III. *Experimental Researches in Electricity.—Seventeenth Series.*

By MICHAEL FARADAY, *Esq., D.C.L. F.R.S. Fullerian Prof. Chem. Royal Institution, Corr. Memb. Royal and Imp. Acadd. of Sciences, Paris, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, &c. &c.*

§ 24. *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.*

1913. 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.

1914. 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*. 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 conduct 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.

1915. The apparatus used was a glass tube (Plate III. fig. 7.) about five inches long

* Annales de Chimie, 1828, xxxvii. p. 242.

and 0·4 of an inch internal diameter, open at both 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 (1881.) 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 (1881.), and when two of the same metal were used, they consisted of the successive portions of the same piece of wire.

1916. The precautions which are necessary for the elimination of a correct result are rather numerous, but simple in their nature.

1917. *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.

1918. *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. 7, (1915.) 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 (1003. 1036. 1037.), and the consequent final superiority of the colder side at which the action was thus necessarily more powerful (1953, &c. 1966. 2015. 2031, &c.). MARIANINI has described many cases of the effects of investing solutions, showing that if two pieces of the same metal (iron, tin, lead, zinc, &c.) be used, the one first immersed is negative to the other, and has given his views of the cause*. 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.

1919. *Effect of motion.*—This investing fluid (1918.) 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 (1881.) 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,

* Annales de Chimie, 1830, xlv. p. 40.

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°*. 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.

1920. The above effect was another reason for heating the acids, &c. (1918.) 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°.

1921. *Effect of air.*—Two platinum wires were put into cold strong solution of sulphuret of potassium (1812.), fig. 7; and the galvanometer was soon at 0°. On heating and boiling the fluid on the side A (1915.) 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 (1933.); 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 (1827.), 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 (1918.), and observing only the first effect.

1922. *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

* 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 reimmersed, 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.

too much detail to be described fully here; but I will briefly point it out and illustrate it by an example or two.

1923. When two platinum wires were compared in hot and cold dilute sulphuric acid (1935.), 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. 7. (1915.) 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 (1919.) facilitated the passing of the current and the deflection increased, but *heating* the platinum side did far more.

1924. *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.

1925. All this resolves 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 (1924.); and platinum hot is as nothing to platina cold, but much to silver either hot or cold.

1926. 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 de-

flection of a galvanometer needle in the circuit, from 12° to 30° or 45°; whilst heat applied to the positive electrode caused no change*.   I have not been able to obtain this nullity of effect at the positive electrode when a voltaic battery was used (1639.); but I have no doubt the present phenomena will prove to be virtually the same as those which that philosopher has described.

1927. 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.

1928. *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. 8.; 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.

1929. *Cleaning the wires.*—That this should be carefully done has been already mentioned (1881.); 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.

1930. Thus the best mode of experimenting (1915.) is to heat the liquid in the limb A or B, fig. 8., 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.

* Bibliothèque Universelle, 1837, vii. 388.

1931. 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.

1932. 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 (1948.) 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 (1948.).

1933. I then used *solution of the sulphuret of potassium* (1812.). As already said, hot platinum is negative in it to the cold metal (1921.); but I do not think the action was thermo-electric. Palladium with a weaker solution gave no indication of a current.

1934. 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.

1935. 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.

1936. *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.

1937. *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 (1848.). It disappears almost entirely when a dilute acid is used (1934.); and what effect does remain indicates that the hot metal is negative to the cold.

1938. 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 (1819.). When the fluid was diluted, and of

specific gravity 1070, like that before used (1932.), the effect was only 1°, and cannot therefore be confounded with the results I have to quote.

1939. The dilute *sulphuric* (1935.) and *nitric* acids used (1934.) 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 (1949. 1950.) ; 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.

1940. In strong nitric acid, again, the hot metal is negative.

1941. 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, &c. 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 (1867.), 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, &c. 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 (1950.) ; and in other cases, again, the hot metal becomes negative instead of positive (1953.).

Cases of one metal and one electrolyte; one junction being heated.

1942. 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.

1943. *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.

1944. *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 (1918.).

1945. *Tin and solution of potassa.*—The hot tin is strongly and constantly positive to the cold.

1946. *Iron and dilute sulphuric acid* (1935.).—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 economize time.

1947. *Dilute solution of yellow sulphuret of potassium*, consisting of one volume of the strong solution (1812.), and eighteen volumes of water.—Iron, silver, and copper, with this solution, gave good results. The hot metal was positive to the cold.

