

values varying from 66 to 200 mm. If, however, we assume, in accordance with the principles explained above, that a constant fraction of the whole energy per gram of liberated hydrogen appears as local heat in the cell, then,  $Q$  denoting the whole heat which appears in the cell,  $L$  the local heat,  $H$  the heat in the wire,  $R$  the resistance of the cell,  $S$  that of the wire, we have

$$\frac{Q-L}{H} = \frac{R}{S};$$

and it is found that on making  $R=32.3$  and  $L=7589$ , this formula will represent the results of experiment very fairly. The last column in the above table gives the value of  $Q$  thus calculated. In general so good an agreement is not to be expected, because  $L$  may and does vary with the strength of the current.

Thus far we have been dealing with the direct results of experiment, but when we inquire into the reason for the existence of this residual electromotive force and of the local development of heat corresponding to it, and, in particular, when we ask why the effect is so much greater with some metals than with others, the answers become less satisfactory. We meet, in fact, with considerable divergence of opinion.

Joule's view was that the effect is due to the affinity of the metal of the electrode for oxygen. This is endorsed to a certain extent by Sir William Thomson, who puts the matter thus:—"In a pair consisting of zinc and tin the electromotive force has been found by Poggendorff to be only about half that of a pair consisting of zinc and copper, and consequently less than half that of a single cell of Smee's. There is therefore an immense loss of mechanical effect in the external working of a battery composed of such elements, which *must* be compensated by heat produced within the cells. I believe, with Joule, that this compensating heat is produced at the surface of the tin in consequence of hydrogen being forced to bubble up from it, instead of the metal itself being allowed to combine with the oxygen of the water in contact with it. A most curious result of the theory of chemical resistance is that, in experiments (such as those of Faraday, *Exp. Res.*, 1027, 1028) in which an electric current passing through a trough containing sulphuric acid is made to traverse a diaphragm of an oxidizable metal (zinc or tin) dissolving it on one side and evolving bubbles of hydrogen on the other, part (if not all) of the heat of combination will be evolved, not on the side on which the metal is being eaten away, but on the side at which the bubbles of hydrogen appear. It will be interesting to verify this conclusion by comparing the quantities of heat evolved in two equal and similar electrolytic cells in the same circuit, each with zinc for negative electrode, and one with zinc the other with platinum or platinized silver for the positive electrode."<sup>2</sup>

Bosscha dissents from the theory of "chemical resistance" thus expounded, and advances a different explanation. According to him, the local heat arises from the energy lost by the liberated ions in passing from the active to the ordinary state. We know that the hydrogen which is being liberated at the surface of an electrode can effect reductions which hydrogen in the ordinary state cannot accomplish; it is liberated in fact in a state of greater intrinsic energy than usual. It is this excess of intrinsic energy which appears as local heat, and gives rise to the residual electromotive force in electrolysis. Different metals possess in very different degrees the power of reducing active hydrogen to the ordinary state; and therefore

<sup>1</sup> *Phil. Mag.*, 1851 (2), p. 556.

<sup>2</sup> The effect here predicted was afterwards observed by Thomson himself, *Rep. Brit. Assoc.*, 1852, and later still by Bosscha, *Pogg. Ann.*, ciii. p. 517.

the proportion of hydrogen which gets away from the electrode in the active state differs according to circumstances. Bosscha's theory is that it is the intrinsic energy thus carried away from the electrode that appears as local heat. Similar remarks apply of course to oxygen, the active form of the gas being probably ozone. As a verification of the theory, the fact is cited that at the surface of a plate of carbon, which possesses in an eminent degree the power of reducing ozone to the ordinary state, the residual electromotive force and local heat are very small. At all events the theory of "chemical resistance" is held to be inadequate to explain the facts; for calculating from some results of his own, combined with those of Lenz and Saweljew, he finds for the residual electromotive force at electrodes of

Pt	Fe	Cu	Sn	Hg	Zn
.45	.49	.64	.86	1.20	1.20;

from which it appears that the order of magnitude of the electromotive forces is not that of the affinities of the metals for oxygen.

*Electrical Measure of Chemical Affinity.*—In a paper<sup>3</sup> sent to the French Academy to compete for a prize offered for the best essay on the heat of chemical combination, Joule elaborates an ingenious method for measuring chemical affinity. By direct observation it is ascertained how much heat is developed in a given time in a certain standard coil of wire, when it is traversed by a current whose strength is measured by means of a tangent galvanometer. Then three readings of the tangent galvanometer are taken—first, when the galvanometer alone is in circuit with the battery, secondly, when the standard coil is also inserted, thirdly, when an electrolytic cell is inserted instead of the coil. The amount of the ions liberated and the heat evolved in the cell during a given time is also observed in the last case. If  $A, B, C$  be the readings of the galvanometer in the three cases, and if  $\alpha$  be the resistance of a metallic wire capable of retarding the current equally with the electrolytic cell,<sup>4</sup> then we easily get, taking the resistance of the standard coil as unity,

$$\alpha = \frac{(A-C)B}{(A-B)C}.$$

Now if the resistance  $\alpha$  were put in the place of the electrolytic cell, the current would be the same; hence by Faraday's law the amount of chemical energy absorbed in the battery would be the same. Also the heat evolved in the rest of the circuit, excluding  $\alpha$ , would be the same. It follows, therefore, that the heat  $H$  which would be evolved in  $\alpha$  is the equivalent of the whole energy given out in the electrolytic cell. If therefore we subtract from  $H$  the heat  $K$  which actually appears in the cell, the remainder  $H-K$  is the heat equivalent of the intrinsic energy of the liberated ions; and, provided they appear finally in the "ordinary" condition,  $H-K$  is the heat which would be developed when they are allowed to combine.

