ceases again, in the absence of coercitive force, as soon as the magnetizing force ceases to act. Such a condition of equilibrium cannot be imagined as produced otherwise than by the simultaneous action of attractive and repulsive forces. There must then be produced a nearly, but not quite, unstable equilibrium of the elementary magnets by the mutual action of all the neighbouring attractive and repulsive molecular forces, if the assumptions of Ampère's theory are to correspond to facts. That a combination of molecular forces fulfilling this necessary requirement can be shown to be possible I do not venture to assert.

XXX. *On the Seat of the Electromotive Forces in the Voltaic Cell.* By PROFESSOR OLIVER J. LODGE, D.Sc.

[Continued from p. 190.*]

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7. **T**HE result of the survey in regard to our special subject of discussion may be summed up thus:—(1) that there is certainly an E.M.F. at the junction of two different substances, or even of the same substance in two different states; and (2) that the total E.M.F. of a circuit is the algebraic sum of all such contact-forces at every junction in the circuit. I do not know that these two propositions could be passed *nem. con.*, but I believe that, provided they are properly understood, the dissenting minority would be a very small one. It is probable that Professor Exner would be in the minority, but I am unable to be sure of any one else.

We can also make a negative proposition which will command almost universal assent—viz. that if in the above second proposition, instead of the sum of the contact-forces at *every* junction, we attend only to the contact-forces at the *metallic* junctions, the proposition will no longer be true. This fact, that the metallic junctions are insufficient to account for all the E.M.F., was established by Becquerel, De la Rive, and

* Scarcely any of this portion was read at Montreal, but it was given in substance to the Society of Telegraph Engineers on March 26th.

others, and still more thoroughly and exhaustively by Faraday. It is the easiest possible thing to make a number of batteries which shall give a current without any metallic junction whatever. Faraday gives some thirty of them*.

One more certain proposition we can lay down—viz. that whenever a current is produced, the energy of the current must be maintained by absorption of heat, or by chemical action, or by gravity, or by some other such agent, not by mere contact.

So much being agreed to, what remains as subject-matter for controversy? This: A voltaic circuit contains at least three junctions; what is the value of the contact force at each of them? and especially to which junction is the major part of the observed E.M.F. due? Is it the zinc-acid? or is it the copper-acid? or is it the zinc-copper? There is no other question. The old chemical and contact controversy has died out, but another controversy remains. Most physicists probably would say today that the major part of the E.M.F. of the cell resides at the zinc-copper junction. This was Volta's view, and this is the view of the text-book writers taught by Sir William Thomson. Some few would say at the zinc-acid junction, and among them I must confess myself.

It is no question between contact and something else; it is a question between a feeble energy-less metal-metal contact, and an active energetic metal-fluid contact with potentialities of chemical action straining across the junction. What is there to distinguish between the two? Electrostatic experiments with air-condensers prove nothing. They add up three E.M.F.s, $\text{air}/\text{M} + \text{M}/\text{M}' + \text{M}'/\text{air}$, and give you the sum. The experimenters usually assume that M/M' is what they are measuring, but there is no proof to be given in support of the assumption, except that if you substitute water for air the effect remains almost unaltered; but then water contains oxygen as the active element the same as air does. Well, then, it may be urged, the effect is the same *in vacuo* and in hydrogen as in air; and to this I answer, Not proven.

Can any further assertions be made with reference to electroscopic experiments as bearing on voltaic theory? Yes, it can be asserted that by adding up the Volta effects for A/B,

* Exp. Res. ii. 2020. Dr. J. A. Fleming describes another of these batteries in Phil. Mag. June 1874, and gives some very cogent and readable arguments in favour of the "chemical theory" of battery E.M.F., suggesting that the difference of potential between the terminals of a battery on open circuit is due to potential chemical combination of the metals and electrolytes. He does not, however, explain the old Volta experiment; and, as Prof. Chrystal has pointed out (*Encyc. Brit.*, "Electricity," p. 99), upholders of the chemical theory are bound to explain this.

for B/C, for C/D. . . and for Z/A, you arrive at the total E.M.F. of the circuit A, B, C A. True, but what then?

The Volta effect you call A/B is really

$$\text{air/A} + \text{A/B} + \text{B/air} ;$$

that you call B/C is

$$\text{air/B} + \text{B/C} + \text{C/air} ;$$

.

and that you call Z/A is

$$\text{air/Z} + \text{Z/A} + \text{A/air}.$$

Add them up, and you get

$$\text{A/B} + \text{B/C} + . . . + \text{Z/A},$$

which *must* be the E.M.F. of a circuit by common sense—*i. e.* without violent experimental disproof, which no one has ever attempted to give. This fact, that the sum of the Volta effects equals the sum of the true forces, in a closed circuit of any conducting materials, has nevertheless caused persons to suppose that air/metal forces are negligibly small. But it is clear that they may have any value they like without affecting the truth of the law. They could only affect it if air/M were not equal to $-M/\text{air}$. The experimental proof of the summation law, therefore, establishes that air/M *is* equal to $-M/\text{air}$, as well as the important fact that the contact-force at each junction is independent of all other junctions of what kind soever.

8. Leaving electrostatic determinations as without bearing on the point at issue, let us ask, Is there no direct and straightforward way of measuring the actual E.M.F. at a particular junction without disturbance from other junctions? The answer is most clearly given by Clerk Maxwell*, thus :—

“ Sir W. Thomson has shown that if Π is the coefficient of Peltier effect or the heat absorbed at the junction by unit current in unit time, then $J\Pi$ is the E.M.F. at that junction acting with the current. This is of great importance, as it is the only method of measuring a local E.M.F.; the ordinary method of connecting up by wires to an electrometer being useless. This Peltier measurement is quite independent of the effect of contact-forces in other parts of the circuit. But the E.M.F. so measured does not account for Volta’s force, which is far greater and often opposite. Hence the assumption that the potential of a metal is to be measured by that of the air in contact with it must be erroneous, and the greater part of Volta’s E.M.F. must be sought for, not at the junction of the two metals, but at one or both of the surfaces

* ‘Electricity and Magnetism,’ vol. i. art. 249. Abbreviated here, because so easy of reference.

which separate the metals from the air or other medium which forms the third element in the circuit."

And in another place he says* :—

"In a voltaic circuit the sum of the E.M.F.'s from zinc to electrolyte, from electrolyte to copper, and from copper to zinc, is not zero, but is what is called the E.M.F. of the circuit—a measurable quantity. Of these three E.M.F.'s only one can be measured by a legitimate process, that namely from copper to zinc. If we cause an electric current to pass from copper to zinc, the heat generated in the conductor per unit of electricity is a measure of the work done by the current, for no chemical or other change is effected. Part of this heat arises from the work done in overcoming ordinary resistance within the copper and the zinc. This part may be diminished indefinitely by letting the electricity pass very slowly. The remainder of the heat arises from the work done in overcoming the E.M.F. from the zinc to the copper, and the amount of this heat per unit of electricity is a measure of the E.M.F. Now it is found by thermoelectric experiments that this E.M.F. is exceedingly small at ordinary temperature, being less than a microvolt, and that it is from zinc to copper†. Hence the statement, deduced from experiments in which air is the third medium, that the E.M.F. from copper to zinc is .75 volt, cannot be correct. In fact, what is really measured is the difference between the potential in air near the surface of copper, and the potential in air near the surface of zinc, the zinc and copper being in contact. The number .75 is therefore the E.M.F., in volts, of the circuit copper, zinc, air, copper, and is the sum of three E.M.F.'s, only one of which has yet been measured."

