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V. Contact electricity of metals

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TABLE II.

Comparison of the Temperatures of the Melting-points of Metals afforded by recent research.

Authority.	Heycock & Neville.	Holborn & Wien.	Holman, Lawrence, & Barr.	D. Berthelot.	The Author.
Date of publication.	1895.	1895.	1896.	1898.	1898.
Instrument	Resistance Pyrometer.	Thermo-couple.	Thermo-couple.	Interference Method	Thermo-couple no. 11.
Calibration data.	0° 100° 444°·53	Porcelain air-thermometer.	0° 444°·53 100° 1072° 218°·2	Expansion of air.	0° 100° 444°·53
Tin	231°·9	......	......	......	232°·1
Bismuth......	......	......	......	......	268·4
Lead	......	......	......	......	325·9
Zinc	418·96	......	......	......	418·2
Aluminium .	654·5	......	660°	......	649·2
Silver.........	960·7	968°	970	962°	961·5
Gold	1061·7	1072	(1072)	1064	1062·7
Copper	1080·5	1082	1095	......	1083·0

V. *Contact Electricity of Metals.* *By* Lord KELVIN, G.C.V.O., D.C.L., LL.D., F.R.S., M.R.I.*

§ 1. WITHOUT preface two 95 years' old experiments of Volta's were, one of them shown, and the other described. The apparatus used consists of: (*a*) a Volta-condenser of two varnished brass plates, of which the lowe plate is insulated in connexion with the gold leaves of a gold-leaf electroscope, and the upper plate is connected by a flexible wire with the sole plate of the instrument; (*b*) two circular discs, one of copper and the other of zinc, each polished and unvarnished. I hold one in my right hand by a varnished glass stem attached to it, while on my left hand I hold the

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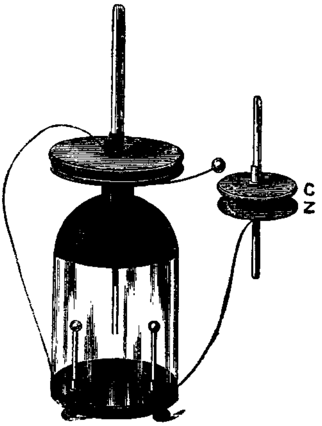
* Communicated by the Author, having been read at the meeting of the Royal Institution on May 21st, 1897.

other, which is kept metallically connected with the sole plate of the electroscope by a thin flexible wire.

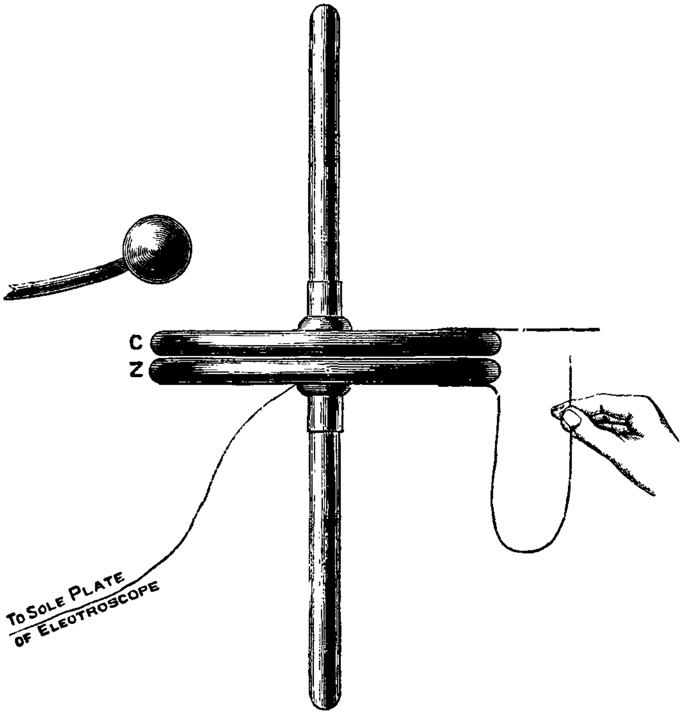
Fig. 1.