In this way Joule found for the heat evolved in the combustion of 1 gm. of copper zinc and hydrogen respectively 594, 1185, 33553.

*Galvanic Batteries.*—It would be inconsistent with our general plan to attempt an exhaustive discussion of all the different electromotors which depend for their energy on chemical action. Wiedemann's *Galvanismus*, or books or telegraphy and other arts in which electricity is applied to technical purposes, may be consulted by the reader who wishes for fuller information. A brief discussion of some typical batteries will, however, be useful, were it only to illustrate the principles we have just been laying down.

All the earlier batteries were one-fluid batteries. The

<sup>3</sup> Noticed in the *Comptes Rendus*, Feb. 1846, and published at length in *Phil. Mag.*, 1852.

<sup>4</sup> Notice that it is not said that  $\alpha$  is equal to the resistance of the electrolyte. Bosscha in the papers we have quoted, either from not having seen the paper we are now analysing, or through a misunderstanding, accuses Joule of error here. The reasoning (*Pogg. Ann.*, ci. p. 540) which he seems to quote from Joule is not to be found in this or in any other of Joule's papers that we know of. Polarization is taken into account by Joule (see *Phil. Mag.*, 1852 (1), p. 485). The criticisms of Verdet, who seems to follow Bosscha, are equally groundless (*Théorie Mécanique de la Chaleur*, t. ii. p. 204).

<sup>5</sup> This word is left purposely a little vague, and is used to avoid a long discussion of points which need not be raised here.

One-fluid batteries. plates usually consisted of zinc and copper, and the exciting fluid was in general sulphuric acid. Various improvements were made by Cruickshank, Wollaston, Hare, and others, in the way of rendering the battery more compact, and of reducing its internal resistance by enlarging the plates. Hare carried the last-mentioned improvement to great lengths; by winding up together in a spiral form sheets of copper and zinc, insulated from each other by pieces of wood, plates of 40 or more square feet surface were obtained. In this way the internal resistance was very much reduced, and powerful heating effects could be obtained. When small internal resistance is no object, the cells of the battery may be filled with sand or sawdust, moistened with the dilute acid. In this form the battery is more portable.

There are two capital defects to which all one-fluid batteries are more or less subject. In the first place, whether there is or is not external metallic connection between the plates, a certain amount of chemical action goes on at the surface of the zinc, which consumes the metal without aiding in the production of the current. To this is given the name of local action. It is supposed to arise from inequalities in the zinc, on account of which one portion of the metal is electropositive to a neighbouring portion; hence local currents arise causing an evolution of hydrogen at some places and solution of the zinc at others. In the second place, when the battery is in action, there is always an evolution of hydrogen at the copper or electronegative plate of the cell, a certain amount of which adheres to the plate and causes a strong electromotive force of polarization. The first of these evils is remedied to a great extent by amalgamating the zinc plate. We thus reduce the surface metal to a fluid condition everywhere, and thereby eliminate differences of hardness and softness, crystalline structure, and so on. The oldest method was to use zinc amalgam for the electronegative metal; but it is now universally the custom to amalgamate the surface of the zinc plates simply, which may be done by rubbing them with mercury under dilute sulphuric acid. No such effective cure has been found for the hydrogen polarization. Smee introduced the plan of using instead of the copper plates thin leaves of platinum or silver foil, which are platinized by the process already described (p. 87). This, in accordance with what we have already seen, diminishes the polarization.<sup>1</sup> A similar result is obtained by using for the electronegative plate cast iron or graphite; the action of the latter is much improved by steeping it in nitric acid.

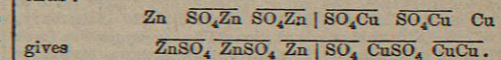
This last fact introduces us to a new principle for improving the action of batteries, viz. the use of an oxidizing agent to get rid of the hydrogen polarization. When the plates of a Smee's battery have been exposed to the air for some time, it is always found that the current is much more energetic than usual just after the first immersion. The improvement is of course only temporary, for the stock of oxygen is soon exhausted, and on raising the plates and dipping them again immediately, the phenomenon does not appear. Davy found that dilute nitric acid acted better than dilute sulphuric acid as an exciting fluid, and the cause of this is the action of the  $\text{HNO}_3$  on the hydrogen evolved at the copper plate. Good instances of this kind of action are furnished by the bichromate battery of Bunsen and the Léclanché cell, which occupy a sort of middle position between one and two fluid batteries.