With every word of Maxwell I cordially agree.

9. While on the theoretical aspect of the subject, it may be well to see what Pellat, as one of the best experimenters on it, has to say. Pellat substantially observes as follows :—

"Does the apparent difference of potential between two metals in contact indicate a real difference of potential between them? In all rigour, No! but the slight variation of its value when different gases or even liquids are used renders it extremely probable that there is such a real difference of potential, and that it is very nearly what is measured in electroscopic experiments."

As to difficulties connected with energy considerations

* Maxwell: Letter to the 'Electrician,' April 26, 1879. Also 'Elem. Electricity,' p. 149.

† Further on (sect. 23) I point out that this statement is not quite true, but it does not affect the main argument.

and mere contact, he refers to Helmholtz* and Clausius†, who, he says, relieve him of all responsibility on this head.

The fact that the voltaic order of the metals is much the same as their order of oxidizability must have struck nearly everybody, and must also have been felt as a difficulty by the upholders of the efficacy of mere contact. Pellat considers he disposes of it thus :—"Since the E.M.F. of a pile is that represented by chemical action, and since by experiment voltaic contact-forces have much the same values as the E.M.F. of piles, it follows that there is some vague relation between A/B and the heats of combination, say of substitution of one metal for another in a salt (as in a Daniell)."

He sums up his experimental conclusions as follows :—

(1) "Two different metals united metallicity are covered, in the state of equilibrium, with electric coats of unequal potential."

(2) "This difference of potential only depends on the superficial coat of metal. It changes notably when the surface is mechanically scratched, becoming always more positive. As the scratching effect disappears with time, so does the extra difference of potential. The state of polish of the surface is immaterial, but traces of foreign substances, forming a coat so thin as to be invisible, are able to modify the value of the observed effect enormously."

(3) "The effect depends somewhat on temperature."

(4) "The pressure and nature of the gas surrounding the metals have a very distinct but extremely feeble influence, but, since the effect produced is a lagging one, it is probably due to some secondary cause, and it is probable that the difference of potential is really independent of the gaseous dielectric."

(5) "The difference of potential between the electric coats on two metals united metallicity has the same value as the E.M.F. of an element of a liquid pile formed by these two

* *Die Erhaltung der Kraft*, p. 47, where Helmholtz develops Volta's original hypothesis about an attraction of matter for electricity, of an amount depending on the kind of matter, so that it gets pulled one way or another across a junction of two dissimilar substances. He points out that the Volta effect is explained if zinc be granted a stronger attraction for electricity than copper has. This view he returns to in his Faraday Lecture 1881, where also he refers to Berzelius's electrical theory of chemical affinity. The opinions of Professor Helmholtz are too weighty to be merely referred to in a footnote, but we may have occasion to consider them later.

† *Die mechanische Behandlung der Elektrizität*, chap. vii. §§ 2 and 3, where Prof. Clausius follows up the above idea by considering the rôle which heat plays in the matter, and thus hypothetically explains the Peltier effect also.

metals, provided that the E.M.F. is determined before any alteration of the metallic surface wetted by the liquid has occurred; but these alterations produce themselves very rapidly."

Pellat's theoretical conclusions being short may also be here quoted, and I will number them on with the others.

(6) "It is extremely probable that the difference of potential between the electric coats which cover two metals connected metallica lly represents the true difference of potential which exists between them. No reason, either theoretical or experimental, can be invoked against the existence of a difference of potential between two metals in contact."

(7) "This last quantity has no connection with the thermoelectric E.M.F. measured by the Peltier phenomenon."

(8) "It has only a vague and distant connection with the difference of oxidizability of the metals."

Concerning these propositions, I may remark that while number 2 is likely to annoy contact theorists (though I know they have methods of explaining it away), numbers 4 and 5 are calculated to restore their equanimity. The five experimental conclusions I accept as in duty bound, only permitting myself to doubt the perfect generality of numbers 4 and 5 under all circumstances; but the three theoretical ones I am unable to wholly accept. Thus with respect to the second part of number 6, I beg entirely to differ from M. Pellat if I am called on to simultaneously admit number 7. Whether one is prepared to accept any of his theoretical conclusions or to reject them all, depends upon how one regards them. If in the way he himself intended, then I reject them all. If with one's own interpretation, then I say that the second part of 6 and 8 are true (though for "only a vague and distant" I would substitute "no"); and 7 is also true if it be held to refer to the quantity first mentioned in number 6, while number 8 refers to the other quantity. Number 6 I should also consider true if the prefix "in" be made to the fourth word.

10. Pellat then proceeds to explain why he considers the Peltier effect to be quite distinct from, and have no relation to, the true E.M.F. of contact. In explaining this he makes use of a piece of unpleasantly plausible reasoning, which I myself have heard Professor Ayrton use, and which, when unexpectedly suggested, is so painfully benumbing that it is worth while to quote it, and to indicate its weak point. Pellat's statement of the argument is rather long; perhaps it can with advantage be abbreviated.

Two metals A and B put into contact are at different potentials, the difference A/B being due to and equal to the E.M.F.

of contact. There is, then, at the junction not only the contact-force E , but also the equal opposite force $-dV$, due to the difference of potential established. Either of these forces alone would resist or aid the passage of electricity across the junction and so give rise to a Peltier effect, but both together will do nothing of the sort; and so if there be any Peltier effect, it must be some small residual phenomenon, or it must be due to some other and totally distinct cause*.

Professor Ayrton's way of putting the argument, which I think he said he got from Sir William Thomson, was something like this. When Q units of electricity are transmitted against a force E , work EQ is done; also when they are transmitted up a difference of potential $V' - V$, work $Q(V' - V)$ is done; but, in an open circuit containing an electromotive junction, $V - V'$ is produced by and is equal to E . Hence, at an electromotive junction no work need be done by a current; in other words, the existence or non-existence of a Peltier effect has nothing to do with the existence or non-existence of a local E.M.F.

The fallacy of the argument, in either form, lies in over-precise specification of locality; it gratuitously asserts as true for *the junction* what is only proved to be true for the whole circuit. It assumes that there can be no work done *at a junction* if it be perfectly easy to drive electricity either way across it—*i. e.* if there be no work done *on the whole*.

11. To exhibit the fallacy, consider a hydrostatic analogy. Two vessels of water connected by a pipe in which is a motor of some kind, which, without leakage, exerts a specified force on the water and maintains a constant difference of potentials, but then remains stationary, doing no further work. We typify it feebly in the diagram by an impracticable close-fitting water-wheel driven by a weight without friction.

