

interest now that the theory of metallic contact, pure and simple, is given up. The following set is given by Faraday:—<sup>1</sup>

HNO <sub>3</sub> (dil.)	H <sub>2</sub> SO <sub>4</sub> (dil.)	HCl	HNO <sub>3</sub> (strong)	KHO.	KHS.	K <sub>2</sub> S <sub>4</sub>
Ag	Ag	Sb	Ni	Ag	Fe	Fe
Cu	Cu	Ag	Ag	Ni	Ni	Ni
Sb	Sb	Ni	Sb	Cu	Bi	Bi
Bi	Bi	Bi	Cu	Fe	Pb	Sb
Ni	Ni	Cu	Bi	Bi	Ag	Pb
Fe	Fe	Fe	Fe	Pb	Sb	Ag
Sn	Pb	Pb	Sn	Sb	Sn	Sn
Pb	Sn	Sn	Pb	Cd	Cu	Cd
Cd	Cd	Cd	Zn	Zn	Zn	Cu
Zn	Zn	Zn	Cd	Zn	Cd	Zn

It will be seen that the order of the metals is not the same for different liquids.

Contact of two liquids.

Just as between different metals and between metals and liquids there is a contact force, so there is a contact force between different liquids. The direct observations of this contact force are very few and uncertain. One thing, however, is settled, viz., that the contact forces between liquids do not universally at least obey the law of Volta, or, at all events, do not form a consistent series with the metals; for a great variety of circuits of one metal and two solutions have been discovered in which the resultant initial electromotive force is not zero. Faraday has even found cases of this kind with one metal and two different strengths of the same solution.

The cell of Becquerel is a favourite illustration of such a circuit. It consists of a porous vessel filled with a solution of potash and immersed in a beaker containing nitric acid; two strips of platinum immersed in the potash and nitric acid respectively form the plates. The current goes in the cell from the potash to the nitric acid. The following additional examples are taken from Wiedemann.<sup>2</sup>

One metal and two liquids.

The current flows from the metal through the liquids in the order named to the same metal again. For brevity, the metal is named only once.

Metal.	1st Fluid.	2d Fluid.
Pt	KHO	Acids
Pt	CuSO <sub>4</sub>	Dil. H <sub>2</sub> SO <sub>4</sub>
Pt	NaCl	ZnCl <sub>2</sub>
Pt	NH <sub>3</sub>	CuSO <sub>4</sub>
L	CaCl <sub>2</sub>	Dil. HNO <sub>3</sub>
M	Conc. H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>
R	KCy	HNO <sub>3</sub>

L stands for Zn, Cu, or Pt.  
M " " Cu, Fe, Pb, Sn, or Ag.  
R " " Ni, Bi, Pt, Hg, Pd, Sb, Fe, C, Ag, Zn, Cu, Cd, or Sn.

A great variety of active voltaic circuits have been formed with two liquids and two metals. The best known class of cases is that in which the metals are in contact, as in the two-fluid batteries of Daniell, Grove, and Bunsen. But Faraday<sup>4</sup> gives a list of some thirty cases in which the fluids and metals are placed alternately, so that there is no metallic contact. He marks the following combinations as powerful:—

Iron	Diluted nitric acid.	Platinum	Green nitrous acid.
Do.	Hydrochloric acid.	Do.	Do. do.
Do.	Solution of com. salt.	Do.	Do. do.
Copper	Potassium sulphide.	Iron	Dil. nitric acid.
Do.	Strong nitric acid.	Do.	Do. do.

It must be carefully noticed that the galvanometer indi-

<sup>1</sup> Exp. Res., 2012. <sup>2</sup> Exp. Res., 1975.  
<sup>3</sup> Galvanismus, Bd. i. § 63. <sup>4</sup> Exp. Res., 2020.

cation in the first instant only is to be considered. After the first rush of electricity the direction even of the current may alter. Above all, no conclusion concerning the value of the initial electromotive force is to be drawn from measurements of the subsequent current. Quantitative determinations of the electromotive force in many of the above cases have been made by various methods, of which an account will be found in Wiedemann's *Galvanismus*, Bd. i. § 230. The most convenient plan is to use Thomson's quadrant electrometer, Lippmann's capillary electrometer, or some other instrument which allows us to measure the electromotive force while no current is passing through the cell. The galvanometer may also be used as in Latimer Clark's modification of Poggendorff's compensation method.

The apparatus may be arranged according to the scheme in fig. 53. ABC denotes part of the resistance in the circuit of the battery K; the circuits A<sub>2</sub>ELB, A<sub>1</sub>FMC each contain a galvanometer, a cell, and a key. The cells E and F are so arranged as to tend to send currents in the same directions as K, but the resistances AB, AC are so adjusted that when the key L or the key M is de-

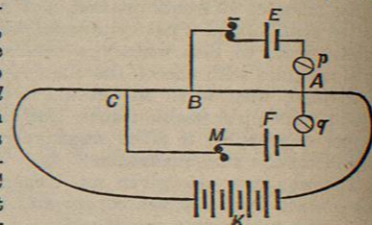


Fig. 53.