The bichromate cell consists of an amalgamated zinc plate, usually suspended between two parallel carbon plates, so that it can be raised or depressed at pleasure. The bichromate solution is made,

<sup>1</sup> Fleeming Jenkin gives '47 volt as the available electromotive force of Smee's cell. The electromotive force when the circuit is broken is much greater. See above, p. 90.

according to Bunsen, by mixing 605 parts of water with 61.3 of potassium bichromate and 116 of sulphuric acid. The electromotive force of the bichromate cell is very great to start with (more than twice that of a Daniell's cell), but it falls very quickly when the external resistance is small. The cell recovers pretty quickly however, and may be used with advantage where powerful currents of short duration are often wanted. In the cell of Léclanché the electronegative metal is replaced by a porous vessel filled with carbon and pounded peroxide of manganese. The exciting liquid used is chloride of ammonium. Chloride of zinc is formed at the zinc plate, and ammonia and hydrogen appear at the negative plate; the latter reduces the  $\text{MnO}_2$ , so that  $\text{H}_2\text{O}$  and  $\text{Mn}_2\text{O}_3$  are formed, while the ammonia is partly dissolved and partly escapes. This element is tolerably constant if it be not used to produce very strong currents, but its great merit consists in being very permanent; for it will keep in condition for months with very little attention, furnishing a current now and then when wanted; hence its extensive use in working electric bells, railway signals, and so on.

It cannot be said that any of the batteries we have described, or in fact any battery on the one-fluid system, satisfies to any great extent the requirements of a constant electromotor, which are to give the same electromotive force whatever the external resistance, and to preserve that electromotive force unaltered for a considerable time. The best solution of the problem to construct a constant battery is the two-fluid principle invented by Daniell; and on the whole, the best application of that principle is the cell originally given by him. This consists essentially of a plate of copper immersed in a saturated solution of copper sulphate, and a plate of zinc immersed in dilute sulphuric acid or zinc sulphate, the copper solution being separated from the other by some kind of diaphragm, usually a porous vessel of unglazed earthenware. The chemical action consists of the solution of the zinc plate to form zinc sulphate, the formation of zinc sulphate at the diaphragm, and the deposition of copper at the copper plate; thus:—



The evolution of hydrogen and the polarization arising therefrom are thus avoided.

A very common arrangement of this cell is a porous vessel, containing the copper plate and the sulphate of copper, with a small store of large crystals to keep the solution saturated. This vessel is dipped into another nearly filled with a semi-saturated solution of zinc sulphate, in which is placed the zinc plate. With a little care to keep the cell clean by occasionally removing some of the zinc solution and diluting to prevent incrustation, to feed the copper solution, so that it may not get weak and deposit hydrogen instead of copper on the copper plate, to keep down the level of the copper solution, which is constantly rising by osmosis (see art. ELECTROLYSIS), and a few other obvious precautions, a battery of Daniell's cells will furnish a very nearly constant current, and keep in order for a long time. It is necessary to keep the current going, otherwise the solutions diffuse through the porous vessel, the result of which is a deposit of copper on the zinc, and other mischiefs, which stop the action of the cell altogether.

Daniell's element has been constructed in a great variety of forms, to suit various purposes. The sawdust Daniell, invented by Sir Wm. Thomson<sup>1</sup> (1858), is very convenient when portability is desired. In this form the copper plate, soldered to a gutta-percha covered wire, is placed at the bottom of a glass vessel and covered with crystals of copper sulphate; over these wet sawdust is sprinkled, and then more sawdust, moistened with a solution of sulphate of zinc, upon which is laid the zinc plate. The cell of Minotto is very similar to this.

In these batteries the sawdust takes the place of the porous diaphragm, and retards the interdiffusion of the fluids. In another class of batteries, of which the element of Meidinger may be taken as the type, the diaphragm is dispensed with altogether, and the action of gravity alone retards the diffusion. In Meidinger's cell the zinc is formed into a ring, which fits the upper part of a glass beaker filled with zinc sulphate. At the bottom of this beaker is placed a smaller beaker, in which stands a ring of copper, with a properly insulated connecting wire. The mouth of the beaker is closed by a lid, with a hole in the centre, through which passes the long tapering neck of a glass balloon, which is filled with

<sup>2</sup> Jenkin, *Electricity and Magnetism*, p. 224.

crystals of copper sulphate; the narrow end of this neck dips into the small beaker, the copper sulphate runs slowly out, and being specifically heavier than the zinc sulphate, it collects at the bottom about the copper ring.

Yet another form of Daniell's element is the tray cell of Sir William Thomson, which consists of a large wooden tray lined with lead, the bottom of which is covered with copper by electrotyping. The zinc is made like a grating, to allow the gas to escape, and is enveloped in a piece of parchment paper bent into a tray-shape, the whole resting on little pieces of wood placed on the leaden bottom of the outer tray. Sulphate of copper is fed in at the edge of the tray, and sulphate of zinc is poured into the parchment. The zincs in these elements are some 40 centimetres square, so that the internal resistance is as low as 0.2 ohm.

One of the best known in this country, and perhaps the most used of all the two-fluid cells, is the element of Grove. This differs from Daniell's element in having nitric acid with a platinum electrode in the porous cell, instead of the copper solution and the copper electrode of Daniell's element. The hydrogen evolved at the platinum is oxidized by the nitric acid, and the polarization thus avoided. The nitrous fumes given off by the chemical action are very disagreeable, and also very poisonous, so that it is advisable to place the battery outside the experimenting room or in a suitable draught chamber. The electromotive force of Grove's cell is a good deal higher than that of Daniell's, and its internal resistance is very much less, .25 ohm being easily attained with a cell of moderate dimensions. On this account the cell is much used for working induction coils, generating the electric light, and so on, notwithstanding that it is troublesome to fit up, and must be renewed every day.

Cells of Bunsen, &c.