$V - V'$ is the equivalent of the force exerted at the junction, and everything is in equilibrium. It is perfectly easy for water to flow from one vessel into the other under the influence of the slightest extra force, for W helps the water up the hill $V - V'$, when the flow is in that direction; and, whenever the flow is reversed, it lets the water gently down again, taking all its energy out of it. If water is made to flow from A to B , say by pouring more into A , the weight W is lowered, or energy disappears (heat absorbed) at the junction; if it is made to flow from B to A the weight is raised, or energy

* Thus it may be, suggests Pellat, due to a slight difference between E and $-dV$ produced by the mere fact of a current passing; *i. e.* contact E.M.F. with electricity at rest may be slightly different from what it is with electricity in motion.

(say heat) is generated at the junction. Thus there is a true Peltier effect at the junction despite the existence of $V - V'$ and its equality to the junction force, and yet no resistance is offered to the flow of water either way. Thus is the first form of the argument controverted.

Fig. 14.

Hydrostatic analogue of the true contact or Seebeck force, and of the real though small difference of potential which it maintains between two metals in contact. A and B represent the two metals, C their junction; W is a weight driving a water-tight wheel until stopped by the difference of potential set up. The hydraulic raising or lowering of the weight represents the Peltier effect.

To pump water from A to B by any other pipe would need work to be done equal to $Q(V - V')$, and to pump water against the force of W, acting alone, would also need work EQ ; but when the water goes from A to B *viâ* W, or *vice versâ*, no work is done on the whole. Quite true: but the conclusion that no work is done *at the junction* by no means follows. Work *must* be done at the junction in proportion to the force there (by inspection of the diagram); and accordingly the existence or non-existence of a Peltier effect has *everything* to do with the existence or non-existence of a local E.M.F. This controverts the second form of the argument.

If the argument be now considered upset, are we to proceed to assert that the difference of potential, or force, concerned in the Volta effect, and the heat-destruction or generation concerned in the Peltier effect, are closely connected, and in fact different ways of observing the same thing? By no means. All we have proved is that the Peltier effect accurately and necessarily represents and measures the true contact-force at a junction. True we have considered a difference of potential $V - V'$ as produced by this contact-force in an incomplete circuit; and so it is. But nothing has been said to imply that this difference of potential has anything to do with what is observed in electrostatic experiments as the Volta effect. So far from this, I will assert that what is

usually observed when two metals are touched and separated is not primarily a difference of potential between the metals at all. They are at different potentials when separated, no doubt, because they are oppositely charged; but they may have been at the same potential until separated. The real Volta effect is almost independent of the true contact-force, and of the difference of potential which it produces. In other words, a good Volta effect can be observed when there was no difference of potential whatever between the metals when in contact.

According to my view the Volta effect is produced, not by a contact-force at the junction of the two metals, but by a

Fig. 15.

Hydrostatic analogue of the Volta effect, or *apparent* difference of potential produced by metallic contact, and of the opposite charges but uniform potential which it maintains between two metals in contact. The vessels are covered by air-tight elastic bags differently stretched.

contact-force at their free surfaces, between the metals and the air or other medium surrounding them. To represent this hypothesis by a hydrostatic model, we shall have to maintain the difference of level in the two connected vessels, not by a force at the junction, but by a force at the surfaces; say by using closed vessels and compressed air, or more pictorially by differently stretched elastic membranes or bladders tied over the tops of the vessels.

Note that the difference of level in this case implies no difference of potential; and, as before, no work is required to transfer water between A and B. Hence it is not easy to distinguish this case from the former; and this difficulty of distinguishing between the two cases is what has given rise to most of the confusion. The only easy criterion is the non-existence in the second case of any Peltier effect at the junction C. Naturally it is possible and common for the two effects to be superposed, but they are essentially independent.

Since the two vessels in the second case are at the same potential, the way to observe the effect is to cut and seal the

pipe at C, and then show that the vessels are differently charged; which is what Volta did. The model does not indeed represent the gradual change of potential induced as the distance between the condenser-plates increases; and it is scarcely worth while to complicate the matter by making a more elaborate model. The thickening of the dielectric layer of a condenser, when its plates are separated, corresponds exactly to the thickening and strengthening of an elastic membrane; and rise of potential in the one case is accurately representable by increase of pressure in the other; but such considerations belong to general electrostatics, and have no special bearing on our present subject.

12. This is perhaps the most convenient place to introduce the notes or condensed statements which I drew up and distributed at the meeting before the discussion. They were intended to be critically exact (allowing of course for mistakes and possible slips) so as to bear analysis; and hence it is probably worth while to reproduce them here with notes and comments.

I. Orthodox Statements believed by the writer to be true in the form here set down.

A. Volta.

i. Two metals in contact ordinarily acquire opposite charges*; for instance, clean zinc receives a positive charge by contact with copper, of such a magnitude as would be otherwise produced under the same circumstances by an E.M.F. of about .8 volt.

ii. This apparent contact E.M.F. or "Volta force" is independent of all other *metallic* contacts wheresoever arranged; hence the metals can be arranged in a numerical series such that the "contact-force" of any two is equal to the difference of the numbers attached to them, whether the contact be direct or through intermediate metals. But whether this series changes when the atmosphere, or medium surrounding the metal, changes, is an open question: on the one side are experiments of De la Rive, Brown, Schulze-Berge; on the other side, of Pfaff, Pellat, Thomson, Von Zahn †. It certainly changes when the free metallic surfaces are in the slightest degree oxidized or otherwise dirty. And in general this "Volta force" is very dependent on all non-metallic contacts.

iii. In a closed chain of any substances whatever, the

* Observe that it is not said that two metals in contact acquire different potentials. Such difference of potential I believe to be only apparent. Compare figs. 14 and 15.

† I put Von Zahn on that side because he himself considers himself there, and because the great bulk of his experiments lean decidedly that way.

resultant E.M.F. is the algebraic sum of the Volta forces measured electrostatically in air for every junction in the chain : neglecting magnetic or impressed E.M.F. [Verified most completely by Ayrton and Perry.]

B. Thomson.

iv. The E.M.F. in any closed circuit is equal to the energy conferred on unit electricity as it flows round it.

[Neglect magnetic or impressed E.M.F. in what follows.]

v. At the junction of two metals any energy conferred on, or withdrawn from, the current, must be in the form of heat. At the junction of any substance with an electrolyte, energy may be conveyed to or from the current at the expense of chemical action as well as of heat.

vi. In a circuit of uniform temperature : if metallic, the sum of the E.M.F.'s is zero by the second law of thermodynamics ; if partly electrolytic, the sum of the E.M.F.'s is equal to the sum of the energies of chemical action going on per unit current per second.

vii. In any closed conducting circuit the total intrinsic E.M.F. is equal to the dynamical value of the sum of the chemical actions going on per unit of electricity conveyed ($\Sigma J\theta\epsilon$), diminished by the energy expended in algebraically generating reversible heat.

viii. The locality of any E.M.F. may be detected, and its amount measured, by observing the reversible heat or other form of energy there produced or absorbed per unit current per second. [This is held by Maxwell but possibly not by Thomson *, though its establishment is due to him.]

