle, closely connected together.

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[1] *Philosophical Transactions*, 1839, p. 27.

CORRESPONDENCE ON ELECTRICITY

FROM THE "PHILOSOPHICAL MAGAZINE," ETC.

On a peculiar Voltaic Condition of Iron, by Professor SCHOENBEIN, *of Bâle; in a Letter to* Mr. Faraday: *with further Experiments on the same subject, by* Mr. FARADAY, *communicated in a Letter to* Mr. Phillips.[1]

To Michael Faraday, D.C.L., F.R.S., etc.

SIR,—As our continental and particularly German periodicals are rather slow in publishing scientific papers, and as I am anxious to make you as soon as possible acquainted with some new electro-chemical phenomena lately observed by me, I take the liberty to state them to you by writing. Being tempted to do so only by scientific motives, I entertain the flattering hope that the contents of my letter will be received by you with kindness. The facts I am about laying before you seem to me not only to be new, but at the same time deserving the attention of chemical philosophers. *Les voici.*

If one of the ends of an iron wire be made red hot, and after cooling be immersed in nitric acid, sp. gr. 1.35, neither the end in question nor any other part of the wire will be affected, whilst the acid of the said strength is well known to act rather violently upon common iron. To see how far the influence of the oxidised end of the wire goes, I took an iron wire of 50′ in length and 0″′.5 in thickness, heated one of its ends about 3″ in length, immersed it in the acid of the strength above mentioned, and afterwards put the other end into the same fluid. No action of the acid upon the iron took place. From a similar experiment made upon a cylindrical iron bar of 16′ in length and 4‴ diameter the same result was obtained. The limits of this protecting influence of oxide of iron with regard to quantities I have not yet ascertained; but as to the influence of heat, I found that above the temperature of about 75° the acid acts in the common way upon iron, and in the same manner also, at common temperatures, when the said acid contains water

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[1] *Lond. and Edinb. Phil. Mag.*, 1836, vol. ix. p. 53.

beyond a certain quantity, for instance, 1, 10, 100, and even 1000 times its volume. By immersing an iron wire in nitric acid of sp. gr. 1.5 it becomes likewise indifferent to the same acid of 1.35.

But by far the most curious fact observed by me is, that any number of iron wires may be made indifferent to nitric acid by the following means. An iron wire with one of its ends oxidised is made to touch another common iron wire; both are then introduced into nitric acid of sp. gr. 1.35, so as to immerse the oxidised end of the one wire first into the fluid, and have part of both wires above the level of the acid. Under these circumstances no chemical action upon the wires will take place, for the second wire is, of course, but a continuation of that provided with an oxidised end. But no action occurs, even after the wires have been separated from each other. If the second wire having become indifferent be now taken out of the acid and made to touch at any of its parts not having been immersed a third wire, and both again introduced into the acid so as to make that part of the second wire which had previously been in the fluid enter first, neither of the wires will be acted upon either during their contact or after their separation. In this manner the third wire can make indifferent or passive a fourth one, and so on.

Another fact, which has as yet, as far as I know, not been observed, is the following one. A wire made indifferent by any of the means before mentioned is immersed in nitric acid of sp. gr. 1.35, so as to have a considerable part of it remaining out of the fluid; another common wire is put into the same acid, likewise having one of its ends rising above the level of the fluid. The part immersed of this wire will, of course, be acted upon in a lively manner. If the ends of the wires which are out of the acid be now made to touch one another, the indifferent wire will instantly be turned into an active one, whatever may be the lengths of the parts of the wires not immersed. [If there is any instance of chemical affinity being transmitted in the form of a current by means of conducting bodies, I think the fact just stated may be considered as such.] It is a matter of course that direct contact between the two wires in question is not an indispensably necessary condition for communicating chemical activity from the active wire to the passive one; for any metal connecting the two ends of the wires renders the same service.

Before passing to another subject, I must mention a fact which seems to be one of some importance. An iron wire curved into a fork is made to touch at its bend a wire provided with an oxidised end; in this state of contact both are introduced into nitric acid of sp. gr. 1.35 and 30°, so as first to immerse in the acid the oxidised end; the fork will, of course, not be affected. If now a common iron wire be put into the acid, and one of the ends of the fork touched by it, this end will immediately be acted upon, whilst the other end remains passive; but as soon as the iron wire with the oxidised end is put out of contact with the bend of the fork, its second end is also turned active. If the parts of the fork rising above the level of the acid be touched by an iron wire, part of which is immersed and active in the acid, no communication of chemical activity will take place, and both ends of the fork remain passive; but by the removal of the iron wire (with the oxidised end) from the bend of the fork this will be thrown into chemical action.