In Bunsen's element the platinum foils of Grove are replaced by carbon. The prime cost of the battery is thus considerably reduced, the more so now that carbons for the purpose have become articles of commerce. The electromotive force of the element thus altered is as great as, or with good carbons even greater than, in Grove's original form; but the internal resistance is greater. There is a difficulty sometimes in obtaining good connection with the carbons, and trouble arises from their fouling; but the fact that this cell is a universal favourite in Germany proves its practical utility. It is comparatively little used in this country.

In the cell of Marié Davy, which is, or was, much used for telegraphic purposes in France, the copper solution and copper plate of Daniell are replaced by a watery paste of protosulphate of mercury, into which is inserted a carbon electrode. The electromotive force of this cell is said to be about 1.5 volts, and its internal resistance to be greater than that of Daniell's cell.

Besides these, various bichromate elements of merit might be described; but we have dwelt long enough on this subject already.

The following table of Latimer Clark's, quoted by Maxwell, will give the reader an idea of the relations as to electromotive force of the commoner elements:—

Daniell.....	H <sub>2</sub> SO <sub>4</sub> + 4Aq	CuSO <sub>4</sub>	1.079
Do.	H <sub>2</sub> SO <sub>4</sub> + 12Aq	CuSO <sub>4</sub>	0.978
Do.	H <sub>2</sub> SO <sub>4</sub> + 12Aq	Cu(NO <sub>3</sub> ) <sub>2</sub>	1.000
Bunsen.....	H <sub>2</sub> SO <sub>4</sub> + 12Aq	HNO <sub>3</sub>	1.964
Do.	H <sub>2</sub> SO <sub>4</sub> + 12Aq	HNO <sub>3</sub> (sp. g. 1.38)	1.888
Grove.....	H <sub>2</sub> SO <sub>4</sub> + 4Aq	HNO <sub>3</sub>	1.956

The electromotive force is stated in volts, and the solutions in the third column are concentrated, unless it is otherwise stated.

**Thermoelectricity.**—We have already alluded to the law of Volta, according to which there can be no resultant electromotive force in a circuit composed solely of different metals; and it will be remembered that we added the condition that all the junctions must be at the same temperature. Seebeck was the first to discover<sup>2</sup> that this law is subject to exception when the junctions are not all at the same temperature. If we form a circuit with an iron wire and a copper wire, and raise the temperature of one of the junctions a little above that of the other, a current flows round the circuit, passing from copper to iron over the hotter junction; similarly, if we solder together a piece of bismuth and a piece of antimony, and connect the free ends with the copper wires of a galvanometer, then when the junction of the bismuth and antimony is heated the galvanometer indicates a current passing from bismuth to antimony over the hot junction. It will be perceived that the second of

<sup>1</sup> Jenkin, *Electricity and Magnetism*, p. 225.  
<sup>2</sup> *Pogg. Ann.*, vi. 1326. The discovery was made about 1821 or 1822.

our two illustrative instances is more complicated than the first, inasmuch as three metals enter into the circuit instead of two. Nevertheless the experimental result is not altered by the intervention of the copper wire (abstraction being made of its resistance), provided the temperatures of the points where it joins the bismuth and antimony respectively be the same. It is easy to give a direct experimental proof of this assertion by inserting between the pieces of bismuth and antimony a piece of copper wire so that the circuit now is Bi.Cu.Sb.Cu.Bi.; if the junctions of the inserted wire with the bismuth and antimony be raised to the same temperature as the BiSb junction in our second experiment, and the junctions with the copper wire of the galvanometer be at the same lower temperature as before, the total electromotive force in the circuit will be the same; and, provided the resistance of the circuit has not been sensibly increased by the interpolation of the copper wire, the galvanometer indication will also be the same as before. The same result is obtained however many different metals we insert between the bismuth and antimony, provided the temperatures of all the junctions be the same and equal to that of the BiSb junction in the original experiment.

The law of Volta therefore still holds if stated thus: *A series of metals whose junctions are all at the same temperature may be replaced by the two end metals of the series without altering the electromotive force in any circuit of which the series forms a part.*

It is not unlikely that the above statement of the fundamental facts concerning thermoelectricity has suggested to the reader two notions:—1st, that the phenomena may be completely explained by a *contact force* at the junctions of the metals which is a function of the temperature of the junction; and 2d, that this contact force is the true contact force of Volta. It is perhaps as well to mention even at this early stage that the first of these notions is certainly not correct, and that the second is not admitted by some of the greatest authorities on the subject.

Seebeck examined the thermoelectric properties of a large number of metals, and formed a thermoelectric series, any metal in which is thermoelectrically related to any following one as bismuth (see above) is to antimony, the electromotive force in a circuit formed of the metals being *ceteris paribus* greater the farther apart they are in the series. The following is a selection from Seebeck's series:—

Bi. Ni. Co. Pd. Pt. Cu. Mn. Hg. Pb. Sn. Au. Ag. Zn. Cd. Fe. Sb. Te.

This series has only a general interest, and is not to be regarded as in any way absolute. Seebeck himself showed the great effect that slight impurities and variations of physical condition may have on the position of a metal in the series. Some specimens of platinum for instance come between zinc and cadmium. Another instance of the same kind is afforded by iron: Joule<sup>3</sup> found the following order to hold—cast iron, copper, steel, smithy iron.