II. *Statements believed by the writer to be false though orthodox.*

ix. Two metals in air or water or dilute acid, but not in contact, are practically at the same potential†. [Sir William Thomson, Clifton, Pellat.]

* The only reason which I can think of as likely to have caused Sir William to doubt or deny the validity of this proposition is given and, I hope, refuted at sections 10 and 11.

† The truth or falsity of this statement may be held to depend on a question of words, viz. the definition of potential. Sir William at the meeting said he had always defined potential as the work done in bringing a unit charge close up to, but not *into*, the body. This definition explains some apparent inconsistency in one or two of his utterances which I had never quite understood. But seeing that there is no difficulty whatever in giving a charge up to a metal body, but rather the contrary, why not define its potential in the more simple manner which followers of his have unconsciously, and I believe universally, adopted, not knowing that they were thus putting themselves out of harmony with him? Given his definition, so that the potential of a body means really not its potential

x. Two metals in contact are at seriously different potentials (*i. e.* differences of potential greater than such millivolts as are concerned in thermoelectricity). [This is held by nearly everybody*.]

xi. The contact-force between a metal and a dielectric, or between a metal and an electrolyte such as water and dilute acid, is small †. [Ayrton and Perry, Clifton, Pellat, and probably Sir William Thomson.]

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13. Before proceeding to the statements embodying my own views, it will be more interesting if I try to explain in a fuller and more connected manner what they are ‡.

Let us regard the air as a dielectric bath of oxygen, in which metals are immersed, and picture a piece of zinc surrounded by oxygen molecules which are straining at it, and

but the potential of the medium close to it, statements Nos. ix. and x. are undoubtedly true; and No. xi. is also true, I suppose, for it then only means that there is not much E.M.F. between the medium close to a metal and that at a little distance.

* It is much more natural to suppose that the potential of a metallic conductor is uniform, whether it is homogeneous or not. Indeed, it is not only more natural, but it is true, that two parts of a conductor *can* only differ in potential by reason of an E.M.F. located at the junction. Now there usually is an E.M.F. at a junction, but it is only of such a magnitude as is concerned in thermoelectricity. This, indeed, does produce a difference of potential between the metals, but nothing else can. N.B. Always provided that by "the potential of a metal" is meant that potential, and not the potential of air near it.

† The experiments supposed to establish this, really prove only that there is very little difference between the air and the water in which a metal is partially immersed. I do not quite know how to understand, on Sir William's plan, the potential of a metal which is half in one medium and half in another.

‡ The reason I set them forth at length is because I had no time at the meeting both to open the discussion and also to properly express my own ideas, and Sir William Thomson was kind enough to tell me to write out the paper completely, and to explain the position I took up fully. This, therefore, I have endeavoured to do.

endeavouring to combine with it. They may indeed partially succeed; but suppose they do not, we have here a strong potential chemical action or chemical strain, which must probably be accompanied by some physical phenomenon. Now remember that oxygen is an electro-negative element; and without endeavouring to examine too precisely what signification is involved in that statement, it will be not out of accord with orthodox views if we assume that it means that at least any dissociated oxygen atoms are negatively charged, each with the characteristic charge of a free dyad atom. Granting something equivalent to this, without pressing the form of expression too closely, we perceive that the strain of the oxygen towards the zinc will result in what I metaphorically call a slackening up, or attempted compression, of the negative electricity in it; *i. e.* in a rise of negative potential. We may therefore say that zinc is at a lower potential than the air surrounding it, and that the step of potential in crossing the boundary from zinc to air is closely connected with the chemical affinity between zinc and oxygen. Observe that this step of potential does not obviously nor probably depend on the amount of oxygen present. It is possible that a few million molecules may be as effective as a large number. Note also that the step of potential is by no means caused by actual oxidation: in so far as the zinc surface is tarnished by oxidation the strain will be diminished and the step of potential become less.

Nothing is said here about the possible effect of the nitrogen, because it is simplest in the first instance to ignore it, though whether experiment will justify this simplicity or not, I do not yet know.

We may go further and assert that if in general the chemical affinity of two substances can be measured by their energies of combination, then the step of potential in the present case may perhaps be calculable from the heat of combustion of zinc.

And one may justify this assertion thus. Let an atom of oxygen combine with an atom of zinc; it will generate an amount of heat h , and its characteristic charge, q , will be given up to the zinc and will thereby fall down the step of potential, v , which separates the zinc from the air. *Now if we suppose that the heat h is the representative and equivalent of the fall of energy $q v$, it follows of course that*

$$v = \frac{J h}{q}.$$

Make the hypothesis and see what comes of it.

14. The oxidation energy of zinc per gramme-equivalent (*i. e.* 65 grammes of zinc or 16 of oxygen) is, according to the determinations of Julius Thomsen, Andrews, and Favre and Silbermann, 85,430, 84,825, and 83,915 respectively.

The amount of electricity needed to deposit a gramme-equivalent of zinc, or of any dyad element, is, according to the modern determination of Lord Rayleigh *, 19,320 units.

Hence the value of $\frac{h}{q}$, which is a ratio evidently independent of the number of atoms dealt with, lies between $\frac{85400}{19320}$ and $\frac{83915}{19320}$ probably. Let us say it is $\frac{85000}{19320}$ or 4.4.

Now J in absolute measure is 42×10^6 ; so the value of v , which is $\left(\frac{Jh}{q}\right)$ according to the above hypothesis, comes out 1.85×10^8 , that is 1.85 volt.

This then, I say, is the step of potential between zinc and air. (To avoid circumlocution I will henceforward speak as if the above hypothesis were admittedly true, and all I now say stands or falls with it.)

All clean bright zinc is thus about 1.8 volt below the potential of the air near it; tarnished or oxidized zinc will exhibit less difference; and it is perhaps possible that perfectly oxidized zinc need show no difference of potential at all between itself and the air. The step of potential by no means therefore depends upon the occurrence of oxidation; it is the oxidation *tendency* which causes it, but so far as oxidation actually takes place the step diminishes.

Proceed to consider a piece of copper similarly. Oxygen molecules are straining at it also, but with less force. The combustion energy of copper per gramme-equivalent is given by the three authorities already quoted as 37,160, 38,290, and 43,770 respectively. These do not agree well, and it is difficult to know which to take; but Thomsen's results are, I believe, generally relied on; so, assuming his, the step of potential between copper and air will be $\frac{.42 \times 37200}{19320}$ volts, that is about

.8 volt. This then is the amount by which clean bright copper differs from the air. Oxidized copper will differ less. Comparing this value for copper with that just obtained for zinc, we perceive that a piece of zinc and a piece of copper are, when separate, not at the same potential; they differ by about a volt from each other. If the zinc is oxidized, they differ less: if the copper is oxidized, they differ more.