1948. *Dilute solution of caustic potassa* (1932.).—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.

1949. *Dilute sulphuric acid* (1935.).—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.

1950. *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.

1951. *Strong nitric acid.*—Hot iron is positive to cold. Both in the hot and cold acid the iron is in its peculiar state (1844. 2001.).

1952. *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 (1950.). 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.

1953. 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 (1918.). 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, pro-

ducing also only a feeble current. Tin gave the same result, but the current was scarcely sensible.

1954. *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 (1918.).

1955. *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.

1956. 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 cognizance of them, except by adding new assumptions to those already composing it (1874.). 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, &c. 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 (1931. 1941.); 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.

1957. 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 (1120.). 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 (1975.), or iron or silver in the same weak acid against copper in the strong acid (1996.). Many of those instances where the hot side ultimately becomes negative, as of zinc in dilute solution of sulphuret of potassium (1953.), or cadmium and lead in dilute nitric acid (1955.), are of this nature; and yet the conditions and result are in perfect agreement with the chemical theory of voltaic excitement (1918.).

1958. 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* (891. 908. 916. 988.). DE LA RIVE in 1836 gave a still more precise enunciation of such a principle†, 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.

1959. 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 (1824, &c. 1878, &c.). 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 (1967.). 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‡.

Cases of two metals and one electrolyte; one junction being heated.

1960. Since heat produced such striking results with single metals, I thought it probable that it might be able to affect the 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.

1961. 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.

1962. 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.

1963. 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

* Philosophical Transactions, 1834, p. 428.   † Annales de Chimie, 1836, lxi. p. 44. &c.
‡ Philosophical Transactions, 1839, p. 97.

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.

1964. *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 (1930.) 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.

1965. 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.

1966. 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 (1953.), 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.

1967. 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 (1959.), 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.

1968. 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, &c., were attended to.

¶. v. *The exciting chemical force affected by dilution.*

1969. 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 inversion of the current took place*. In 1828 DE LA RIVE carried these and similar cases much further, especially in voltaic combinations of copper and iron with lead†. In 1827 BECQUEREL‡ 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§ made many such experiments with one metal and a fluid in different states of dilution, which I think of very great importance.

1970. 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 (1874.), exactly those influences at the points of contact in the various cases, which the prior results, ascertained by experiments, would require.

1971. The form of apparatus used was the bent tube already described (1915.) fig. 7. The precautions before directed with the wires, tube, &c., 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‖, but whose influence in the present researches requires explanation.

1972. Figs. 9 and 10 represent the two arrangements of fluids used. The part below *m* in thè 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

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* Annales de Chimie, 1823, xxii. p. 361.   † Ibid. 1828, xxxvii. p. 234.
‡ Ibid. 1827, xxxv. p. 120.   § Ibid. 1828, xxxvii. p. 240, 241.
‖ Traité de l'Électricité, ii. p. 81.

nearly so. Whenever the current existed it was from the weak to the strong acid through the liquid.

1973. When the tube was arranged, as in fig. 9, 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.

1974. I occasionally used the tube with dilute acid on one side only, fig. 9, and sometimes that with dilute acid on both sides, fig. 10. I will call the first No. 1. and the second No. 2.

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1975. In illustration of the general results I will describe a particular case. Employing tube No. 1. with strong and dilute nitric acid*, 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 gavanometer-needle could be held stifly 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.

1976. On repeating the experiments with the substitution of platinum, gold, or even palladium for the copper, scarcely a sensible effect was produced (1973.).

1977. *Strong and dilute nitric acid*.*—The following single metals being compared with themselves in these acids, gave most powerful results of the kind just described with copper (1975.); 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 up together. Iron and lead show the alternations of state in the tube No. 2. as beautifully as copper (1975.).

1978. *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. (1974.) with this and the strongest acid. But as this degree of dilution produced very little effect with the iron, as compared with what a

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* The dilute acid consisted of three volumes of strong nitric acid and two volumes of water.

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 (1973.).

1979. 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.

1980. *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 (1973.), 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.

1981. *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 (1973.).

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 (1985.).

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1982. 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 (1874. 1956. 1985. 2006. 2014. 2063.); 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 (1808.) 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.

1983. 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.

1984. 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 (1980. 1981.), though it does with nitric and sulphuric acids (1977. 1978.); 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.

1985. 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? (1977. 1984.) Or if, to avoid *this 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?