Thermoelectric series have been given by Hankel, Thomson, and others, but we need not reproduce them here. It may be well, however, to direct the attention of the reader to the properties of metallic sulphides and of alloys which in many cases occupy extreme positions in the thermoelectric series. Alloys present anomalies in their thermoelectric properties somewhat similar to those already noticed in our discussion of their conductivity. These properties have been much studied with a view to practical applications in the construction of thermopiles. Considerable progress has been made in this direction (see above p. 11), notwithstanding the fact that many of the alloys most distinguished for their thermoelectric power are very brittle and have a tendency to instability under the continued action of heat.<sup>4</sup>

<sup>3</sup> *Phil. Mag.*, 1857.  
<sup>4</sup> For further information consult Wiedemann, *Galv.*, Bd. § 59<sup>a</sup> &c.

Thermo-electromotive force.

Many measurements of the electromotive force of thermoelectric couples have been made by Matthiessen,<sup>1</sup> Wiedemann,<sup>2</sup> E. Becquerel,<sup>3</sup> and others, but the results are of no great value owing to the effect of impurities and the want of sufficient data to determine all the thermoelectric constants of any one couple (see below, p. 99). Numerical data, such as they are, will be found in Wiedemann, Fleeming Jenkin's *Electricity and Magnetism*, or Everett's *Illustrations of the Centremetre-gramme-second System of Units*. It will give the reader an idea of the order of the magnitudes involved to state that the electromotive force at ordinary temperatures of a BiSb couple is somewhere about 11700 C. G. S.<sup>4</sup> absolute units when the difference between the temperatures of the junctions is 1° C. The corresponding number for a CuFe couple is 1600 or 1700.

Thermoelectric currents, or at least what may very likely be such, have been obtained in circuits other than purely metallic, *e. g.*, in circuits containing junctions of metals and fluids,<sup>5</sup> metals and melted salts,<sup>6</sup> fluids and fluids.<sup>7</sup> The phenomena in all these cases are complicated, and the results more or less doubtful; so that no useful purpose could be served by discussing the matter here. The same remark applies to the curious electrical phenomena of flames,<sup>8</sup> of which no proper explanation, so far as we know, has as yet been given.

Experiments of Magnus.

The experiments of Magnus<sup>9</sup> have shown that in a circuit composed entirely of one metal, every part of which is in the same state as to hardness and strain, no thermoelectromotive force can exist, no matter what the variations of the section or form of the conductor or what the distribution of temperature in it may be (so long as there is neither discontinuity of form nor abrupt variation of temperature).

This statement is of great importance, as we shall see, in the theory of thermoelectricity. Its purport will be all the better understood if we dwell for a little on the three limitations which accompany it.

The great effect of the hardness or softness and crystalline or amorphous structure of a metal on its electric properties was observed by Seebeck soon after the discovery of thermoelectricity.<sup>10</sup> The effect of temper in wires may be shown very neatly by the following experiment due to Magnus. On a reel formed by crossing two pieces of wood are wound several turns of hard-drawn brass wire softened in a number of places adjacent to each other on the reel. The free ends of the wire being connected with a galvanometer, and the parts of the wire lying between neighbouring hard and soft portions being heated, a thermoelectric current of considerable strength is obtained, whose direction is from soft parts to hard across the heated boundaries. Effects of a similar kind were obtained with silver, steel, cadmium, copper, gold, and platinum. In German silver, zinc, tin, and iron, the current went from hard to soft across the hotter boundary.

Sir William Thomson made a number of experiments on the effect of strain on the electric properties of metals. The results, some of them very surprising, are contained in his Bakerian Lecture,<sup>11</sup> along with many other things of great importance for the student of thermoelectricity.

Two of his experiments may be described as specimens.

<sup>1</sup> *Pogg. Ann.*, 1858.  
<sup>2</sup> *Ann. de Chim. et de Phys.*, 1864.  
<sup>3</sup> That is, roughly, .000117, if we take for our unit the electromotive force of a Daniell's cell.  
<sup>4</sup> By Walker, Faraday, Henrich, Gore, and others; see Wiedemann, Bd. i. § 639, &c.  
<sup>5</sup> Andrews, *Phil. Mag.*, 1837; Hankel, Wiedemann (*l. c.*), Gore, *Phil. Mag.*, 1864.  
<sup>6</sup> Nobili, Wiedemann, Becquerel; see Wiedemann, *l. c.*  
<sup>7</sup> See Wiedemann, *l. c.*  
<sup>8</sup> *Pogg. Ann.*, 1851.  
<sup>9</sup> *Pogg. Ann.*, 1856.  
<sup>10</sup> *Phil. Trans.*, 1856.

They afford convenient lecture-room illustrations of the subject under discussion. (1.) A series of copper wires A, B, C, D, E, F, G, &c., are suspended from a horizontal peg. A and B, C and D, E and F, &c., are connected by short horizontal pieces of copper wire, all lying in the same horizontal line, and B and C, D and E, F and G, &c., are connected by a series of pieces lying in another horizontal line below the former. An arrangement is made by means of which the alternate wires A, C, E, G, can be more or less powerfully stretched, while B, D, F, &c., are comparatively free. A piece of hot glass is applied to heat either the upper or lower line of junctions. A thermoelectric current is then observed passing from the stretched to the unstretched copper across the hot junctions. This thermoelectric current increases with the traction up to the breaking point. But the most remarkable point that comes out in such experiments is that when we free the wire after powerful traction, leaving it with a permanent set, there is still a thermoelectric current; but the direction is now from the soft or unstrained towards the permanently strained parts across the hot region. (2.) Iron gives similar results, only the direction of the current is in each case opposite to that in the corresponding case for copper. The following experiment exhibits this in a very elegant manner. One end of a piece of carefully annealed iron wire is wound several times round a horizontal peg, the free end being slightly stretched by a small weight, and connected with one terminal of a galvanometer. The other end of the wire is wound a few times round one side of a rectangular wooden frame, the free end being stretched by a small weight and connected with the other terminal of the galvanometer. The parts of the wire on the peg or the part on the frame is then heated, and weights are hung to the frame. As the weight increases, the deflection of the galvanometer goes on increasing. If we stop a little short of rupture, and gradually decrease the weight, the deflection of the galvanometer gradually decreases to zero, changes sign before the weight is entirely removed, and finally remains at a considerable negative value when the wire is again free.