pressed, no current is indicated by *p* or *q*. When this is so, we must obviously have  $E = V_A - V_B$ ,  $F = V_A - V_C$ , &c.,  $V_A, V_B, V_C$  denoting the potentials at A, B, and C. Hence, if P, Q, R denote the resistances in AB, AC, and in the whole circuit of K,

$$E = \frac{P}{R} K, \quad F = \frac{Q}{R} K.$$

If K were a constant battery, and its internal resistance were either known or else so small as to form only an inappreciable fraction of R, then each of the equations just written might be used singly, and we might operate with one cell and one galvanometer, comparing the electromotive force of the cell with K. In general, however, this will not be possible, and then we have, eliminating K and P

$$\frac{E}{F} = \frac{P}{Q},$$

from which we get the ratio of E to F independent of the variation of K and R. We can by this method therefore find the ratio of the electromotive force of a given combination to that of a standard cell, when no current is passing through either. The process would be perfect in practice if a standard cell could be constructed whose absolute constancy could be relied on.

Contact force from polarization.—The flow of electricity through the cell is accompanied by a deposition of the products of chemical decomposition on the plates, which alters the surface contact forces. This constitutes the phenomenon of polarization, which we have already partially studied. It will be useful to consider a little more in detail some of the forms in which it is met with.

The products of electrolysis which accumulate at the electrodes may be simply held in solution or precipitated, or they may combine chemically with the solution; they may be deposited as a crust on the electrode, or they may enter into more or less intimate connection with it. Several of these different effects may occur together; but in almost all cases the result is the same, viz. a great weakening of the current after the first instant or so. This weakening of the current might be due either to a transition resistance caused by the alterations at the electrodes, or to an op-

posing electromotive force arising from the alteration of the contacts. The former was the explanation adopted in the earlier researches of Poggendorff and Fechner; but there can be no doubt about the existence of the latter effect, and Lenz showed that it was sufficient to account for the facts observed. It has been usual, therefore, to neglect the transition resistance altogether in the great majority of cases. It is certain, however, that it really exists in some instances. Consider the case of two electrolytic cells containing concentrated sulphuric acid, the electrodes being in the one copper plates, in the other platinum plates. Either of these cells inserted into a voltaic current will weaken the current, but for different reasons. In both cases hydrogen is freed at the negative electrode, and reduces sulphur from the strong acid, the effect of which is not great either way, for if the negative electrode be replaced by a fresh plate the weakening of the current remains. At the positive electrode oxygen is evolved, which oxidizes the copper in the one case and is deposited on the platinum in the other,—in both cases replacing the positive electrode by a fresh plate will cause momentary increase in the current; but the copper plate which served as positive electrode if tested against a fresh copper plate gives very little return current, whereas the positive platinum plate similarly tested gives a very powerful one. In the one cell the weakening of the current was due to the resistance of a crust of non-conducting copper oxide, in the other it was due to the contact force at the surface of the oxygenated platinum.<sup>1</sup>

Transition resistance.

Gas polarization.

The polarization which arises from the deposition of gas on the electrodes is, if we except the case where peroxides are formed, by far the most powerful form, and has been much studied ever since voltaic batteries were used. Experiments like the one just quoted prove decisively that the electromotive force has its seat at the surface of the electrode itself, and is due to local alterations there. The certainty of this fact gives the study of the phenomenon great theoretical importance, since we may hope thereby to arrive at some idea of the nature of the contact force.

It is also certain that in most cases each electrode contributes separately to the whole electromotive force, for if we remove the polarized plates the adhering gas goes with them, and each plate is found to be electrically different when tested against a fresh or unpolarized plate. We may also take measures to remove the deposited gas by washing the plates with water, potash, or nitric acid, or by igniting them; and it is found that the more energetic the chemical agency thus employed the more thoroughly is the polarization destroyed.

It seems clear, therefore, that it is the mere fact of the presence of the gas on the electrode in some form or other which causes the electrical difference. We may go still further and produce the phenomenon by depositing gas by means other than electrolytic. If a piece of platinum foil be immersed in hydrogen it absorbs the gas, as has been shown by Graham. A piece of foil thus treated is positive to a piece of freshly ignited foil when both are placed in dilute sulphuric acid. The same result is obtained by saturating the liquid in the neighbourhood of the foil with hydrogen.<sup>2</sup> The activity thus conferred on the plate may be again destroyed by immersing it in chlorine or bromine, or even in oxygen, by igniting it, and so on. Similarly, if we dip a fresh piece of foil into chlorine or bromine, it will become negative to a fresh plate. The effect obtained by dipping the foil in oxygen in the ordinary state is very small, the oxygen deposited by electrolysis must therefore be in a different state to that condensed during mere im-

mersion in the gas. This is probably due to the fact that electrolytically generated oxygen contains ozone (see art. ELECTROLYSIS); and in accordance with this we find that a platinum foil ozonized by being held in the electric brush proceeding from a charged conductor, or rubbed with phosphorus, is negative to a fresh plate in dilute sulphuric acid.