As all the phenomena spoken of in the preceding lines are, no doubt, in some way or other dependent upon a peculiar electrical state of the wires, I was very curious to see in what manner iron would be acted upon by nitric acid when used as an electrode. For this purpose I made use of that form of the pile called the *couronne des tasses*, consisting of fifteen pairs of zinc and copper. A platina wire was connected with (what we call) the negative pole of the pile, an iron wire with the positive one. The free end of the platina wire was first plunged into nitric acid sp. gr. 1.35, and by the free end of the iron wire the circuit closed. Under these circumstances the iron was not in the least affected by the acid; and it remained indifferent to the fluid not only as long as the current was passing through it, but even after it had ceased to perform the function of the positive electrode. The iron wire proved, in fact, to be possessed of all the properties of what we have called a passive one. If such a wire is made to touch the negative electrode, it instantaneously becomes an active one, and a nitrate of iron is formed; whether it be separate from the positive pole or still connected with it, and the acid be strong or weak.

But another phenomenon is dependent upon the passive state of the iron, which phenomenon is in direct contradiction with all the assertions hitherto made by philosophical experimenters. The oxygen at the anode arising from the decomposition of water contained in the acid does not combine with the iron serving as the electrode, but is evolved at it, just in the same manner as if it were platina, and to such a volume as to bear the ratio of

1 : 2 to the quantity of hydrogen evolved at the cathode. To obtain this result I made use of an acid containing 20 times its volume of water; I found, however, that an acid containing 400 times its volume of water still shows the phenomenon in a very obvious manner. But I must repeat it, the indispensable condition for causing the evolution of the oxygen at the iron wire is to close the circuit exactly in the same manner as above mentioned. For if, *exempli gratiâ*, the circuit be closed with the negative platina wire, not one single bubble of oxygen gas makes its appearance at the positive iron; neither is oxygen given out at it, when the circuit is closed, by plunging first one end of the iron wire into the nitric acid, and by afterwards putting its other end in connection with the positive pole of the pile. In both cases a nitrate of iron is formed, even in an acid containing 400 times its volume of water; which salt may be easily observed descending from the iron wire in the shape of brownish-yellow-coloured streaks.

I have still to state the remarkable fact, that if the evolution of oxygen at the anode be ever so rapidly going on, and the iron wire made to touch the negative electrode within the acid, the disengagement of oxygen is discontinued, not only during the time of contact of the wires, but after the electrodes have been separated from each other. A few moments holding the iron wire out of the acid is, however, sufficient to recommunicate to it the property of letting oxygen gas evolve at its surface. By the same method the wire acquires its evolving power again, whatever may have been the cause of its loss. The evolution of oxygen also takes place in dilute sulphuric and phosphoric acids, provided, however, the circuit be closed in the manner above described. It is worthy of remark, that the disengagement of oxygen at the iron in the last-named acids is much easier stopped, and much more difficult to be caused again, than is the case in nitric acid. In an aqueous solution of caustic potash oxygen is evolved at the positive iron, in whatever manner the circuit may be closed; but no such disengagement takes place in aqueous solutions of hydracids, chlorides, bromides, iodides, fluorides. The oxygen, resulting in these cases from the decomposition of water, and the anion (chlorine, bromine, etc.) of the other electrolyte decomposed combine at the same time with the iron.

To generalise these facts, it may be said that independently of the manner of closing the circuit, oxygen is always disengaged at the positive iron, provided the aqueous fluid in which it is immersed do not (in a sensible manner) chemically act upon it; and that no evolution of oxygen at the anode in contact with iron under any circumstances takes place, if besides oxygen another anion is set free possessed of a strong affinity for iron. This metal having once had oxygen evolved at itself, proves always to be indifferent to nitric acid of a certain strength, whatever may be the chemical nature of the fluid in which the phenomenon has taken place.