These experiments of Sir Wm. Thomson's were repeated by Le Roux. The results of the two experimenters are not very concordant. This may be due to differences in the qualities of the materials with which they worked, or to the fact that Le Roux<sup>12</sup> worked at higher mean temperatures than Thomson.<sup>13</sup>

Le Roux also repeated the experiments of Magnus, confirming his general result, but adding the two last qualifications given above. He found, contrary to the result of Magnus, that when a lateral notch is filed in a wire and one side heated, there is in general a thermoelectric current, which is greater, up to a certain limit, the deeper the notch. He also found that when two wires of the same metal, with flat ends, are pressed together, so that one forms the continuation of the other, and the wire on one side of the junction is heated, no current is obtained; but he observed a current in all cases where there was dissymmetry,—*e. g.*, where an edge of one end was pressed on the flat surface of the other, where the wires overlapped or crossed, or where the chisel-shaped end of one wire fitted into a notch in the end of the other, and the axes of the wires were inclined, and so on.

Whether a very abrupt variation in temperature in a continuous part of a metallic wire would produce a thermoelectromotive force is a question which possesses little physical interest, since it is impossible to realize the

<sup>12</sup> *Ann. de Chim. et de Phys.*, 1867.  
<sup>13</sup> Wiedemann, Bd. i. § 610. It appears from a note at the end of Le Roux's paper (*l. c.*) that Sir Wm. Thomson has lately repeated some of his experiments and confirmed his former results.

imagined conditions. There can be no doubt, however, that, when the two unequally heated ends of a wire composed of the same metal throughout are brought together, a thermoelectric current is in general the consequence. Such currents were, it appears, observed by Ritter<sup>1</sup> in 1801, when cold and hot pieces of zinc wire were brought into contact. Becquerel, Matteucci, Magnus, and others have experimented on this subject. The results obtained are, no doubt, greatly influenced by the state as to oxidation, &c., of the surfaces of the metals experimented on, as has been pointed out by Franz and Gangain. The experimental conditions are, in truth, very complicated, and a discussion of the matter would be out of place here.<sup>2</sup> We may mention, however, that, at the instance of Professor Tait, Mr Durham<sup>3</sup> made experiments on the transient current which arises when the unequally heated ends of a platinum wire are brought into contact. It was found that the first swing of a galvanometer of moderately long period was proportional to the temperature difference and independent of the mean temperature through a considerable range.

Cumming, who experimented on thermoelectricity about the same time as Seebeck, and apparently independently, discovered the remarkable fact that the thermoelectric order of the metals is not the same for high temperatures as for low. He found that, when the temperature of the hot junction in a circuit of iron and copper, or iron and gold, is gradually raised, the electromotive force increases more and more slowly, reaches a maximum at a certain temperature T, then decreases to zero, and finally changes its direction. The higher the temperature of the colder junction, so long as it is less than T, the sooner the reversal of the electromotive force is obtained. If the temperature of the hot junction be T + τ, where τ is small, then the reversal of the electromotive force takes place when the temperature of the colder junction is T - τ. If both junctions, A and B, be at the temperature T, then either heating or cooling A will cause a current in the same direction round the circuit, and either heating or cooling B will cause a current in the opposite direction.

The reversal of the current may be shown very conveniently in the manner recommended by Sir Wm. Thomson.<sup>4</sup> A circuit is formed by soldering an iron wire to the copper terminal wires of a galvanometer. If one junction be at the temperature of the room and the other at 300° C. or thereby, a current flows from copper to iron across the hotter junction; but, if we raise the temperature of both junctions over 300° C., one being still a little hotter than the other (which can be managed by keeping both in a lamp flame, one in a slightly hotter place than the other), then the current will flow from iron to copper across the hot junction. If both junctions be allowed to cool, the difference between their temperatures remaining the same, the current will decrease, becoming zero when the mean temperature of the two junctions is about 280° C.; and, on still further lowering the mean temperature, it will set again in the opposite direction, i.e., from copper to iron across the hot junction. The fundamental facts of thermoelectric inversion were confirmed by Becquerel,<sup>5</sup> Hankel,<sup>6</sup> Svanberg,<sup>7</sup> &c.; but the matter rested there till it was taken up<sup>8</sup> by Sir Wm. Thomson<sup>9</sup> in the course of his classical researches on the applications of the laws of thermodynamics to physical problems.