The gas battery of Grove is a remarkable instance of the electromotive properties of gas-coated metals. Two long glass tubes A and B are arranged in the two necks of a Woulfe's bottle. The upper ends of the tubes are closed, but pierced by two platinum wires, to which are fastened two long strips of platinum foil (which are sometimes platinized)<sup>3</sup> reaching to very near the lower ends of the tubes. The bottle and part of the tubes are filled with some liquid, say dilute sulphuric acid, and hydrogen introduced into B and oxygen into A. This may be very conveniently done by sending an electric current from A to B and decomposing the dilute acid, but it may be done in other ways as well. This arrangement has an electromotive force comparable with that of a Daniell's cell (see below, p. 88), and if the original volume of hydrogen in B be twice that of the oxygen in A it will continue to send the current through a closed circuit, the gas gradually disappearing in the tubes until none is left, when the current stops. These gas elements may be connected up in series, &c., and used like ordinary battery cells.

If the tube B be filled with ordinary hydrogen and A with liquid only, a current in the same direction as before is observed; but the liquid in A is decomposed and hydrogen evolved, which produces an opposing electromotive force and stops the current. If A contain oxygen and B fluid only, the current lasts for a very short time unless the oxygen contain ozone. This is in accordance with what we have already seen.

Grove<sup>4</sup> has given an electromotive series for the different gases and metals as follows:—

Chlorine.	Metals which do not decompose water.	Alcohol.
Bromine.		Sulphur.
Iodine.		Phosphorus.
Nitric oxide.	Camphor.	Carbonic oxide.
Carbonic acid.	Volatile oils.	Hydrogen.
Nitrogen.	Olefiant gas.	Metals which decompose water.
	Ether.	

In this series any member is positive to any preceding member.

We have already remarked that the polarization in many cases comes on very rapidly. In cases where the electromotive force of the battery is not sufficient to produce a continuous evolution of gas, the current after the first rush dies away very rapidly. There are cases, however, in which a small current continues to flow for a very long time. Such currents are not accompanied by any visible evolution of gas, and it is clear that they could not be so accompanied, for, if the electromotive force of the battery be under a certain limit, the amount of chemical energy absorbed by the current per unit of time is less than the intrinsic energy of the ions liberated in a unit of time. It was originally supposed, therefore, that, besides this electrolytic conduction proper, fluids conducted to a slight extent like metals. But Helmholtz<sup>5</sup> has shown that no such assumption is necessary, and has pointed out that when the fluid holds gas in solution a sort of electrolytic conduction may take place which involves, it is true, liberation of the ions, or at least of an ion, but so that the final result does not imply absorption of more energy than the battery can furnish per unit of time in accordance with Faraday's law of electrolytic conduction.

Suppose, for instance, that the dilute sulphuric acid in an ordinary voltammeter held H in solution. When the current passes, O appears at the anode and unites with the H in solution to form water; a corresponding quantity of H is thereby liberated at the cathode, which is either absorbed by the platinum electrode or diffuses towards the anode, to combine in its turn with the appearing oxygen. It is obvious that the liberation of the ion in such a case does not involve absorption of energy to the extent necessary when both H and O are disengaged from water. A current might therefore be kept up under such circumstances for a long time by an electro-

<sup>3</sup> This is best accomplished by washing the foils in hot nitric acid, and then using them to decompose a solution of platonic chloride with the current of two cells of Grove.  
<sup>4</sup> Phil. Trans., 1845.

<sup>5</sup> Poag. Ann., 1873.

<sup>1</sup> Wiedemann, Bd. i. § 455.

<sup>2</sup> See Macaluso's experiments, Wiedemann, Nachträge, § 53.

motive force under that of a cell of Daniell. Helmholtz has given the name of electrolytic convection to this species of electrolytic conduction. He has shown that the phenomenon comes to an end when the liquid is perfectly freed from gas. The absorption of the gases by the electrodes plays a great part here, and gives rise in gas-free liquids to a phenomenon analogous to the residual discharge. When the battery is first turned on, a rush of electricity takes place, then there is a small current which gradually dies away. The first rush is like the instantaneous charge of a condenser; the small current which arises from the slow penetration of the ions into the platinum corresponds to the formation of latent charge. When the voltmeter is disconnected from the battery and discharged through a galvanometer, we have a first rush due to the part of the ions accumulated on the surface of the platinum, and then a gradually decreasing current due to the emergence of the gas which had penetrated into the metal. When the electromotive force which presses the gas into the electrode is removed, the absorbed gas will move very nearly in accordance with the ordinary law of diffusion, and the rate of its reappearance will depend very little on the electromotive force at the surface of the electrode. Consequently the residual current furnished by such an apparatus will not depend on its external resistance. A sudden increase of the external resistance will simply cause the current to diminish until sufficient surface density has been attained to raise the electromotive force to the value required to keep up the same current as before through the increased resistance; and the converse will happen if the external resistance be decreased.

This passage of the gas into the substance of the electrode has, at the instance of Helmholtz, lately been investigated by Root.<sup>2</sup> He finds that in certain cases, when only one side of a platinum foil is exposed to electrolysis, the deposited gas, whether H or O, actually passes through and produces the corresponding polarization on the other side of the foil.