I have made a series of experiments upon silver, copper, tin, lead, cadmium, bismuth, zinc, mercury, but none showed any resemblance to iron, for all of them were oxidised when serving as positive electrodes. Having at this present moment neither cobalt nor nickel at my command, I could not try these magnetic metals, which I strongly suspect to act in the same manner as iron does.

It appears from what I have just stated that the anomalous bearing of the iron has nothing to do with its degree of affinity for oxygen, but must be founded upon something else. Your sagacity, which has already penetrated into so many mysteries of nature, will easily put away the veil which as yet covers the phenomenon stated in my letter, in case you should think it worth while to make it the object of your researches.

Before I finish I must beg of you the favour of overlooking with indulgence the many faults I have, no doubt, committed in my letter. Formerly I was tolerably well acquainted with your native tongue; but now, having been out of practice in writing or speaking it, it is rather hard work to me to express myself in English.

It is hardly necessary to say that you may privately or publicly make any use of the contents of this letter.—I am, Sir, your most obedient Servant,

C. T. SCHOENBEIN,
BÂLE, *May* 17, 1836. Prof. of Chem. in the University of Bâle.

DEAR PHILLIPS,—The preceding letter from Professor Schoenbein, which I received a week or two ago, contains facts of such interest in relation to the first principles of chemical electricity, that I think you will be glad to publish it in your *Philosophical Magazine*. I send it to you unaltered, except in a word or two here and there; but am encouraged by what I consider the Professor's permission (or rather the request with which he has honoured me), to add a few results in confirmation of the effects described, and illustrative of some conclusions that may be drawn from the facts.

The influence of the oxidised iron wire, the transference of the inactive state from wire to wire, and the destruction of that state, are the facts I have principally verified; but they are so well described by Professor Schoenbein that I will not add a word to what he has said on these points, but go at once to other results.

Iron wire, as M. Schoenbein has stated, when put *alone* into strong nitric acid, either wholly or partly immersed, acquires the peculiar inactive state. This I find takes place best in a long narrow close vessel, such as a tube, rather than in a flat broad open one like a dish. When thus rendered quiescent by itself, it has the same properties and relations as that to which the power has been communicated from other wires.

If a piece of ordinary iron wire be plunged wholly or in part into nitric acid of about specific gravity 1.3 or 1.35, and after action has commenced it be touched by a piece of platina wire, also dipping into the acid, the action between the acid and the iron wire is instantly stopped. The immersed portion of the iron becomes quite bright, and *remains* so, and is in fact in the same state, and can be used in the same manner as the iron rendered inactive by the means already described. This protecting power of platina with respect to iron is very constant and distinct, and is the more striking as being an effect the very reverse of that which might have been anticipated prior to the knowledge of M. Schoenbein's results. It is equally exerted if the communication between it and the iron is not immediate, but made by other metals; as, for instance, the wire of a galvanometer; and if circumstances be favourable, a small surface of platina will reduce and nullify the action of the acid upon a large surface of iron.

This effect is the more striking if it be contrasted with that produced by zinc; for the latter metal, instead of protecting the iron, throws it into violent action with the nitric acid, and determines its quick and complete solution. The phenomena are well observed by putting the iron wire into nitric acid of the given strength, and touching it in the acid alternately by pieces of platina and zinc: it becomes active or inactive accordingly; being preserved by association with the platina, and corroded by association with the zinc. So also, as M. Schoenbein has stated, if iron be made the negative electrode of a battery containing from two to ten or more pairs of plates in such acid, it is violently acted upon; but when rendered the positive electrode, although oxidised and dissolved, the process, comparatively, is extremely slow.

Gold has the same power over iron immersed in the nitric acid that platina has. Even silver has a similar action; but from its relation to the acid, the effect is attended with peculiar and changeable results, which I will refer to hereafter.

A piece of box-wood charcoal, and also charcoal from other sources, has this power of preserving iron, and bringing it into the inactive state. Plumbago, as might be expected, has the same power.

When a piece of bright steel was first connected with a piece of platina, then the platina dipped into the acid, and lastly the steel immersed, according to the order directed in the former cases by Professor Schoenbein, the steel was preserved by the platina, and remained clear and bright in the acid, even after the platina was separated from it, having, in fact, the properties of the inactive iron. When immersed of itself, there was at first action of the usual kind, which, being followed by the appearance of the black carbonaceous crust, known so well in the common process of examining steel, the action immediately ceased, and the steel was preserved, not only at the part immersed, but upon introducing a further portion, it also remained clean and bright, being actually protected by association with the carbon evolved on the part first immersed.