* "4.025 grammes of silver are deposited by an Ampère current in an hour" (Montreal Address). This gives the electrochemical equivalent of silver .01118, and of hydrogen .0010352.

Now put the zinc and copper into direct metallic contact, and neglect for the present the third of a millivolt of E.M.F. developed at the junction, which acts so as to drive positive electricity from copper to zinc. A rush of electricity must take place from the copper to the zinc to equalize their potential; it is impossible that they can remain at different potentials when directly united: all parts of a conductor must be at a uniform potential, and the rush has taken place because they were not so when put into contact.

15. Picturing to ourselves the effect as produced by the straining oxygen atoms, we shall perceive that they could not get at either metal when separate: first, because they surrounded it everywhere, and strained equally on all sides; and second, because, being all charged with negative electricity, they could not move in on all sides at once without, so to speak, compressing the electricity in the body and giving it an absolute charge. But directly the copper touched the zinc the oxygen atoms were cleared away at the point of contact, and the stress of those at the rest of its surface was no longer counterbalanced. Moreover, they *can* now all move nearer to the zinc because a way of escape for electricity is provided into the copper, whose surrounding oxygen atoms will be thus driven back somewhat further from the surface, until the dielectric strain, assisting the chemical strain on the copper surface and opposing it on the zinc surface, prevents further displacement, and equilibrium is again attained. The electricity which escaped from the zinc to the copper was negative electricity (oxygen being essentially an electro-negative element), the negatively charged oxygen atoms have moved a little nearer to the zinc than their normal distance: *i. e.* the thickness of its layer of negative electricity is reduced, or its surface is positively charged; the negative layer on the copper has been slightly thickened—its surface is negatively charged.

This is a pictorial way of representing the process, and may be regarded as somewhat fanciful; it is, however, the way in which the theory originally occurred to me, and it permits more insight into the processes than a mere statement in terms of potential can; though it may well be that the imagined processes are but distant likenesses of the real ones.

The oxygen atoms have moved nearer to the zinc; it is now more easily oxidized than before. The copper, on the other hand, is by contact with zinc somewhat protected.

Observe that the contact has not developed any force; it has only, by sweeping away the oxygen from the point of contact, enabled previously existing forces to do work and produce their effect.

The air surrounding the metals in contact is in a state of slight dielectric strain, such as would be produced by two pieces of any one metal of similar size and position, charged so as to differ in potential from each other by a volt.

Zinc and copper plates in contact may therefore be regarded as the plates of a condenser, but they form a peculiar condenser, for they are not really at different potentials; the whole step of potential which throws the air into its state of dielectric strain is located on their bounding surfaces.

Let s and s' be the electrostatic capacity of the zinc and the copper respectively; think of them as two independent spheres united by a fine wire; and let x be their common potential; then the zinc has, by the fact of contact, gone up $1\cdot8+x$, and the copper has gone down $x-\cdot8$; and, since the quantity of electricity which left the one went to the other, it follows that—

$$s(1\cdot8-x)=s'(x-\cdot8)$$

$$\text{or} \quad x = \frac{1\cdot8s + \cdot8s'}{s+s'}$$

There is no necessary relation between s and s' in general, but in the ordinary form of the Volta experiment the two plates are of equal size and shape; in which case $s=s'$, and $x=1\cdot3$ volt below the potential of the unconstrained air.

All this is wholly unlike a condenser investigation. To treat it as a condenser we must consider the air-surfaces close to the two metals as the plates of the condenser, and we can then speak of its electrostatic capacity S in the ordinary way, and say that it is in the present case charged with the E.M.F. of a volt.

The quantity of electricity on either plate of such a condenser is $S(1\cdot8-\cdot8)$ or S ; hence

$$s(1\cdot8-x)=s'(x-\cdot8)=S(1\cdot8-\cdot8).$$

And the general relation between the three S 's is like that of two Leyden jars in cascade, viz.,

$$S = \frac{s s'}{s+s'}$$

If the two pieces of metal are circular disks each of radius r , and at a distance z apart, the value of S is of course $\frac{r^2}{4z}$.

In Volta's form of the experiment, two plates are put near each other, connected for an instant, then removed from each other, and the potential of one of them observed. This

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measures $\frac{S(1.8 - .8)}{s + x}$, where x is the capacity of the electrometer used.

In Pellat's form the charges acquired by contact are neutralized, and the oxygen atoms driven back to their normal distance, by an extraneous E.M.F. carefully adjusted until the plates, after separation, exhibit no charge. This measures $1.8 - .8$ directly.

16. So far I have spoken as if I were sure that (granting the hypothesis) the potential of clean zinc is 1.8 volt below the air; but I am not really sure that this is anything better than an approximation. The fact that no actual combination occurs makes the matter perhaps a little indefinite. If an oxygen atom unites with a zinc atom, one has a right to say distinctly that q has stepped down v ; but suppose they are only facing one another, and wishing to combine, are we justified then in asserting that the step v is ready for q to go down, and that it is the same v as before? It almost seems to depend on whether chemical attraction becomes greater as two atoms approach one another, or becomes less.

Suppose, first, it becomes greater, which is the natural hypothesis, then the v calculated from data obtained by permitting the combination to occur will be too large for the step of potential caused by the attraction of metal for oxygen over a standard distance. On the other hand, the differential force urging electricity across a junction of two metals, which is observed in the Volta effect, may be somewhat greater than simply the differences in their pull reckoned at standard distances, because the approach of atoms to the zinc will increase it on this side, and the recession of atoms from the copper will decrease it on that. Hence the Volta effect may perhaps be expected to agree better with calculation than the air/metal potential-difference does, if this latter could be experimentally observed, which it never yet has been.

Next, suppose that chemical attraction becomes less as atoms approach: the step of potential between a metal and air will now be greater than that calculated from chemical data; nevertheless the Volta effect will be somewhat less than that due to the differences of such steps for two metals, and may thus possibly agree pretty well with calculation.

The agreement or non-agreement of Volta effects with calculation does not therefore quite establish the accuracy of our calculated metal-air contact-forces. But we have no right to assume that even Volta effects will agree with calculation particularly well so long as our data are so slender. They have no chance of accurately agreeing unless the metals used

are pure and perfectly clean—a most difficult condition to attain for even a few seconds.

Before leaving this subject it may be well to point out that, whereas the *calculation* of a Volta effect depends on data obtained by allowing oxygen atoms to approach the metal so as completely and actually to combine, the *experimental determination* by Kohlrausch's and similar methods depends on letting the atoms approach somewhat nearer to one metal and recede somewhat further from another; while the *compensation form* of the experiment employed by Pellat and others depends upon forcing back and restoring the atoms to their original or standard positions. Now if the views here just expressed have any sense or signification whatever in actual fact, it would be very natural to suppose that the numbers obtained in these three ways might be slightly different. But to specify the direction in which we should expect the differences, if any, to lie would require us to have made up our minds as to the probable variation of chemical attraction with distance. Assuming an inverse variation, the Pellat method should give the least, the Volta or Kohlrausch method the next, and the calculation method the greatest, value for the Volta effect.