To commence the experiment I place one disc resting on the other, and lift the two till the upper touches a brass knob connected by a stiff metal wire with the lower plate of the Volta condenser. I break this contact and then lift the upper plate of the condenser; you see no divergence of the gold leaves. This proves that no disturbing electric influence sufficient to show any perceptible effect on our gold-leaf electroscope is present. Now I repeat what I did, with only this change—I hold the lower disc with the upper disc resting on it two or three centimetres below the knob. I then with my right hand lift the upper plate of the Volta-condenser; you see a very slight divergence between the shadows of the gold leaves on the screen. I can just see it by looking direct at the leaves from a distance of about half a metre. Still holding the lower plate firmly in my left hand in the same position, and holding the upper plate by the top of its glass stem in my right, at first resting on the lower plate I lift it and let it down very rapidly a hundred times, so as to produce one hundred cycles of operation—break contact between discs, make and break contact between upper disc and knob, make contact between discs. Lastly, I lift the upper plate of the condenser; you see now a great divergence of the gold leaves, many of you can see it direct on the leaves, while all of you can see it by their shadows on the screen. Now, keeping the upper plate of the condenser still unmoved, I bring a stick of rubbed sealing-wax into the neighbourhood of the electroscope; you see the divergence of the leaves is increased. I remove the sealing-wax and the divergence diminishes to what it was before. This proves that the gold leaves diverge in virtue of resinous electricity upon them, and therefore that the insulated plate of the condenser received resinous electricity from the copper disc. If now I interchange the two discs so that the upper is zinc and the lower copper, and repeat the experiment, you see that the rubbed sealing-wax diminishes the divergence as it is brought from a distance into the neighbourhood, and that a glass rod rubbed with silk increases the divergence. Hence we conclude that in the separation of two discs of copper and zinc the copper carries away resinous electricity and the zinc vitreous electricity.

§ 2. *Experiment* 2.—The same apparatus as in Experiment 1, except that the polished zinc and copper discs have their opposed faces varnished with shellac, and are provided with wires soldered to them for making metallic connexion between them when the upper rests on the lower, as shown in Fig. 2. All operations are the same as in Experiment 1, but now with this addition—when the upper disc rests on the lower, make and break metallic contact by hand as shown in the diagram. The results are the same as those of Experiment 1, except that the quantity of electrification given to the gold leaves by a single cycle of operations is generally greater than in Experiment 1, for this reason: In Experiment 1 at the instant of breaking contact between the zinc

Fig. 2.



and copper there is generally some degree of inclination between the two discs, while at the corresponding instant of Experiment 2 they are parallel and only separated by the insulating coats of varnish. If great care is taken to keep the discs as nearly as possible parallel at the instant of separation, the effect of a single separation may be made greater in Experiment 1 than in Experiment 2 (see § 3 below).

§ 3. An instructive variation of Experiment 1 may be made by giving a large inclination, 5°, or 10°, or 20°, of the upper plate to the lower, while still in contact and at the instant of separation. By operating thus the experiment may be made to fail so nearly completely that no divergence of the leaves will be observed even after one hundred cycles.

§ 4. These two experiments, with the variation described in § 3, put it beyond all doubt that Volta's electromotive force of contact between two dissimilar metals is a true discovery. It seems to have been made by him about the year 1801; at all events he exhibited his experiments proving it in that year to a Commission of the French Institute (Academy of Sciences). It is quite marvellous that the fundamental experiment (§ 1 above), simple, easy, and sure as it is*, is not generally shown in courses of lectures on electricity to students, and has not been even mentioned or referred to in any English text-book later than 1845, or at all events not in any one of a large number in which I have looked for it, except in the 'Elementary Treatise on Electricity and Magnetism,' founded on Joubert's '*Traité Élementaire d'Électricité*,' by Foster and Atkinson, 1896 (p. 136). The only other places in which I have seen it described in the English language are Roget's article in the '*Encyclopædia Metropolitana*' referred to above; Tait's 'Recent Advances in Physical Science,' 1876; and Professor Oliver Lodge's most valuable, interesting, and useful account of all that had been done for knowledge of contact electricity from its discovery by Volta till 1884, in his Report to the British Association of that year, 'On the Seat of the Electromotive Forces in the Voltaic Cell.'