It might at first sight be expected that in all cases where the electromotive force in the circuit is sufficient to produce continual evolution of the ions the polarization would be the same. This is not by any means the case, however, owing to the fact that the final state of the liberated ions varies with the strength of the current, or, more correctly speaking, with the current density, i.e., the amount of electricity which crosses unit section of the electrode in unit time. When H<sub>2</sub> and O are being liberated from dilute H<sub>2</sub>SO<sub>4</sub>, this depends mainly on the formation of variable quantities of ozone and H<sub>2</sub>O<sub>2</sub>. This variation of the physical state and intrinsic energy of the liberated ions, is a fact of the greatest importance in the art of electro-metallurgy. A better instance could not be given than Gore's electrolytic modification of antimony, whose intrinsic energy is strikingly manifested by its explosive properties.

The effect of enlarging the surface of the electrode in diminishing the polarization in the case where the maximum polarization is not reached was noticed above (p. 48). It has also the effect of diminishing the maximum of polarization in the case where the ions are completely set free. Platinizing has the same effect. Thus Poggendorff<sup>3</sup> found for the maximum polarization 2.12 to 2.32<sup>4</sup> for bright platinum plates, while it was only 1.83 to 1.85 for platinized plates. The effect of platinizing on the hydrogen and oxygen polarization was about equal for strong currents, but greater on the hydrogen polarization when the current was weaker. On the other hand, by using small platinum points to decompose water in Wollaston's manner, Buff<sup>5</sup> found the polarization as high as 8.31.

Poggendorff<sup>6</sup> and Crova<sup>7</sup> have investigated the dependence of the maximum of polarization on the current density. It follows from their researches that it can be represented by  $A - B^{-1}$ , I being the current density.

It would appear that the maximum of polarization is decreased by increasing the temperature of the cell. The

effect, however, in some cases at least which have been adduced to prove this, might be explained by the decrease of the internal resistance of the cell.

Agitating the electrodes, stirring the liquid in their neighbourhood, or any other process which tends to dissipate the deposit on the electrode, leads, as might be expected, to a diminution of the polarization. The effect of increased pressure in retarding or helping electrolysis might be appreciable in certain cases. Suppose that an electrochemical equivalent of the ions, during liberation under a pressure  $p$ , increases in volume by  $v$ , then during the passage of a unit of electricity work to the extent  $pv$  is done; the electromotive force required to free the ions must therefore have a part equal to  $pv$  which may increase or decrease as the process goes on. If the ions be gases which obey Boyle's law very nearly, then  $pv$  is constant, so long as the temperature remains the same; so that we cannot expect, within reasonable limits, to check the electrolysis of dilute sulphuric acid by conducting it in a closed vessel.<sup>8</sup>

We have repeatedly drawn attention to the rapidity with which the polarization decays in the first few instants after the plates are connected through a circuit of moderate resistance. Direct proofs of this have been given by Beetz<sup>9</sup> and Edlund<sup>10</sup>. The former shows that the oxygen polarization decays much more rapidly than the hydrogen polarization, which is not to be wondered at, considering the greater readiness of platinum to absorb hydrogen; with palladium electrodes the difference would doubtless be still more marked. The reader may also consult an interesting paper on this subject by Bernstein<sup>11</sup> who concludes that in a certain case the polarization diminished by  $\frac{1}{2}$  to  $\frac{1}{10}$  of its value in about  $\frac{1}{100}$  of a second.

There seems to be little reason to doubt the substantial accuracy of the facts just mentioned; and the reader will not fail to see the application to the theory and practice of the measurement of the electromotive forces of inconstant electromotors, a category under which, unfortunately for the electrician, all known voltaic batteries must be classed. The remark applies with double force to the measurement of the electromotive force of polarization. Many measurements of the latter have been made. We quote a few, to give the reader a general idea of the magnitudes involved; into a discussion of the methods we cannot enter here.

Hydrogen and Oxygen Polarization of bright Platinum Plates.<sup>12</sup>

Whole Polarization.	H Polarization.	O Polarization.	Observer.
2.33	...	...	Wheatstone.
2.56	...	...	Buff.
2.31	1.15	1.16	Svanberg.
2.33	1.16	1.16	Poggendorff.
...	1.15	...	Beetz.

Polarization of Platinum Plates with different Gases compared with the Electromotive Force of Platinum Plates with the same Gas against a fresh Platinum Plate in Grove's Gas Battery.<sup>13</sup>

Gas	Polarization.	Pt.GiPt.
I	.171	.161
Br	.329	.323
Cl	.505	.466
H	.910	.814
Cl and H	1.375	1.335

<sup>1</sup> Within certain limits, of course. <sup>2</sup> Pogg. Ann., 1876.  
<sup>3</sup> Wiedemann, Bd. i. § 480; Pogg. Ann., 1847.  
<sup>4</sup> Unless otherwise stated, our unit of the electromotive force is for the present the electromotive force of a Daniell's cell.  
<sup>5</sup> Wiedemann, Bd. i. § 473; Pogg. Ann., 1867.  
<sup>6</sup> Pogg. Ann., 1864. <sup>7</sup> Ann. de Chim. et de Phys., 1863.

<sup>8</sup> Maxwell, vol. i. § 263. Other matters of great interest are stated there. See also the instructive analysis of the phenomena of polarization in §§ 294-271. <sup>9</sup> Pogg. Ann., 1856.  
<sup>10</sup> Pogg. Ann., 1852; see also Wiedemann, Bd. i. § 495 &c.  
<sup>11</sup> Pogg. Ann., 1875. <sup>12</sup> From Wiedemann, Bd. i. § 478.  
<sup>13</sup> Beetz, quoted in Wiedemann; Pogg. Ann., 1853.