But all these ideas complicate the matter somewhat, and they are quite possibly unnecessary. If it be considered that we have no data at present, it may be permitted to work on the simplest hypothesis, viz. that the step v is independent of how nearly chemical action has occurred—that it is the same for atoms straining at one another at their normal distance as for atoms on the verge of combination. And it may be argued in favour of this view that we really have some data, viz. these.

If it were not true, results obtained by Pellat's method could not be expected to agree exactly with those obtained by Kohlrausch's (of which Ayrton and Perry's or Clifton's may be taken as the best examples). Now results obtained by these different methods do agree very fairly well; exact agreement cannot be predicated, for the most trifling circumstances cause large variations in the Volta effect, but no decided disagreement is observable. Again, if it were not true, the Volta effect observed when two metals far apart in the series (*e.g.* zinc and platinum) were employed would be inconsistent with the results obtained by using metals nearer together, say zinc and tin, or tin and platinum; and if this were so, the metals could not be arranged in the linear series which eighty years ago Volta showed they could be. These arguments throw no light on what may happen *just* before actual combination, still they are encouraging as far as they go.

17. Let us therefore endeavour to suppress further qualms, and calculate a series of metal-air contact-forces from the heats of combustion; remembering that all we have to do, in order to convert heats of combustion per dyad gramme-equivalent into volts, is to divide by $\frac{19320 \times 10^9}{42 \times 10^6}$, that is by 46,000.

But the decision as to what numbers we shall take to represent heats of combustion is a matter of some difficulty, for not only do the numbers obtained by different observers for the same reaction differ, sometimes considerably, but it is not obvious when different oxides are formed which of them we are to consider as most applicable to the case of the Volta experiment. Perhaps one should take the most common or stable oxide; perhaps, seeing that no combination is supposed actually to occur, and since the metal is, so to speak, in excess, it is most reasonable to take the lowest oxide which the substance will form. It may be that the data are not known for this; it may even be that they have only been obtained for the hydrate instead of for the oxide.

I must therefore do the best I can, and quote several numbers wherever there is obvious doubt. I imagine that J. Thomsen's are the most reliable when they are available.

But it must be remembered all through, that since it is only the *tendency* to chemical action which is the cause of the Volta effect, whereas combination-heats are obtained by permitting or causing the combination to actually occur, the numbers obtained by calculation are not likely to be quite right; and they may be expected to err on the side of excess, the calculated number being higher than the actual value if directly observed.

Energy of Combination of Metals with Oxygen.

Metal.	Molecule.	Authority.	Heat of formation.	The same reduced to Volts.	Extreme values.	Mean or probable value.
Zinc	Zn,O	Thomsen	85430	1·85		
		Joule	77000	1·66		
		Andrews	84825	1·84		
		Favre and Silbermann }	83915	1·82		
Tin	Zn,O,H ₂ O	Thomsen	82600			
	Sn,O	Andrews.....	67100	1·46		
	Sn,O,H ₂ O	Thomsen	68090			
	$\frac{1}{2}$ (Sn,O ₂)	Andrews.....	67680			
	SnO,O	"	69584			
Lead	Pb,O	Thomsen	50300	1·15		
	"	F. and S.	55350	1·20		

Table (continued).

Metal.	Molecule.	Authority.	Heat of formation.	The same reduced to Volts.	Ex-treme values.	Mean or probable value.
Iron	Fe_2O	F. and S.	75656	1.64		
	Fe_2O_3	Thomsen	68280	1.48		
	$\frac{1}{3}(\text{Fe}_2\text{O}_3)$	"	63730			
Nickel.....	$\frac{1}{3}(\text{Fe}_2\text{O}_3)$	Andrews.....	66448	1.44		
	Ni_2O_3	Thomsen	60840	1.32		
Cobalt	Co_2O_3	"	63400	1.38		
	Cu_2O	"	37160	.81		
Copper	"	Andrews.....	38290	.83		
	"	F. and S.	43770	.95		
	Cu_2O	Thomsen	40810	.89		
Mercury.....	Cu_2O	Joule	37486	.81		
	Hg_2O	Thomsen	30660	.67		
Silver	Hg_2O	"	42200	.92		
	Ag_2O	"	5900	.13		
Hydrogen ...	"	F. and S.	12226	.27		
	H_2O { gas	Thomsen	68360	1.49		
	liquid	"	78000	1.70		
Potassium ...	"	Dulong, Hess, Grassi, Joule, Berthelot	79600	1.72		
	$2(\text{K}, \text{H}_2\text{O})$	Thomsen	208000			
	$2(\text{K}, \text{H}_2\text{O}, \text{aq.})$	"	232920			
Sodium	$\text{K}_2\text{O}, \text{aq.}$	"	164560	3.56		
	K_2O	Woods	136000	2.95		
	$2(\text{Na}, \text{H}_2\text{O})$	Thomsen	204060			
Calcium	$2(\text{Na}, \text{H}_2\text{O}, \text{aq.})$	"	223620			
	$\text{Na}_2\text{O}, \text{aq.}$	"	155260	3.36		
	Na_2O	Woods	151600*	3.28		
Barium	"	Hypothetical.....	130000	2.82		
	Ca_2O	Thomsen	131360	2.85		
	$\text{Ca}_2\text{O}, \text{H}_2\text{O}$	"	146400			
Strontium ...	$\text{Ca}_2\text{O}, \text{aq.}$	"	149400	3.24		
	Ba_2O	"	130380	2.84		
	$\text{Ba}_2\text{O}, \text{H}_2\text{O}$	"	148000			
Magnesium ..	$\text{Ba}_2\text{O}, \text{aq.}$	"	158260			
	Sr_2O	"	130980	2.84		
	$\text{Sr}_2\text{O}, \text{H}_2\text{O}$	"	148180			
Palladium ...	$\text{Sr}_2\text{O}, \text{aq.}$	"	157780	3.41		
	Mg_2O	"	145860	3.16		
	$\text{Mg}_2\text{O}, \text{H}_2\text{O}$	"	148960			
Cadmium ...	$\text{Pd}_2\text{O}, \text{H}_2\text{O}$	"	22710	.50		
Thallium ...	$\text{Cd}_2\text{O}, \text{H}_2\text{O}$	"	65680	1.43		
Manganese...	TL_2O	"	42240	.92		
Aluminium...	$\text{Mn}_2\text{O}, \text{H}_2\text{O}$	"	94770	2.05		
Lithium.....	$\frac{1}{3}(\text{Al}_2\text{O}_3, 3 \text{H}_2\text{O})$	"	129600	2.81		
Arsenic	$\text{Li}_2\text{O}, \text{aq.}$	"	166520	3.62		
Bismuth.....	$\frac{1}{3}(\text{As}_2\text{O}_3)$	"	51530	1.12		
	$\frac{1}{3}(\text{Bi}_2\text{O}_3)$	Woods	13200	.29		

* This number for sodic oxide agrees with Thomsen's value for the hydrated oxide, whereas for K, Ba, Sr, Ca the oxide is distinctly below the hydrate. By analogy, one would expect to have to subtract some 25,000 from the hydrated oxide $\text{Na}_2\text{O}, \text{aq.}$, and this gives the 130,000 which I put down as a hypothetical number for Na_2O .