§ 5. The reason for this unmerited neglect of a great discovery regarding properties of matter is that it was overshadowed by an earlier and greater discovery of its author, by which he was led to the invention of the voltaic pile and crown of cups, or voltaic battery, or, as it is sometimes called, the

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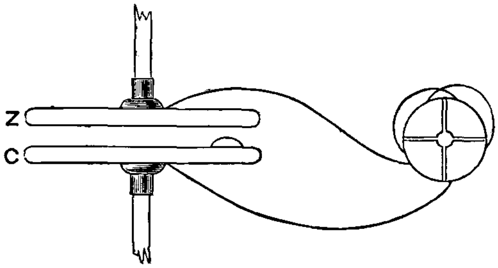
* Fully and clearly described in Roget's article on "Galvanism," in the '*Encyclopædia Metropolitana*,' vol. iv. edition 1845, p. 210.

galvanic battery. Knowing, as we now know, both Volta's discoveries, we may describe the earlier most shortly by saying that the simple experiment (§ 1 above), demonstrating the later discovery, is liable to fail if a drop of water is placed on the lower of the two polished plates. It fails if (see fig. 4 below) the last connexion between the zinc and copper, when the upper disc is lifted, is by water. It would not fail (see fig. 6 below) nor be sensibly altered from what is found with the dry polished metals, if the upper disc were slightly tilted in the lifting, so as to break the water arc before the separation between the metals, and secure that the last connexion is contact of dry metals. To show this to you more readily than by a Volta condenser with gold-leaf electroscope, I shall now use instead my quadrant electrometer without condenser.

(1) Holding the copper disc connected with the metal case of the electrometer in one hand, with my other hand I hold by a glass handle the zinc disc, which you see is connected by a fine wire with the insulated quadrants of the electrometer. I first place the zinc resting on the copper, both being polished and dry. You now see the spot of light at the point marked O on the scale, which I call the metallic zero. I now lift the zinc disc two or three millimetres from resting on the copper, and you see the spot of light travelling largely to the right, which proves that vitreous electricity has passed from the zinc disc through the connecting wire to the insulated quadrants of the electrometer. I lower the zinc disc down to rest again on the copper disc ; you see the spot of light again comes back to the metallic zero.

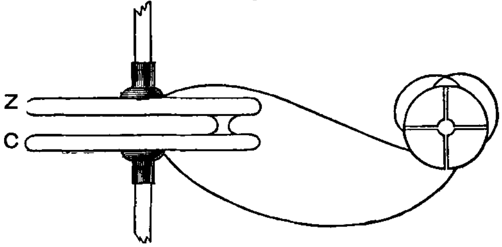
(2) I now raise the zinc disc, and with a little piece of wet wood (or a quill pen) place a little mound of water on the copper disc, as shown in fig. 3. I bring down the zinc disc to touch the top of the little mound of water, keeping it parallel to the copper disc so that there is no metallic contact

Fig. 3.



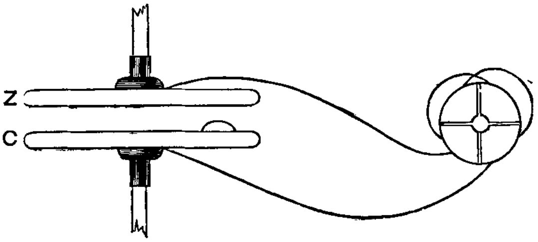
between them (fig. 4); you see that the spot of light moves to the left and settles at a point marked E (which I call the electrolytic zero of our circumstances), a few scale-divisions to the left of the metallic zero. This motion and settlement is the simplest modern exhibition of Volta's greatest discovery.

Fig. 4.



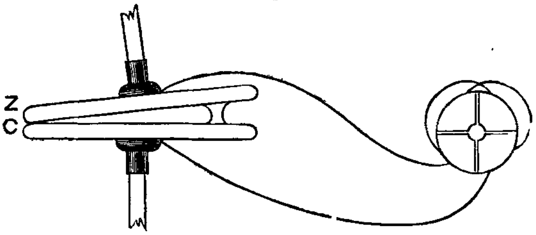
(3) Now that the spot of light has settled, I lift the zinc disc a millimetre till the water-column is broken, and then two or three centimetres farther (fig. 5); the spot of light does not move, it remains at E. I lower the zinc disc again: still no motion of the spot of light, not even when the zinc again touches the little mound of water.

Fig. 5.



(4) Now I tilt the zinc disc slightly till it makes a dry metallic contact with the copper, as shown in fig. 6; while

Fig. 6.



the water arc still remains unbroken. You see the spot of light, at the instant of metallic contact, suddenly leaves E and moves to the right, and settles quickly at the metallic zero after a few vibrations through diminishing range.