When the iron is in this peculiar inactive state, as M. Schoenbein has stated, there is not the least action between it and the nitric acid. I have retained such iron in nitric acid, both alone and in association with platina wire for thirty days, without change; the metal has remained perfectly bright, and not a particle has been dissolved.

A piece of iron wire in connection with platina wire was entirely immersed in nitric acid of the given strength, and the latter gradually heated. No change took place until the acid was nearly at the boiling-point, when it and the iron suddenly entered into action, and the latter was instantly dissolved.

As an illustration of the extent and influence of this state, I may mention that with a little management it can be shown that the iron has lost, when in the peculiar state, even its power of precipitating copper and other metals. A mixture of about equal parts of a solution of nitrate of copper and nitric acid was made. Iron in the ordinary, or even in the peculiar state, when put into this solution, acted, and copper was precipitated;

but if the inactive iron was first connected with a piece of platina dipping into the solution, and then its own prepared surface immersed, after a few seconds the platina might be removed, and the iron would remain pure and bright for some time. At last it usually started into activity, and began to precipitate copper, being itself rapidly corroded. When silver is the metal in solution, the effect is still more striking, and will be referred to immediately.

I then used a galvanometer as the means of connection between the iron and other metals thus associated together in nitric acid, for the purpose of ascertaining, by the electric currents produced, in what relative condition the metals stood to each other; and I will, in the few results I may have to describe, use the relations of platina and zinc to each other as the terms of comparison by which to indicate the states of these metals under various circumstances.

The oxidised iron wire of Professor Schoenbein is, when in association with platina, exactly as another piece of platina would be. There is no chemical action, nor any electric current. The iron wire, rendered inactive either by association with the oxidised wire or in any other way, is also as platina to the platina, and produces no current.

When ordinary iron and platina in connection by means of the galvanometer are dipped into the acid (it matters not which first), there is action at the first moment on the iron, and a very strong electric current, the iron being as zinc to the platina. The action on the iron is, however, soon stopped by the influence of the platina, and then the current instantly ceases, the iron now acting as platina to the platina. If the iron be lifted into the air for a moment until action recommences on it, and be then reimmersed, it again produces a current, acting as zinc to the platina; but as before, the moment the action stops, the current is stopped also.

If an active or ordinary, and an inactive or peculiar iron wire be both immersed in the nitric acid separately, and then connected either directly or through the galvanometer, the second does not render the first inactive, but is itself thrown into action by it. At the first moment of contact, however, a strong electric current is formed, the first iron acting as zinc, and the second as platina. Immediately that the chemical action is re-established at the second as well as the first, all current ceases, and both pieces act like zinc. On touching either of them in the acid with a piece of platina, both are protected, and cease to act; but there is no current through the galvanometer, for both change together.

When iron was associated with gold or charcoal, the phenomena were the same. Using steel instead of iron, like effects ensued.

One of the most valuable results in the present state of this branch of science which these experiments afford, is the additional proof that *voltaic electricity is due to chemical action, and not to contact.* The proof is equally striking and decisive with that which I was able to give in the sixth part of my *Experimental Researches* (par. 615). What indeed can show more evidently that the current of electricity is due to chemical action rather than to contact, than the fact that though the contact is continued, yet when the chemical action ceases, the current ceases also?

It might at first be supposed that in consequence of the peculiar state of the iron, there was some obstacle, not merely to the *formation* of a current, but to the *passage* of one; and that, therefore, the current which metallic contact tended to produce could not circulate in the system. This supposition was, however, negatived by removing the platina wire into a second cup of nitric acid, and then connecting the two cups by a compound platina and iron wire, putting the platina into the first vessel, and the iron attached to it into the second. The second wire acted at the first moment, producing its corresponding current, which passed through the first cup, and consequently through the first and inactive wire, and affected the galvanometer in the usual way. As soon as the second iron was brought into the *peculiar* condition, the current of course ceased; but that very cessation showed that the electric current was not stopped by a want of conducting power, or a want of metallic contact, for both remained unchanged, but by the absence of chemical action. These experiments, in which the current ceases whilst contact is continued, combined with those I formerly gave, in which the current is produced though contact does not exist, form together a perfect body of evidence in respect to this elementary principle of voltaic action.