<sup>1</sup> Wiedemann, Bd. i. § 627.  
<sup>2</sup> Consult Wiedemann, Bd. i. § 627, &c., and Mascart, t. ii. § 932. &c.  
<sup>3</sup> Proc. R. S. E., 1871-2.  
<sup>4</sup> Bakerian Lecture, Phil. Trans., 1856, p. 699.  
<sup>5</sup> Ann. de Chim. et de Phys., 1826.  
<sup>6</sup> Pogg. Ann., 1844.  
<sup>7</sup> Pogg. Ann., 1853; cf. Wiedemann, Bd. i. § 623.  
<sup>8</sup> In consequence, it appears, of a remark of Joule's, cf. Proc. R. S. E., 1874-5, p. 417.  
<sup>9</sup> Trans. R. S. E., 1851.

Thermoelectric inversion. Cumming.

The application of the first law of thermodynamics leads to no difficulty; and it indicates that the heat absorbed according to Peltier's law, in the ordinary case when a current passes from copper to iron across the hotter of the junctions, minus the heat evolved at the colder junction where the current passes from iron to copper, is to be looked on as a source of part at least of the energy of the thermoelectric current. If absorption or evolution of heat occur anywhere else than at the junctions, this must be taken account of in a similar manner.

The application of the second law is of a more hypothetical character. It is true that the Peltier effects, as we may for shortness call the heat absorption and evolution at the junctions, are reversible in this sense that we might suppose the thermoelectric current, whose energy arises wholly or partly from the excess of the heat absorbed at the junction A over that evolved at the junction B, used to drive an electromagnetic engine and raise a weight; and that we might suppose the potential energy thus obtained again expended in sending, by means of an electromagnetic machine, a current in the opposite direction round the circuit, absorbing heat at B, evolving heat at A, and thus restoring the inequality of temperature. This process, however, must always be accompanied by dissipation of energy, (1) by the evolution of heat in the circuit according to Joule's law, and (2) by conduction from the hotter towards the colder parts of the wires. The first of these effects varies as the square of the current strength, while Peltier's effect varies as the current strength simply; so that the former might be made as small a fraction of the latter as we please by sufficiently reducing the current, and thus, theoretically speaking, eliminated. The second form of dissipation could not be thus got rid of, and could only be eliminated in a circuit of infinitely small thermal but finite electric conductivity, a kind of circuit not to be realized, as we know (see above p. 51). Still it seems a reasonable hypothesis to assume that the Peltier effects, and other heat effects if any, which vary as the first power of the strength of the current, taken by themselves are subject to the second law of thermodynamics. Let us now further assume that all the reversible heat effects occur solely at the junctions. Let Π, Π' denote the heat (measured in dynamical equivalents) absorbed and evolved, at the hot and cold junctions respectively in a unit of time by a unit current. Let E be the electromotive force of an electromotor maintaining a current I, in such a direction as to cause absorption of heat at the hot junction. Then, if R be the whole resistance of the circuit, we have, by Joule's law and the first law of thermodynamics,

$$EI + \Pi I - \Pi' I = RI^2, \dots (1),$$

supposing the whole of the energy of the current wasted in heat. Hence we get

$$I = \frac{E + \Pi - \Pi'}{R} \dots (2).$$

It appears then that, owing to the excess of the absorption of heat at the hot junction over the evolution at the cold junction, there arises an electromotive force Π - Π' helping to drive the current in the direction giving heat absorption at the hot junction. We may suppose (and shall henceforth suppose) that E = 0, and then the current will be maintained entirely by the thermoelectromotive force.

If we now apply the second law, we get

$$\frac{\Pi}{\theta} - \frac{\Pi'}{\theta'} = 0,$$

θ and θ' being the absolute temperatures of the hot and cold junctions. Hence

$$\frac{\Pi}{\theta} = \frac{\Pi'}{\theta'} \dots (3);$$

or, in other words, Π = Cθ, where C is a constant depend-

ing only on the nature of the metals. In accordance with this, the thermoelectromotive force in the circuit would be C(θ - θ'); that is, it would be proportional to the difference between the temperatures of the junctions. Now this conclusion is wholly inconsistent with the existence of thermoelectric inversions. We must therefore either deny the applicability of the second law, or else seek for reversible heat effects other than those of Peltier. This line of reasoning, taken in connection with another somewhat more difficult, satisfied Sir Wm. Thomson that reversible heating effects do exist in the circuit elsewhere than at the junctions. These can only exist where the current passes from hotter to colder parts of the same wire or the reverse. Thomson was thus led to one of the most astonishing of all his brilliant discoveries; for he found, after a series of researches distinguished alike for patience and experimental skill, that an electric current absorbs heat in a copper conductor when it passes from cold to hot, and evolves heat in iron under similar circumstances. This phenomenon was called by its discoverer the electric convection of heat. He expressed the facts above stated by saying that positive electricity carries heat with it in an unequally heated copper conductor, and negative electricity carries heat with it in an unequally heated iron conductor. The first statement is perhaps clearer; the value of the one given by Thomson consists in the suggestion which it conveys of a valuable physical analogy with the transport of heat by a current of water in an unequally heated pipe.<sup>1</sup>

If two points AB of a uniform linear conductor, in which a current I is flowing from A to B, and evolving heat, be kept at the same constant temperature, but for the electric transport of heat the temperature distribution would be symmetrical about a point of maximum temperature half way between A and B. Owing to the electric transport of heat, the maximum will be shifted towards A in iron, towards B in copper.<sup>2</sup> This remark contains the principle of the experiments made by Thomson to detect the new effect.