1986. 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 in 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.

1987. 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.

1988. 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 (1973.); but the results were then almost nothing, and showed that the phenomena could not be so accounted for.

1989. 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 (1988.) was positive to tin in the moderate or the 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.

1990. 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. 11 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.

1991. 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 (1979. 1989.), but rather look for them in platinum or gold, which, however, produce no results of the kind (1976. 1988.).   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 (1981.).   Nay, more, that with the same acid, and merely by changing the proportion of dilution, such alteration of the order must take place (1986. 1988.).

1992. Thus it appears, as before remarked (1982.), 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.

1993. 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 (1915.) ; 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, re-arranging the fluid, and re-immersing the wires, the tin into the weak, and the lead into the strong portion.   DE LA RIVE has already stated * 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 (1918.) : 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.

1994. *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.

1995. *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 in strength.   Still there were great variations in degree ; thus iron in strong acid was only a little positive to silver in weak

* Annales de Chimie, 1828, xxxvii. p. 240.

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.

1996. *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 (1974.), 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 (1975.). Copper in weak acid was positive to silver, iron, 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.

1997. 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 above one hundred different ways in the same acid, merely by the effect of dilution.

1998. 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.

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1999. 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.

2000. 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.

2001. These, therefore, are *finally* cases of such an inversion (1999.); 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 (1843. 1951. 2033.), 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.

2002. *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 (1918.); and though the effect might easily pass unobserved, the case cannot be allowed to stand, as fulfilling the statement made (1999.).

2003. *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 (1999.).

2004. 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 (1995.) or from potassa (1994.) 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.

2005. 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 (1997. 1998.), 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 (1829. 1833.) is confirmed by the present.

2006. 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 (1874. 1982. 1991. 2014. 2060.), then how *utterly unlike* such contact must be to that of the numerous class of conducting solid bodies (1809. 1867.); and where, to give the assumption any show of support, is the case of such contact (apart from chemical action) producing such currents?

2007. That it cannot be an alteration of contact force by mere dilution at one side (2006.) 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 (1976.), there was no sensible current, or only one so small as to be unimportant.

2008. A still stronger proof is afforded by the following result. I arranged the tube, fig. 9 (1972.), with strong solution of yellow sulphuret of potassium (1812.) 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 (2049.), 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.

2009. 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 (1959.).

¶ vi. *Differences in the order of the metallic elements of voltaic circles.*

2010. 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* (943.); and in 1828 DE LA RIVE showed many inversions in different cases† (1877.); gave a strong

* Elements of Chemical Philosophy, p. 149.   † Annales de Chimie, 1828, xxxvii. 232.

contrast in the order of certain metals in strong and dilute nitric acid*; 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 †.

2011. I have pursued this subject in relation to several solutions, taking the precautions before referred to (1917, &c.), 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 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.

2012. In further illustration of this subject I will take ten metals, and give their order in seven different solutions.

Dilute nitric acid.	Dilute sulphuric acid.	Muriatic acid.	Strong nitric acid.	Solution of caustic potassa.	Colourless bi-hydrosulphuret of potassium.	Yellow hydro-sulphuret 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.

2013. 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 (1812.) 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.

2014. The displacements appear to be most extraordinary, as extraordinary as those consequent on dilution (2005.); and thus show that there is no general ruling influence of fluid conductors, or even of acids, alkalies, &c. 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

* Annales de Chimie, 1828, xxxvii. p. 235.　　　　　　　† Ibid., p. 243.

most extraordinary manner, following all the contortions of the string of facts (1874. 1956. 1992. 2006. 2063.), and yet never showing a case of the production of a current by contact alone, i. e. unaccompanied by chemical action.

2015. 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 (1997.) 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 produced, as the chemical actions producing these decay or are exhausted; the consequent result being well seen in the effect of the investing fluids produced (1918. 1953. 1966.).

2016. 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 (2040. 2052.), 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.*

2017. 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 (1799.), I purpose adding a few

observations and facts to show the number of these cases, and their force. In the Eighth Series of these Researches* (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 simple circuit, without any contact of metals (880, &c.). It was further shown, that when a pair of zinc and platinum plates were excited at one end by dilute nitro-sulphuric acid (880.), or solution of potash (884.), or even in some cases a solution of common salt (885.), decompositions might be produced at the other end, of solutions of iodide of potassium (900.) protochloride of tin (901.), sulphate of soda, muriatic acid, and nitrate of silver (906.); or of the following bodies in a state of fusion; nitre, chlorides of silver and lead, and iodide of lead (902. 906.); no metallic contact being allowed in any of the experiments.