Maximum of polarization.

Polarization of various Metals measured with Thomson's Quadrant Electrometer.<sup>1</sup>

Oxygen Plate.	Hydrogen Plate.	Polarization.	No. of Cells in Polarizing Battery.
Freshly ignited Pt.	Pt	1.64-2.30	1-8
Pt	Pd	1.50-1.85	1-4
Pd	Pt	1.60-1.91	1-4
Pt	Fe	2.16	3
Fe	Pt	0	3
Fe	Fe	0	3
Al	Al	1.09-5.20	1-6

Although the polarization by gas deposits has absorbed so much of the attention of physicists, it is by no means a solitary instance. The phenomenon is universal. It appears even with zinc plates in zinc sulphate, and copper plates in copper sulphate. The nearest approach to unpolarizable electrodes is the case of amalgamated zinc plates in zinc sulphate, originally discovered by Du Bois Reymond. When the sulphate solution is neutral, the polarization, as may be shown by immersing a large number of plates in series in the solution, is extremely small.

For an account of polarization at the surface of two liquids observed by Du Bois Reymond, and other kindred matters, and for many other facts which we have passed over in silence, the reader may consult Wiedemann's *Galvanismus*. Some account will be found in the article *ELECTROLYSIS* of the remarkable phenomenon of the "passivity of iron, and of the powerful polarization arising from the formation of superoxides, on which depends the action of the secondary pile of Planté."

Application of the Laws of Energy to the Voltaic Circuit.—In the classical series of researches by which Joule laid the foundations of the laws of energy, a considerable share of attention is devoted to the energetics of the electric current. Guided by the great idea which he was gradually developing, Joule made experimental determinations of the amount of energy of various kinds evolved in the electric circuit. We have already seen how he measured the quantity of heat developed in a metallic conductor, and in an electrolyte.<sup>2</sup> This quantity was found to vary as the product of the resistance of the conductor into the square of the current strength, account being taken of disturbances at the electrodes in the case of electrolytes.

These disturbances were considered in the first memoir and allowed for. The accuracy of the view taken of them, to which Joule was led by the opinion of Faraday, that the solution of the oxide in the voltaic cell had no active share in producing the electric current, was justly questioned, implicitly by Sir Wm. Thomson<sup>3</sup> in 1851, and explicitly by Bosscha<sup>4</sup> in 1859.

In a later memoir, however,<sup>5</sup> Joule made a direct experimental investigation of these secondary effects, and shows how they can be accounted for. His results have not been shaken by subsequent investigators; and the general conclusions to be drawn from them are not in the least affected by the theory of secondary action, which is suggested in the paper. These, so far as we are now concerned with them, are as follows:—

"1st. In an electrolytic cell there are three distinct obstacles to the voltaic current. The first is resistance to conduction; the second is resistance to electrolysis without chemical change<sup>6</sup> [arising simply from the presence of

<sup>1</sup> Tait, *Phil. Mag.*, 1869. This method is in some respects one of the best for measurements of the kind.  
<sup>2</sup> *Phil. Mag.*, 1841. <sup>3</sup> *Phil. Mag.*, 1851 (2), p. 554.  
<sup>4</sup> Pogg. Ann., cviii. p. 319.  
<sup>5</sup> *Mem. Lit. and Phil. Soc. Manchester*, 2d ser. vii., 1843.  
<sup>6</sup> This resistance is, in more modern language, an "opposing electromotive force."  
<sup>7</sup> The meaning of "without chemical change" will be seen directly.

chemical repulsion];<sup>8</sup> and the third is resistance to electrolysis, accompanied by chemical changes.

"2d. By the first of these (the resistance to conduction) heat is evolved exactly as it is by a wire, according to the resistance and the square of the current; and it is thus that a part of the heat belonging to the chemical actions of the battery is evolved. By the second a reaction on the intensity<sup>9</sup> of the battery occurs, and wherever it exists heat is evolved exactly equivalent to the loss of heating power in the battery arising from its diminished intensity. But the third resistance differs from the second, inasmuch as the heat due to its reaction is rendered latent, and thus lost to the circuit.

"3d. Hence it is that, however we arrange the voltaic apparatus, and whatever cells of electrolysis we include in the circuit, the whole caloric of the circuit is exactly accounted for by the whole of the chemical changes.

"4th. As was discovered by Faraday, the quantity of current electricity<sup>10</sup> depends upon the number of atoms which suffer electrolysis in each cell; and the intensity depends on the sum of chemical affinities. Now both the mechanical and heating powers of a current are (per equivalent of electrolysis in any one of the battery cells) proportional to its intensity. Therefore the mechanical and heating powers of the current are proportional to each other.

"5th. The magnetic electrical machine enables us to convert mechanical power into heat by means of the electric currents which are induced by it; and I have little doubt that, by interposing an electromagnetic engine in the circuit of a battery, a diminution of the heat evolved per equivalent of chemical change would be the consequence, and this in proportion to the mechanical powers obtained."<sup>11</sup>

The above statement of Joule's contains, in a form which seems to us neither ambiguous nor obscure,<sup>12</sup> an exposition of the leading experimental principles of the energetics of the electric circuit. Besides the papers of Joule we have mentioned, two others on the electrical origin of the heat of chemical combination ought to be read in connection with this subject.<sup>13</sup> The now famous tract of Helmholtz, "Ueber die Erhaltung der Kraft," which appeared in 1847, shortly after these papers of Joule, did much, by its able statement of the issues, to advance this branch of electrical science, and should be consulted by every thorough student.