With respect to the state of the iron when inactive in the nitric acid, it must not be confounded with the inactive state of amalgamated or pure zinc in dilute sulphuric acid. The distinction is easily made by the contact of platina with either in the respective acids, for with the iron such association does nothing, whereas with the zinc it develops the full force of that metal and generates a powerful electric current. The iron is in fact as if it had no attraction for oxygen, and therefore could not act on the electrolyte present, and consequently could produce no current. My strong impression is that the surface of the iron is oxidised, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation; and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface, no reiteration of the attraction of successive particles of the iron on the elements of successive portions of the electrolyte, and therefore not those successive chemical actions by which the electric current (which is definite in its production as well as in its action) can be continued.

In support of this view, I may observe, that in the first experiment described by Professor Schoenbein, it cannot be doubted that the formation of a coat of oxide over the iron when heated is the cause of its peculiar and inactive state: the coat of oxide is visible by its colour. In the next place, all the forms of experiment by which this iron, or platina, or charcoal, or other voltaic arrangements are used to bring ordinary iron into the peculiar state, are accompanied by a determination of oxygen to the surface of the iron; this is shown by the electric current produced at the first moment, and which in such cases always precedes the change of the iron from the common to the peculiar state. That the coat of oxide produced by common means might be so thin as not to be sensible and yet be effectual, was shown by heating a piece of iron an inch or two from the end, so that though blue at the heated part, the end did not seem in the slightest degree affected, and yet that end was in the peculiar state. Again, whether the iron be oxidised in the flame much or only to the very slight degree just described, or be brought into the peculiar state by voltaic association with other pieces or with platina, etc., still if a part of its surface were removed even in the smallest degree and then the new surface put into contact with the nitric acid, that part was at the first moment as common iron; the state being abundantly evident by the electrical current produced at the instant of immersion.

Why the superficial film of oxide, which I suppose to be formed when the iron is brought into the peculiar state by voltaic association, or occasionally by immersion alone into nitric acid, is not dissolved by the acid, is I presume dependent upon the peculiarities of this oxide and of nitric acid of the strength required for these experiments; but as a matter of fact it is well known that the oxide produced upon the surface of iron by heat, and showing itself by thin films of various colours, is scarcely touched by nitric acid of the given strength though left in contact with it for days together. That this does not depend upon the film having any great thickness, but upon its peculiar condition, is rendered probable from the fact that iron oxidised by heat, only in that slight degree as to offer no difference to the eye, has been left in nitric acid of the given strength for weeks together without any change. And that this mode of superficial oxidation, or this kind of oxide, may occur in the voltaic cases, is rendered probable by the results of the oxidation of iron in nitrate of silver. When nitrate of silver is fused and common iron dipped into it, so as to be thoroughly wetted, being either alone or in association with platina, the iron does not commence a violent action on the nitrate and throw down silver, but it is gradually oxidised on the surface with exactly the same appearances of colour, uniformity of surface, etc., as if it were slowly oxidised by heat in the air.

Professor Schoenbein has stated the case of iron when acting as the positive electrode of a *couronne des tasses*. If that instrument be in strong action, or if an ordinary battery be used containing from two to ten or more plates, the positive iron instantly becomes covered in the nitric acid with a coat of oxide, which though it does not adhere closely still is not readily dissolved by the acid when the connection with the battery is broken, but remains for many hours on the iron, which itself is in the peculiar inactive state. If the power of the voltaic apparatus be very weak, the coat of oxide on the iron in the nitric acid often assumes a blue tint like that of the oxide formed by heat. A part of the iron is however always dissolved in these cases.

If it be allowed that the surface particles of the iron are associated with oxygen, are in fact oxidised, then all the other actions of it in combination with common iron and other metals will be consistent; and the cause of its platina-like action, of its forming a strong voltaic current with common iron in the first instance, and then being thrown into action by it, will be explained by considering it as having the power of determining and disposing of a certain portion of hydrogen from the electrolyte at the first moment and being at the same time brought into a free metallic condition on the surface so as to act afterwards as ordinary iron.

I need scarcely refer here to the probable existence of a very close connection between the phenomena which Professor Schoenbein has thus pointed out with regard to iron, and those which have been observed by others, as Ritter and Marianini, with regard to secondary piles, and A. de la Rive with respect to peculiar affections of platina surfaces.