2018. 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 (1831.), or green nitrous acid (1844.), or the solution of potassa (1854.); for here no metallic contact was allowed, and chemical action was the evident and only cause of the currents produced.

2019. The following 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 the 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.

2020.

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.	

2021. 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		
Gold		Dilute nitric acid
Platinum		Dilute sulphuric acid
Palladium		Muriatic acid
Silver	Strong nitrous acid, or strong solution of sulphuret of potassium. Iron	Solution of vegetable acids
Nickel		Iodide of potassium
Copper		Iodide of zinc
Lead		Solution of salt
Tin		Many metallic solutions.
Zinc		
Cadmium		

2022. To these cases must be added the many in which one metal in a uniform acid gave currents when one side was heated (1942, &c.). Also those in which one metal with an acid strong and diluted gave a current (1977, &c.).

2023. In the cases where by dilution of the acid one metal can be made either positive or negative to another (1996, &c.), 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.

2024. That it is easy to construct batteries without metallic contact was shown by Sir HUMPHRY DAVY in 1801*, 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†, 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.

2025. Let $a\,b$, $a\,b$, $a\,b$, fig. 12, Plate III., 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 (1979, &c.). Such an arrangement will give an effective battery.

2026. If the acid used be the sulphuric, and the metal employed be iron, the current

* Philosophical Transactions, 1801, p. 397. Also Journals of the Royal Institution, 1802, p. 51; and NICHOLSON's Journal, 8vo, 1802, vol. i. p. 144.

† Quarterly Journal of Science, viii. 177; or Annales de Chimie, xi. 190. (1819.)

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 ———→.

2027. Strong and weak solutions of potassa being employed in the tubes, then the single metals zinc, lead, copper, tin, and cadmium (1981.), will produce a similar battery.

2028. If the arrangement be as in fig. 13, in which the vessels 1, 3, 5, &c. contain strong sulphuric acid, and the vessels 2, 4, 6, &c. dilute sulphuric acid; and if the metals *a, a, a,* are tin, and *b, b, b,* are iron (1979.), 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.

¶ viii. *Considerations of the sufficiency of chemical action.*

2029. Thus there are no want of cases in which chemical action alone produces voltaic currents (2017.); 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.

2030. *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* 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.

2031. *Where chemical action has been, but diminishes or ceases, the electric current diminishes or ceases also.*—The cases of tin (1882. 1884.), lead (1885.), bismuth (1895.), and cadmium (1905.), in the solution of sulphuret of potassium, are excellent instances of the truth of this proposition.

2032. If a piece of grain tin be put into strong nitric acid, it will generally exert no action, in consequence of the film of 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 (1918.), and the current ceases with it. Each scratch upon the surface of the tin reproduces the series of phenomena.

2033. The case of iron in strong nitric acid, which acts and produces a current at the first moment (1843. 1951. 2001.), but is by that action deprived of so much of its activity, both chemical and electrical, is also a case in point.

* Annales de Chimie, 1827, xxxv. 122. Bibliothèque Universelle, 1838; xiv. 129, 171.

2034. 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.

2035. The effect of the investing fluid already referred to in the cases of tin (1919.) and cadmium (1918.), some of the results with two metals in hot and cold acid (1966.), and those cases where metal in a heated acid became negative to the same metal in cold acid (1953, &c.), 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.

2036. *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.

2037. 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, &c. (1838. 1937.), then no currents, and of course no such alterations in direction, are produced.

2038. *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 (1867.). 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 (1843. 1853. 1825. 1829.). These are very striking facts.

2039. *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. 14.; 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. 15., where, in imitation of a former experiment (889.), 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. 15., chemical action commences, and a powerful current is produced, though without metallic or any additional contact. To observe this with the apparatus, fig. 14., a drop of water was put in at *b*. At first there was no chemical 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.

2040. *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.*

2041. 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*, showed that crystallized *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†, 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‡, 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.

2042. 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 acid. 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.

2043. In 1835 M. MUNCKE§ 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‖. M. SCHŒN-BEIN 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¶. My own results confirm those of M. DE LA RIVE, for by direct experiment I find that the

* Annales de Chimie, 1802, xl. 224.   † Ibid. 1835, lx. 164, 171.