Numbers obtained from unsatisfactory oxides and hydrates like those of aluminium, arsenic, and bismuth, are not likely to be useful for our present purpose. I know of no better data yet available however.

It is now easy to write down a Volta series obtained by pure calculation from heats of combustion. We can then see how far it agrees with the results of direct experiment. The principle on which I determine which of the preceding numbers to select is simply to choose Thomsen's when it refers to the simplest oxide, and in other cases to take what one can get. Metals about which there is obvious uncertainty, as for instance sodium, aluminium, bismuth, &c., are omitted.

Calculated Volta Series.

Lithium and Magnesium	3.0	Nickel		1.32
Potassium		Lead		1.15
Calcium, &c.		Thallium		.92
Zinc		Copper		.81
Iron		Mercury		.67
Tin		Palladium		.5
Cadmium		Silver		.13
Cobalt				

To compare this series with those obtained by experiment, we may as well take zinc as the metal of reference, and write down the Volta effect between it and the other metals, first as abstracted from the above table, and then as found by different observers. Strictly, one ought first to subtract Peltier forces from the observed numbers before comparing them with theory; but these forces are too small to make any appreciable difference.

Volta Effects in Air.

Comparison between Theory and Experiment.

Metal pair.	Calculated from heats of oxidation.	Observed by				
		Pellat.		Ayrton and Perry.		Clifton.
		Clean.	Scratched.	Using commer- cial zinc.	Using amal- gamated zinc.	
Zinc:—						
Tin	.39	.25	.35	.28	.46	
Lead	.70 or .65	.15	.31	.20	.35	
Iron	.21 or .4	.56	.70	.60	.74	.75
Nickel	.53	.47	.63	...	...	
Copper	1.04 or .9	.71	.86	.75	.89	.85
Mercury ...	1.18	...	...	1.06	1.20	1.07
Silver	1.71 or 1.58	.91	1.12	...	...	
Platinum ...		...	...	.98	1.13	

The alternative calculated number sometimes given is merely to show the kind of variation probable in those cases from uncertainty of data. In each case of agreement the calculated number is a little higher than the observed, as was to be expected. No reason occurs to me for the breakdown and apparent interchange, in the case of lead and iron, but such vague guesses as may occur to every one.

Measurements of the E.M.F. between clean metals plunged into distilled water or weak acid, have been made by Clifton and by Beetz*. I suppose one is justified in calling them:—

Volta Effects in Water.

Metal pair.	Calculated from heats of oxidation.	Observed by	
		Beetz.	Clifton.
Zinc:—			
Copper	1.0	.98	82 to 92 1.3 (Smee).
Silver.....	1.7	1.23	
Platinum	1.8 or less.	1.52	
Sodium amalgam:—			
Zinc	1.0	.78	
Copper	2.0	1.79	
Silver.....	2.6	2.05	
Platinum	2.8	2.31	

I do not wish to blink the fact that some of the numbers in the former of the above tables afford a rather poor support to my theory; but it must be remembered, on the other hand, that they are not relative numbers only that we have calculated, but absolute; and the fact that the heats of combustion reduced to volts are numbers of the same order of magnitude as the Volta effects, is of itself a strong confirmation of the belief that chemical strain at the air-contacts is the real cause of the apparent contact-force at the junction of two metals.

The agreement of the numbers, though not exact, seems to me too close to be the result of accident. One may, I think, claim that the hypothesis whence the calculated numbers are obtained is justified by the figures as far as they go. It is not put forward as a completed theory, but only as a first step to such a theory. I believe it to be a step in the direction of the truth, but it requires working out and elaborating by a scientific chemist.

18. Not many measurements of metal pairs have been made, even in air; for mere permutations such as copper-tin, tin-silver, &c. follow at once from the numbers given above by Volta's series-law; but in gases other than air one has at

* *Ann. der Physik*, x. p. 348 (1880).

present no experimental guidance beyond the barest qualitative one given by Mr. Brown, that copper-nickel reverses its sign when changed from air to hydrochloric acid, and that copper-iron is reversed in sulphuretted hydrogen. But satisfactory observation in these gases is difficult, because they not only *tend* to attack the plates, but they *do* attack them; and so a film is formed and everything is rendered uncertain.

Another complication results from the fact that, when metals are taken out of air and put into a foreign gas, they are already coated with a film of oxygen, and it is not clear in what way this will affect the action of the new gas. It may have to be replaced almost by substitution; the affinity to be considered in chlorine, for instance, being something like $M, Cl_2 - M, O$. In a compound like HCl , the hydrogen also may have to be provided for, the resulting chemical strain being, for instance, $M, Cl_2 - M, Cl + H_2, O - 2(H, Cl)$; but the consideration of the hydrogen affinities will not affect *differences*, and therefore will leave comparisons with experiment unaffected. Taking the metals as clean, however, and without air-films, we must suppose the following series to be right.

Energies of Combination of Metals with Chlorine; and
Calculated Volta Series in that Gas.

Metal.	Molecule.	Authority.	Heat of Combination.	Calculated Volta series, in Volts.
Zinc	Zn, Cl_2	Thomsen.	97210	2.1
	"	F. and S.	100592	
	"	Andrews.	101316	
Lead	Pb, Cl_2	Thomsen.	82770	1.8
	"	F. and S.	89450	
Iron	Fe, Cl_2	Thomsen.	82050	1.78
	"	F. and S.	99302	
Nickel		No data.		
Copper	Cu, Cl_2	Thomsen.	51630	1.12
	"	F. and S.	59048	
	"	Andrews.	60988	
Mercury	Hg, Cl_2	Thomsen.	63160	1.38
Silver	$2(Ag, Cl)$	"	58760	1.28
	"	F. and S.	69600	
	"	Thomsen.	44000	
Hydrogen ...	$2(H, Cl)$	"	78640	.96
	$2(H, Cl, aq.)$	"	78640	
	$2(H, Cl)$	F. and S.	47566	
	$2(H, Cl)$	Alvia.	48174	
Potassium ...	$2(K, Cl)$	Thomsen.	211220	4.62
	"	F. and S.	201920	
	"	Andrews.	208952	
Sodium	$2(Na, Cl)$	Thomsen.	195380	4.24

This series will hold, as far as *differences* are concerned, for hydrochloric acid also; because, whatever effect the hydrogen

affinity may have in changing the numbers, it will have the same effect on all.

It is easy to write down the hypothetical series in bromine and iodine in the same way:—

Calculated Volta Series in Bromine and Iodine.

Metal.	In Bromine.	In Iodine.
Potassium	3·85	3·50
Zinc... ..	1·74	...
Lead	1·40	·87
Silver.....	1·10	·60
Copper	·89	·23
Hydrogen	·40	—·13

All this supposes the metals to be perfectly clean, and not covered with a film of foreign gas like oxygen. On the hypothesis that the metal has been taken recently out of air, and that the film of oxygen with which it is covered has to be torn from the metal, though it was not actually combined with it, the Volta series in chlorine or hydrochloric acid would be quite different, and more like this.