In my *Experimental Researches* (par. 212) I have recorded a case of voltaic excitement, which very much surprised me at the time, but which I can now explain. I refer to the fact stated, that when platina and iron wire were connected voltaically in association with fused nitrate or chloride of silver, there was an electric current produced, but in the reverse direction to that expected. On repeating the experiment, I found that when iron was associated with platina or silver in fused nitrate or chloride of silver, there was occasionally no current, and when a current did occur it was almost constantly as if the iron was as platina, the silver or platina used being as zinc. In all such cases, however, it was a thermo-electric current which existed. The volta-electric current could not be obtained, or lasted only for a moment.

When iron in the peculiar inactive state was associated with silver in nitric acid sp. gr. 1.35, there was an electric current, the iron acting as platina; the silver gradually became tarnished and the current continued for some time. When ordinary iron and silver were used in the nitric acid there was immediate action and a current, the iron being as zinc, to the silver as platina. In a few moments the current was reversed, and the relation of the metals was also reversed, the iron being as platina, to the silver as zinc; then another inversion took place, and then another, and thus the changes went on sometimes eight or nine times together, ending at last generally in a current constant in its direction, the iron being as zinc, to the silver as platina: occasionally the reverse was the case, the predominant current being as if the silver acted as zinc.

This relation of iron to silver, which was before referred to, page 324, produces some curious results as to the precipitation of one metal by another. If a piece of clean iron is put into an aqueous solution of nitrate of silver, there is no immediate apparent change of any kind. After several days the iron will become slightly discoloured, and small irregular crystals of silver will appear; but the action is so slow as to require time and care for its observation. When a solution of nitrate of silver to which a little nitric acid had been added was used, there was still no sensible immediate action on the iron. When the solution was rendered very acid, then there was direct immediate action on the iron; it became covered with a coat of precipitated silver: the action then suddenly ceased, the silver was immediately redissolved, and the iron left perfectly clear, in the peculiar condition, and unable to cause any further precipitation of the silver from the solution. It is a remarkable thing in this experiment to see the silver rapidly dissolve away in a solution which cannot touch the iron, and to see the iron in a clean metallic state unable to precipitate the silver.

Iron and platina in an aqueous solution of nitrate of silver produce no electric current; both act as platina. When the solution is rendered a little acid by nitric acid, there is a very feeble current for a moment, the iron being as zinc. When still more acid is added so as to cause the iron to precipitate silver, there is a strong current whilst that action lasts, but when it ceases the current ceases, and then it is that the silver is redissolved. The association of the platina with the iron evidently helps much to stop the action.

When iron is associated with mercury, copper, lead, tin, zinc, and some other metals, in an aqueous solution of nitrate of silver, it produces a constant electric current, but always acts the part of *platinum*. This is perhaps most striking with mercury and copper, because of the marked contrast it affords to the effects produced in dilute sulphuric acid and most ordinary solutions. The constancy of the current even causes crystals of silver to form on the iron as the negative electrode. It might at first seem surprising that the power which tends to reduce silver on the iron negative electrode did not also bring back the iron from its peculiar state, whether that be a state of oxidation or not. But it must be remembered that the moment a particle of silver is reduced on the iron, it not only tends to keep the iron in the peculiar state according to the facts before described, but also acts as the negative electrode; and there is no doubt that the current of electricity which continues to circulate through the solution passes essentially between it and the silver, and not between it and the iron, the latter metal being merely the conductor interposed between the silver and the copper extremities of the metallic arrangement.

I am afraid you will think I have pursued this matter to a greater length than it deserves; but I have been exceedingly interested by M. Schoenbein's researches, and cannot help thinking that the peculiar condition of iron which he has pointed out will (whatever it may depend upon) enable us hereafter more closely to examine the surface-action of the metals and electrolytes when they are associated in voltaic combinations, and so give us a just knowledge of the nature of the two modes of action by which particles under the influence of the same power can produce either local effects of combination or current affinity.[1]—I am, my dear Phillips, very truly yours,

M. FARADAY.

ROYAL INSTITUTION, *June* 16, 1836.