An extremely important contribution to the experimental evidence for the law of energy in the case of electric currents was furnished by the researches of Favre.<sup>14</sup> He uses a calorimeter, which is virtually a mercury thermometer with an enormous bulb, into which are inserted a number of test-tube shaped vessels all opening outwards. When a heated body is placed in one of these vessels its heat is quickly communicated to the mercury in the calorimeter, and the amount of heat thus communicated is measured by the expansion of the mercury, which is measured as usual by noting the displacement along a capillary tube. Into one of the recesses of the bulb of this calorimeter containing a quantity of dilute sulphuric acid was introduced 33 grm. of granulated zinc. The heat evolved during its dissolution was 18682 units (gramme-degrees C.). Five of the recesses were then furnished with dilute sulphuric acid of the same strength as before, and into them were put five elements of Smee (amalgamated zinc and

<sup>8</sup> The brackets here are ours; they contain Joule's theoretical view with which we are not now concerned.  
<sup>9</sup> In modern phrase, "electromotive force."  
<sup>10</sup> That is, current strength.  
<sup>11</sup> This he experimentally verified, *Phil. Mag.*, 1843.  
<sup>12</sup> Cf. Verdet, *Théorie Mécanique de la Chaleur*, § 327.  
<sup>13</sup> *Phil. Mag.*, 1842 (1), and 1843 (1).  
<sup>14</sup> *Ann. de Chim. et de Phys.*, 1854.

platinized copper). These were joined up in circuit by means of very thick copper wire, and the heat developed during the solution of 33 grm. of zinc observed as before. The result was 18674 units, *i.e.*, almost exactly the same as before. A small electromagnetic engine was next introduced into the circuit, and the heat observed, first, when it was at rest; secondly, when it was in motion, but consuming all its energy in heat owing to friction, &c.; and thirdly, when it was doing work in raising a weight. The quantities of heat in the three cases were 18667, 18657, and 18374 units respectively. In the first four experiments, therefore, the heat developed in the circuit is sensibly the same, the mean being 18670; the heat developed in the last case is less than this by 296, which is the equivalent of the potential energy conferred on the raised weight. From this result the value of the mechanical equivalent of heat ought to be 443. This differs considerably from the best value (423 to 425), but not more so than might be expected from experimental errors.

Theory of Sir Wm. Thomson

*Dynamical Theory of the Electromotive Force of the Battery.*—In two very important papers published in the *Philosophical Magazine* for 1851, Sir William Thomson laid the foundations of the Dynamical Theory of Electrolysis, one of the objects of which, to use very nearly his own words, is to investigate, for any circuit, the relation between the electromotive force, the electrochemical equivalents of the substances operated on, and the dynamical equivalent of the chemical effect produced in the consumption of a given amount of the materials, and by means of this relation to determine in absolute measure from experimental data the electromotive force of a single cell of Daniell's battery, and the electromotive force required for the electrolysis of water.

Thomson's law

The relation sought for is found as follows. Let  $E$  be the electromotive force<sup>1</sup> of the battery. Then, by the definition of electromotive force,  $E$  is the whole work done in the circuit by a unit current during a unit of time. This work may appear as heat developed in the conductors or at the junctions according to the laws of Joule and Peltier, as the intrinsic energy of liberated or deposited ions, as work done by electromagnetic forces, as "local heat" in the battery (see below, p. 91), or otherwise. Let  $e$  be the electrochemical equivalent of any one of the elements which take part in the chemical action from which the energy of the current is derived, *i.e.*, the number of grammes of that element which enter into the chemical action during the passage of unit current for a second; and let  $\theta$  be the thermal equivalent of that amount of chemical action in the battery into which exactly a gramme of the element in question would enter,—in other words, the amount of heat that would be developed were the whole energy of the amount of chemical action just indicated spent in heat. Then it is obvious that the energy of the chemical action that takes place in the battery during the passage of unit current for a unit of time is  $J\theta e$ , where  $J$  is Joule's equivalent. Hence, by the principle of conservation, we must have

$$E = J\theta e;$$

or, in words, the electromotive force of any electrochemical apparatus is, in absolute measure, equal to the dynamical equivalent of the chemical action that takes place during the passage of unit current for a unit of time.

The value of  $J$  is known, being  $4156 \times 10^4$  in absolute units. The value of  $e$  has been found by various experimenters (see below, p. 104), the most accurate result being probably that deduced from the experiments of Kohlrausch, *viz.*  $e = .003411$  for zinc.

<sup>1</sup> All our quantities are measured, of course, in C. G. S. absolute units.