The first experiment in which the effect was satisfactorily established was made with a conductor ABCDEFG, formed of a number of strips of iron bound together at A, C, E, and G, but opened widely at B, D, and F, to allow these parts to be thoroughly heated or cooled. At O and E small cylindrical openings allowed the bulbs of two delicate mercurial thermometers to be inserted in the heart of the bundle of strips. The part D of the conductor was kept at 100° C. by means of boiling water, and the parts B and F were kept cool by a constant stream of cold water. The current from a few cells of large surface was sent for a certain time from A to G, then for the same length of time from G to A, and so on. In this way the effects of want of symmetry were eliminated, and the result was that the excess of the temperature at E over that at C was always greatest when the current passed from G to A; whence it follows, as stated above, that a current of positive electricity evolves heat in an iron conductor when it passes from cold to hot.

Le Roux<sup>3</sup> has made a series of interesting experiments on the Thomson effect in different metals. He found that the effect varies as the strength of the current, and gives the following numbers representing its relative magnitudes in different metals. In lead the effect is insensible.

	+		
Sb	64	Fe	31
Cd	31	Bi	31
Zn	11	Arg	25
Ag	6	Pt	18
Cu	2	Al	0.1
		Sn	0.1

We may now apply the mathematical reasoning given above, taking into account Thomson's effect.

<sup>1</sup> Trans. R. S. E., 1851.  
<sup>2</sup> See Verdet, Théorie Mécanique de la Chaleur, t. ii. § 250.  
<sup>3</sup> Ann. de Chim. et de Phys., 1867

Suppose for simplicity we have a circuit of two metals only. Let Equate the current go from A to B over the hot junction, and let the heat absorbed in passing from a point at temperature θ to a neighbouring point at temperature θ + dθ in A be σ<sub>1</sub>dθ per unit of current son. per unit of time; let σ<sub>2</sub>dθ be the corresponding expression for B. Then it is obvious, from the result of Magnus (see above, p. 95), that σ<sub>1</sub> and σ<sub>2</sub> can be functions of the temperature merely; they depend, of course, on the nature of the metal, but are independent of the form or magnitude of the section of the conductor. The first and second laws now give respectively

$$E = \Pi - \Pi' + \int_{\theta'}^{\theta} (\sigma_1 - \sigma_2) d\theta \dots (4),$$

$$0 = \frac{\Pi}{\theta} - \frac{\Pi'}{\theta'} + \int_{\theta'}^{\theta} \frac{\sigma_1 - \sigma_2}{\theta} d\theta \dots (5),$$

where E is the whole thermoelectromotive force, and Π and Π' are the same functions of θ and θ' respectively. By differentiation we get from (5)

$$\frac{d}{d\theta} \left( \frac{\Pi}{\theta} \right) + \frac{\sigma_1 - \sigma_2}{\theta} = 0 \dots (6);$$

whence we easily get

$$E = \int_{\theta'}^{\theta} \frac{\Pi}{\theta} d\theta \dots (7),$$

or

$$\frac{\Pi}{\theta} = \frac{dE}{d\theta}$$

This last equation enables us to determine E in terms of Π, and conversely.

When the difference between the temperatures of the junctions is very small, equal to dθ say, the thermoelectromotive force is

$$\frac{\Pi}{\theta} d\theta \dots (8).$$

The coefficient  $\frac{\Pi}{\theta}$  by which we must multiply the small temperature difference to get the electromotive force is called by Thomson the thermoelectric power of the circuit. If we have a circuit of three metals, A, B, C, all at the same temperature θ, then we know that

$$\frac{\Pi_{BC} + \Pi_{CA} + \Pi_{AB}}{\theta} = 0, \dots (9);$$

whence

or, in other words, the thermoelectric power of B with respect to A is equal to the difference between the thermoelectric powers of a third metal C with respect to A and B respectively.

Thus far we have been following Thomson. But as yet Tait<sup>4</sup> we have no indication how σ, the coefficient of the Thomson convection effect, depends on the temperature. Thomson himself seems (see his Bakerian Lecture, l. c., p. 706) to have expected that σ would turn out to be constant. Certain considerations concerning the dissipation of energy led Tait, however, to conjecture that σ is proportional to the absolute temperature. If we adopt this conjecture, Thomson's equations give us at once the values of the Peltier effect and the electromotive force in the circuit. If σ = k.θ, σ<sub>2</sub> = k<sub>2</sub>θ, we get from (6) and (7) successively<sup>4</sup>

$$\Pi = (k_1 - k_2)(\theta_{12} - \theta)\theta \dots (10),$$

$$E = (k_1 - k_2)(\theta - \theta') \{ \theta_{12} - \frac{1}{2}(\theta + \theta') \} \dots (11),$$

where θ<sub>12</sub> is the neutral temperature. Also, since in a circuit of uniform temperature there are no Thomson effects, and the sum of the Peltier effects is zero, we get for any three metals

$$(k_2 - k_3)\theta_{23} + (k_3 - k_1)\theta_{31} + (k_1 - k_2)\theta_{12} = 0 \dots (12).$$

Taking up the idea of a thermoelectric diagram originally suggested by Thomson, Tait has shown how to represent the above results in a very elegant and simple manner. Suppose we construct a curve whose abscissa is the absolute temperature θ, and whose ordinate is the thermoelectric power of some standard metal with respect to the

<sup>4</sup> Tait, Proc. R. S. E., 1870-1-2.