Hypothetical Volta Series of Air-coated Metals in Chlorine or HCl.

Silver	1·8
Lead	1·2
Iron	1·1
Copper	·9
Zinc	·85

Unfortunately I can get no data for the heat of chlorination of nickel; but assuming it not very different from iron, the above series gives copper and nickel in the right order, as observed by Mr. Brown, whereas the other one did not. I have no experiments with which to compare the numbers.

Calculated Volta Series of Clean Metals in Sulphur or Sulphuretted Hydrogen.

Metal.	Heat of Sulphurization per gramme equivalent.	Volts.
Potassium	91276	1·95
Zinc	41880	·87
Iron	35506	·76
Lead	19112	·41
Copper	18266	·39
Silver.....	11048	·34
Hydrogen	5482	·12

But it will be observed that this is nothing like the order to be expected in sulphuretted hydrogen ; for it is popularly known that copper is more easily sulphurized in this gas than iron. Now assuming that the metal had been covered with an air-film, and that the oxygen of this has to be replaced by sulphur, the chemical tendency, instead of being M, S , is something more like $M, S-M, O$, or possibly $M, S-M, O + H_2, O-H_2, S$; and either of these will give a quite different order. Data are given on p. 624 of Naumann's *Gmelin-Kraut*, vol. i., for the neutralization-heats of various bases by H_2S , such as $CuO + H_2S$, &c. These are something like what we want, and from them we reckon the following :—

Hypothetical Volta Series, in Sulphur or Sulphuretted Hydrogen, of Metallic Oxides, and possibly of Air-coated Metals.

Metal.	Heat of reaction, $MO + H_2S = MS + H_2O$.	Volts.
Silver.....	55800	1.20
Mercury	41700	1.04
Copper	31600	.68
Lead	26600	.57
Zinc	19200	.41
Iron	14600	.31
Sodium	7700	.16

The series so obtained gives copper and iron in their proper order ; but it is scarcely likely to be really correct, because it assumes that the *oxides* of the metals are exposed to the gas rather than the metals themselves. It is quite possible that it is not very incorrect for tarnished metals, *i. e.* metals coated with a film of oxide ; but for ordinarily clean metals, coated, not with a film of oxide, but with a film of oxygen, it is nothing but a rough approximation, given because we have no better data.

It is to be noted that, as the film of oxygen diffuses away, the Volta-effect depending on it must diminish ; until at length the active affinity causing the chemical strain is nothing more than M, S or perhaps $M, S-H_2, S$. A gradual falling off and ultimate even reversal of sign was observed by Mr. Brown in both HCl and H_2S . In so far as actual chemical action occurs and a film of chloride or sulphide forms, so far of course also will the effect diminish ; because it depends essentially on the unsatisfied chemical strain, not on the accomplished chemical action.

Additional Note, March 13th, 1885.

On page 176 of the March Number of the Philosophical Magazine I quote from Von Zahn and others an extraordinary statement, ascribed to Professor Exner, that a thermopile ceases to work in a vacuum; saying at the same time that I had been unable to find the statement myself in Exner's writings. For a sufficient reason as it now turns out, because it is not there.

Turning over some back volumes of 'Nature' recently, I accidentally came across a letter from Prof. Exner in vol. xxiii. p. 170, December 1880, denying that he had ever said such a thing, and maintaining that his memoirs were quite clear on the subject of the relation, or rather want of relation, between voltaic and thermoelectric phenomena. This is perfectly true; Prof. Exner has expressed himself on this subject with decision, and finds fault with Prof. Edlund for ever confusing the two distinct things together.

In the same volume of 'Nature,' on page 312, appears a note from Professor Young acknowledging that he ought to have been more careful to refer to the original statement, and giving one of the "Physical Notes" of 'Nature,' p. 156, vol. xxii., as his authority. This "Physical Note" quotes from *l'Electricité*; and so the error, however originally manufactured, gets handed on from one paper to another.

One of the memoirs which I have unfortunately overlooked in my historical sketch of the experimental work done in connection with the subject has come to hand this morning, through the kindness of the authors, MM. E. Bichat and R. Blondlot, of Nancy. It was published in the *Comptes Rendus* (1883), t. xc. pp. 1202 et 1293, and in the *Journal de Physique*, 2^e série, ii. p. 533, and is an attempt to measure the Volta-effect for two liquids. The method employed involves the use of three vessels, A, B, C, of which A and C contain one liquid and B the other. A and B are then connected by a liquid siphon with porous diaphragm [the capillary E.M.F. possibly excited by this diaphragm is bad]; and the potential of the air between B and C is then rendered uniform [or, commonly speaking, the potentials of B and C are equalized] by making one of the liquids drip inside a cavity kept moist with the other. A and C are connected by platinum electrodes through a compensation resistance-box and battery to a quadrant-electrometer, and the difference of potential between them measured. The arrangement is highly ingenious, but the difficulties of definite and certain measurement must be considerable.

The same physicists have quite recently made a determination, not of the Volta-effect, but of the true contact-force between two liquids, by the use of mercury electrodes; employing for this purpose a theorem of Helmholtz, that if by judicious polarization the capillary constant of a mercury-liquid surface be made a maximum, then between the mercury and the liquid there is no difference of potential*.

Their account of this last determination has not yet been published, but it will appear shortly (before this is printed probably) in the *Comptes Rendus*.

The theorem gives evidently an admirably simple method of measuring liquid / liquid contact-force, if it can be made to work practically.

MM. Bichat and Blondlot apparently hope, by a comparison of the two methods, the results of which are quite different (in accordance with the views expressed in the present communication), to be able to obtain values for air / liquid contacts. This would be a most important and useful piece of work: the only difficulty in accomplishing it is the difficulty of getting both sets of measurements thoroughly dependable. I hope they may succeed in overcoming all obstacles.

[To be continued.]

XXXI. *The Uses of a Line-Divider.*

By Miss SARAH MARKS†.

THE ordinary method of dividing a given straight line AB into any number of equal parts (fig. 1), without using a special instrument, is to draw a line AC at any angle to it, to cut off from AC the given number of equal parts AD', D'E', &c., to join M, the last of the points so taken, to B, and from D', E', &c. to draw lines parallel to MB, meeting AB in D, E, &c. These points D, E, &c. divide AB into the required number of equal parts. This is exactly the method adopted in using the line-divider.

It consists of a hinged rule with a firm joint, having the left-hand limb fitted to slide in an undercut groove upon the plain rule. Both limbs are bevelled on their inner edges, and the left one is divided both on the bevel and on the top into eighths, quarters, half-inches, and inches, which are consecutively numbered, beginning at the hinged end, so that any

* *Monatsberichte der Berliner Akad.* November 3, 1881.

† Communicated by the Physical Society. Read February 14, 1885.