We may find  $\theta$  by direct calorimetric experiments on the heat developed in the circuit. In this way Joule found for the thermal equivalent of the chemical action of a Daniell's cell during the solution of 65 grammes of zinc 47670 (grm. deg. C.), and Raoult<sup>2</sup>, by a somewhat similar process, obtained the number 47800. These give for the heat equivalent of the chemical action during the solution of 1 grm. zinc 733 and 735 respectively. Substituting these values in our formula, we get for the electromotive force of Daniell's cell in absolute C. G. S. units  $1.039 \times 10^8$  or  $1.042 \times 10^8$ .

But we may proceed in a totally different way to find the value of  $\theta$ . Direct observations have been made on the heat evolved in a great variety of chemical actions, and from these experiments we can calculate, with a considerable degree of accuracy, the value of  $\theta$ , and thus deduce the electromotive force of a battery from purely chemical data. This method of procedure must of course be adopted if we wish to test the dynamical theory. Now, neglecting refinements concerning the state in which the copper is deposited, the state of concentration of the solution, &c., the chemical action in a Daniell's cell may be stated to be the removal of the Cu from  $\text{CuSO}_4$  in solution, and the substitution of Zn in its place. Now, Favre and Silbermann have found for the heat developed in this chemical action 714 (grm. deg. C.) per grm. of zinc. This will give, by the above formula, for the electromotive force of Daniell's element  $1.012 \times 10^8$ . The chemical action might also be stated as the combination of zinc with oxygen, and the solution of the zinc oxide thus formed in sulphuric acid, the separation of copper oxide from sulphuric acid, and of the copper from the oxygen. The quantity of heat evolved in the first two actions per grm. of zinc is, according to Andrews,  $1301 + 369 = 1670$  (grm. deg. C.), and that absorbed in the last two actions  $588 + 293 = 881$ . Hence  $\theta = 789$ ; this gives  $1.118 \times 10^8$ . Professor G. C. Foster<sup>3</sup> has calculated from Julius Thomson's experiments values 805, 1387, and 617 of  $\theta$  for the cells of Daniell, Grove, and Smee respectively; the values of the electromotive forces corresponding to these are  $1.141 \times 10^8$ ,  $1.966 \times 10^8$ , and  $.875 \times 10^8$ . These results are in fair agreement with the different values of the electromotive force obtained from direct experiment.

Limit of electro motive force for electrolysis.

It follows from Thomson's theory that a certain minimum electromotive force is necessary to decompose water; and he calculated from the data of Joule that this minimum was 1.318 times the electromotive force of a Daniell's cell. Favre and Silbermann found for the heat developed in the formation of  $\text{H}_2\text{O}$  68920, from which we conclude that the minimum electromotive force required to electrolyse water is  $68920 \div 47800$ , *i.e.*, 1.44 times that of a Daniell's cell.<sup>4</sup>

*Development of Heat at the Electrodes.*—In a remarkable paper,<sup>5</sup> which we have already quoted, Joule investigated directly the disturbing effect of the electrodes on the heat

<sup>2</sup> Wiedemann, Bd. ii. 2, § 1118.  
<sup>3</sup> Everett, *Illustrations of C. G. S. System of Units*, p. 77. No reference to the source is given.  
<sup>4</sup> Verdet (*Théorie Méc. de la Chaleur*, tom. ii. p. 207) states that Favre was the first to point this out, but gives no citation. It seems unlikely that Favre considered the matter so early as 1851. (See Violle's bibliography at the end of Verdet's volume.)

<sup>5</sup> *Mem. Lit. and Phil. Soc. Manchester*. ser. 2, vol. vii., 1843. This paper seems to have been in a great measure lost sight of. In his earlier papers (*Pogg. Ann.*, clii. § 504, 1858) Bosscha says he had not seen it. Poggendorff, in a note, p. 504, appreciates it in a manner which appears to us unjust. This may have arisen from misunderstanding of Joule's terminology, however. Verdet (*Chaleur*, tom. ii. p. 204) does not seem to have been acquainted with it. It is mentioned in the bibliography by M. J. Violle, however, under 1846, which is the date of the volume of the *Memoirs* in which it was published. The paper was actually read Jan. 1843.

developed in an electrolyte. His method was as follows. A coil of wire whose resistance was known in terms of a certain standard was inserted in the circuit of six Daniell's elements, and the heat evolved in it carefully measured by immersing it in a calorimeter. The resistance of the rest of the circuit, including that of the battery, was found by interpolating a known resistance in the circuit and observing, by means of a tangent galvanometer, the ratio in which the current was reduced. (The assumption is here made that the electromotive force of a Daniell's cell is constant for different currents.) Knowing the heat evolved in a part of the circuit of known resistance, and knowing the resistance of the whole circuit, the heat evolved according to Joule's law in the whole circuit during the oxidation of 65 grammes of zinc can be calculated from the indications of the tangent galvanometer previously compared with a voltmeter. Hence the thermal equivalent  $\theta$  of the work done by the electromotive force of a Daniell's cell during the solution of 65 grm. zinc can be found. The value of  $\theta$  arrived at by Joule in this way is 47670 (grm. deg. C.).