‡ Ibid. 1836, lxi. 40; and Bibliothèque Universelle, 1836, i. 152, 158.

§ Bibliothèque Universelle, 1836, i. 160.   ‖ Ibid. 1836, i. 162, 154.

¶ Philosophical Magazine, 1838, xii. 226, 311; and Bibliothèque Universelle, 1838, xiv. 155.

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 (1822.) at common temperatures, and after an hour filtered and tested in the same manner, and found to contain plenty of lead.

2044. 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.

2045. 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 (1120.) 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.

2046. 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 (2045.), and found to be strongly negative to metallic platinum in the solution of 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.

2047. The same effect is well shown by the action of oxidized iron. If a plate of iron be oxidized 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 (1840.). But if it be oxidized 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.

2048. 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 (2045.).

2049. This result is one of those effects which has to be guarded against in the experiments formerly described (1826. 1886.). 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.

2050. 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.

2051. 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 (2050.) was applied to it also, with the same result.

2052. 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 (1869.), though they are excellent conductors of electricity, and can readily carry the currents formed by other and more effectual means.

2053. With such a mass of evidence for the efficacy and sufficiency of chemical

action as that which has been given (1878. 2052.); with so many current circuits without metallic contact (2017.) and so many non-current circuits with (1867.); 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.*

2054. 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 suchlike solid conductors* (1809. 1867.). A very brief consideration is, I think, sufficient to show how little support these phenomena give to the theory in question.

2055. 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.

2056. Admitting contact force, we may then assume that heat either increases or diminishes the electromotive force of contact. For if in fig. 16. 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.

2057. 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 (2012.). 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† : how is it consistent with the contact theory of the voltaic pile?

2058. Again, if silver and antimony form a thermo circle (fig. 17.), 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. 18.), and the junction x be heated, the current is from the bismuth to the silver; and assuming that heat increases the force of con-

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* See FECHNER's words, Philosophical Magazine, 1838, xiii. p. 206.
† Annals of Philosophy, 1823, vi. 177.

tact (2056.), 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 (2012.) are used; so that metallic contact like that of 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.

2059. 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 (2012.).

2060. 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 thermo-metallic 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.

2061. 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 (2012.), 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.

2062. 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 (2069. 2071. 2073.).

2063. 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 (2060.) and made, not only to vary uncertainly for each metal, but to vary also in direct conformity with the variation of chemical action (1874. 1956. 1992. 2006. 2014.).

2064. 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* are quite sufficient to authorize that conclusion.

¶ x. *Improbable nature of the assumed contact force.*

2065. 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.

2066. It is assumed by the theory (1802.) 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 (1738. 1743.).

2067. 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.

2068. This is in no respect consistent with known actions. If in relation to chemical

* Annales de Chimie, 1829, xli. 355. xlvi. 275.

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 (1739.), 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 (921. 924.) proportionate to the amount of chemical force consumed (868.).

2069. But the contact theory, which is obliged, according to the facts, to admit that the acting particles are not changed (1802. 2067.) (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 (2071.). 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*;) 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.

2070. 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†? There is no sufficient pro-

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* Memorie della Società Italiana in Modena, 1837, xxi. 232, 233, &c.

† 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.

bable 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.

2071. 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 (1790.), is there a pure creation of force; a production of power without a corresponding exhaustion of something to supply it*.

2072. 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.

2073. 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 (2069.). Then would

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* (*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.

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.

Royal Institution,
December 26, 1839.

NOTE.

2074. In a former series (925, &c.) 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*.

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†.

For myself, I had made exception of the hydracids (929.) on theoretical grounds. I had also admitted that oxyacids when in solution might in such cases produce small currents of electricity (928. 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 oxidizement of zinc, I do not think that the *quantity* of electricity is at all increased or affected by the combination of the oxide with the acid (933. 945.), still the latter circumstance cannot go altogether for nothing. The researches of Mr. DANIELL on the nature of compound electrolytes‡ ties together the electrolyzation 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 electrolyzations, and at the zinc in the ordinary active pile, are, in principle, closely connected together.

* Bibliothèque Universelle, 1838, xiv. 129. 171. Comptes rendu, i. p. 455. Annales de Chimie, 1827, xxxv. 122.

† Philosophical Magazine, 1838, xiii. p. 382; or POGGENDORF's Annalen, xlii. p. 76.

‡ Philosophical Transactions, 1839, p. 97.