Letter from MR. FARADAY *to* MR. Brayley *on some former Researches relative to the peculiar Voltaic Condition of Iron reobserved by Professor* SCHOENBEIN, *supplementary to a Letter to* Mr. Phillips, *in the last Number.*[2]

ROYAL INSTITUTION, *July* 8, 1836.

MY DEAR SIR,—I am greatly your debtor for having pointed out to me Sir John F. W. Herschel's paper on the action of nitric acid on iron in the *Annales de Chimie et de Physique;* I read it at the time of its publication, but it had totally escaped my memory, which is indeed a very bad one now. It renders one-half of my letter (supplementary to Professor Schoenbein's) in the last number of the *Philosophical Magazine,* page 57 (or page 321 of this volume), superfluous; and I regret only that it did not happen to be recalled to my attention in time for me to rearrange my remarks, or at all events to add to them an account of Sir John Herschel's results. However, I hope the editors of the *Phil. Mag.* will allow my present letter a place in the next number; and entertaining that hope I shall include in it a few references to former results bearing upon the extraordinary character of iron to which M. Schoenbein has revived the attention of men of science.

"Bergman relates that upon adding iron to a solution of silver in the nitrous acid no precipitation ensued." [3]

Keir, who examined this action in the year 1790,[4] made many excellent experiments upon it. He observed that the iron acquired a *peculiar or altered* state in the solution of silver;

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[1] *Exp. Researches*, Pars. 682, 732.

[2] *Lond. and Edinb. Phil. Mag.* 1836, vol. ix. p. 122.

[3] *Phil. Trans.* 1790, p. 374.

[4] *Ibid.* pp. 374, 379.

that this state was only superficial; that when so altered it was inactive in nitric acid; and that when ordinary iron was put into strong nitric acid there was no action, but the metal assumed the *altered* state.

Westlar, whose results I know only from the *Annales des Mines* for 1832,[1] observed that iron or steel which had been plunged into a solution of nitrate of silver lost the power of precipitating copper from its solutions; and he attributes the effect to the assumption of a negative electric state by the part immersed, the other part of the iron having assumed the positive state.

Braconnot in 1833[2] observed that filings or even plates of iron in strong nitric acid are not at all affected at common temperatures, and scarcely even at the boiling-point.

Sir John Herschel's observations are in reality the first which refer these phenomena to electric forces; but Westlar's, which do the same, were published before them. The results obtained by the former, extracted from a private journal dated August 1825, were first published in 1833.[3] He describes the action of nitric acid on iron; the altered state which the metal assumes; the superficial character of the change; the effect of the contact of other metals in bringing the iron back to its first state; the power of platina in assisting to bring on the altered or prepared state; and the habits of steel in nitric acid: he attributes the phenomena to a certain *permanent electric state of the surface of the metal.* I should recommend the republication of this paper in the *Philosophical Magazine.*

Professor Daniell, in his paper on Voltaic Combinations[4] (Feb. 1836), found that on associating iron with platina in a battery charged with nitro-sulphuric acid, the iron would not act as the generating metal, and that when it was afterwards associated with zinc it acted more powerfully than platina itself. He considers the effect as explicable upon the idea of a force of heterogeneous attraction existing between bodies, and is inclined to believe that association with the platina cleanses the surface of the iron, or possibly causes a difference in the mechanical structure developed in this particular position.

In my letter, therefore, as published in the *Philosophical Magazine* for the present month (July), what relates to the preserving power of platina on iron ought to be struck out, as

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[1] *Annales des Mines*, 1832, vol. ii. p. 322; or *Mag. de Pharm.* 1830.

[2] *Annales de Chimie et de Physique*, vol. lii. p. 288.

[3] *Ibid.* 1833, vol. liv. p. 87.

[4] *Phil. Trans.* 1836, p. 114.

having been anticipated by Sir John Herschel, and also much of what relates to the action of silver and iron, as having been formerly recorded by Keir. The facts relating to gold and carbon in association with iron; the experimental results as to the electric currents produced; the argument respecting the chemical source of electricity in the voltaic pile; and my opinion of the cause of the phenomena as due to a relation of the superficial particles of the iron to oxygen, are what remain in the character of contributions to our knowledge of this very beautiful and important case of voltaic condition presented to us by the metal iron.—I am, my dear Sir, yours very truly,

M. FARADAY.

E. W. Brayley, Esq.
London Institution.

INDEX

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