Electrolytic cells of various construction were then inserted into the circuit. The electromotive force resisting the passage of the current through the cells was found by taking the number of battery cells just sufficient to produce electrolysis, observing the current, then increasing the number of cells by one and observing the current again. If  $i$  be the current in the first case, corrected to bring it to the value it would have had if the resistance of the whole circuit had been the same as in the second case, and  $j$  the current in the second case, then,  $E$  being the number of battery cells used in the first case, the electromotive force  $Z$  opposing the current is given by

$$Z = E - \frac{i}{j}$$

the unit being the electromotive force of a Daniell's cell.  $Z$  being known and assumed constant for different currents within certain limits, the resistance of the whole circuit, electrolyte included, can be found by Ohm's method as above. The amount of heat  $H$  which ought to be developed in the electrolyte by Joule's law can then be calculated. The amount of heat  $H$  actually developed was observed. It was found that  $H$  is in general greater than  $H$ , the difference per electrolysis of 65 grm. zinc with various electrodes is shown in the following table:—

Electrode.		Z	H - H	L	Z - L
+	-				
Pt	Amg. Zn	2.81	66300	1.39	1.42
Pt	Pt	2.47	53000	1.11	1.36
Ag <sup>1</sup>	Ag <sup>1</sup>	1.75	16400	.34	1.40
Pt <sup>1</sup>	Pt <sup>1</sup>	1.90	28800	.60	1.29
Pt <sup>1</sup>	Pt <sup>1</sup>	1.90	26700	.56	1.34

<sup>1</sup> Platinized.

The electrolyte in all these cases was dil.  $\text{H}_2\text{SO}_4$ , excepting the last case, where it was a solution of potash of sp. g. 1.063. In all the cases the chemical process is finally the same or very nearly so, *viz.*, the freeing of the elements of water, hydrogen and oxygen; in the ordinary gaseous<sup>1</sup> state, and the transference of a certain quantity of  $\text{H}_2\text{SO}_4$  from the negative to the positive electrode, or of alkali in the opposite direction. Yet the values of  $H' - H$  (which we may call the local heat) are very different. It will be seen, however, that the values of  $H' - H$  and  $Z$  rise and fall together; and, if we calculate the electromotive forces ( $L$ ) corresponding to the values of  $H' - H$ , by dividing by 47670, which was found for the thermal equivalent of the electro-

<sup>1</sup> The amount of oxygen that finally escapes in the active state as ozone is very small.

motive force of a Daniell's cell, and subtract the values of Local  $L$  thus found from  $Z$ , we get results which are not far from constant. The mean of the values of  $Z - L$  is 1.36, the thermal equivalent of which is 64800, which is not very different from 68900, the heat evolved in the combination of 2 grm. of H with 16 grm. of O to form water. It appears, therefore, that the local heat corresponds to the excess of the electromotive force of polarization over the electromotive force requisite to separate water into its component gases. In other words, the work done by the current against this residual electromotive force is accounted for by the local heat  $H' - H$  developed in the cell (see Joule's statement above, p. 89). A glance at the column  $L$  in the above table shows that this residual electromotive force depends greatly on the nature of the electrodes. Thus when the positive and negative electrodes are plates of platinum and zinc respectively the residual electromotive force is 1.39, whereas with platinized silver plates it is only .34. Local heat and the corresponding electromotive force play a very important part in the working of batteries. Owing to this cause there is an evolution of heat in the cell itself which varies with the strength of the current, and uses up a certain definite fraction of the energy furnished by the solution of the zinc. By sufficiently increasing the external resistance, the amount of heat developed in the cell according to the law  $JH = RI^2$  can be made as small a fraction as we please of the whole heat thus developed; but the amount of local heat generated in the cell during the solution of 65 grm. zinc is not greatly altered in this way, at least not in a cell of Daniell, or in any other of the so-called constant batteries. Did our space permit we might quote a great variety of experimental results to illustrate the principles we have been discussing. Most of these investigations are due to the French physicists Favre and Silbermann, whose researches have greatly advanced this department of the science of energy.

Very copious extracts from the memoirs of these and other physicists who have worked in this department will be found in Wiedemann, Bd. ii. 2, §§ 1121 *seqq.* The reader who desires to follow this interesting subject to the sources will find his labour much lightened by referring to M. J. Violle's excellent bibliography of the mechanical theory of heat, appended to the second volume of Verdet's *Théorie Mécanique de la Chaleur*. Much has been done for the theory of the subject by a series of papers on the mechanical theory of electrolysis by Bosscha,<sup>2</sup> in which the somewhat complicated phenomena involved are analysed in a remarkably clear and able way. Any reader who desires to know what has been done in this department will do well to consult these papers. We quote the following as an example of Favre and Silbermann's results and of the calculations of Bosscha.

The heat evolved in a cell of Smee<sup>3</sup> and in platinum wires of different lengths through which it was circuited was measured with the following result:—

Heat in cell.	Heat in wire.	Length of wire.	Heat in cell calc.
13127	4965	25 mm.	13528
11690	6557	50 "	11788
10439	7746	100 "	10188
8992	9030	200 "	9048

The heat in each case is that evolved during the liberation of 1 grm. of hydrogen in the cell. If we assume that the whole heat in the cell and in the wire is generated according to Joule's law, and calculate on this hypothesis the resistance of the cell in mm. of the wire, we should get

<sup>2</sup> *Pogg. Ann.*, cli., cliii., cv., cviii., 1857, &c.  
<sup>3</sup> Amalgamated zinc and platinized copper.

Local heat and residual electromotive force.

Favre and Silbermann, Bosscha