(5) Lastly, I break the metallic contact, and hold the zinc disc again parallel to the copper (fig. 4) with the water connexion still remaining unbroken between them ; the spot of light shows no sudden motion ; it creeps to the left till, in half a minute or three-quarters of a minute, it reaches its previous steady position on the left. This is the now well-known phenomenon (never known to Volta) of the recovery of a voltaic cell from electrolytic polarisation after a metallic short-circuit.

§ 6. The succession of experiments described in § 5, interpreted according to elementary electrostatic law, proves the following conclusions :—

(1) When the dry and polished discs of zinc and copper are metallically connected and held parallel, their opposed faces are oppositely electrified, the zinc with vitreous electricity, and the copper with resinous electricity, in quantities varying inversely as the distance between them when this is small in comparison with the diameter of each.

(2) The opposed polished faces are non-electrified when polished portions of the zinc and copper surfaces are connected by water, and when there is no metallic connexion between them. Or, if not absolutely free from electrification, they may be found slightly electrified, zinc resinously or vitreously, and copper vitreously or resinously, according to differences in respect to cleanness, polish, or scratching or burnishing, as explained in § 16 below ; and according to polarisational or other difference in the wetted portions of the surfaces.

If instead of pure water we take a weak solution of common salt, or carbonate of soda, or sulphate of zinc or ammonia, we find results but little affected by the differences of the liquids.

§ 7. But if the polished surface of either the copper or the zinc is oxidized, or tarnished in any way, notably different results are found when the experiments of § 5 are repeated with the disc or discs thus altered.

For example, hold the copper disc, with its polished side up, over a slab of hot iron, or a spirit-lamp, or a bunsen-burner, till you see a perceptible change of colour, due to oxidation of the previously polished face. Then allow the copper to cool, and repolish a small area near one edge ; place a little mound of water upon this area, and operate as in § 5 (2), (3). The water connexion between polished zinc and polished copper brings the spot of light to the same electrolytic zero E as before. But now, when we lift the zinc disc and break the water connexion, the spot of light moves to the right, instead of remaining steady as it does when both the dry opposed surfaces are polished. If next we tarnish the zinc disc by heat, as we did for the copper disc, and repeat the experiment with wholly polished copper, and with the zinc disc oxidized where dry, and polished only where wet by the water connexion, we find still the same electrolytic zero E ; but now the spot of light moves to the left when we lift the zinc disc and break the water connexion.

§ 8. The experiments of § 7, interpreted in connexion with those of § 5, prove that there are dry contact voltaic actions between metallic copper and oxide of copper in contact with it, and between metallic zinc and oxide of zinc in contact with it; according to which, dry oxide of copper is resinous to copper in contact with it, and dry oxide of zinc is resinous to zinc in contact with it, just as copper is resinous to zinc in contact with it. We may verify this conclusion by another interesting experiment. Taking, for instance, the oxidized copper plate, with a little area polished for contacts, put a little mound of copper, instead of the mound of water, on this area for contact with the upper plate; and for the upper plate take polished copper instead of polished zinc. If we operate now as in § 7, the spot of light settles at the metallic zero O when the metallic contact is made, instead of at the electrolytic zero E, as it did when we had water connexion between zinc and copper. But now, just as in § 7, the spot of light moves to the right when the contact is broken and the upper plate lifted, which proves that vitreous electricity flows into the electrometer from the upper plate, when its distance from the lower plate is increased after breaking the metallic contact. We conclude that when the two plates were parallel, and very near one another, and when there was metallic connexion between them, vitreous and resinous electricities were induced upon the opposed surfaces of metallic copper and oxidized copper respectively. This statement, which we know from § 7 to be also true for zinc compared with oxidized zinc, is probably also true for every oxidizable metal compared with any one of its possible oxides. It is true, as we shall see later (appended paper of 1880–81; also Erskine-Murray's paper referred to in § 15), even for platinum in its ordinary condition in our atmosphere of 21 per cent. oxygen and 79 per cent. nitrogen, voltaically tested in comparison with platinum which has been recently kept for several minutes or several hours in an atmosphere of pure oxygen, or even in an atmosphere of 95 per cent. oxygen and 5 per cent. nitrogen.

§ 9. Hitherto we have had no means of measuring the amount of the Volta-contact electric force between dry metals, except observation of the degrees of deflexion of the gold leaves of an electroscope, or of the spot of light of the quadrant electrometer, consequent upon operations performed upon different pairs of metals, with dimensions and distances of motion exactly the same, and comparison of these deflexions with the steady deflexion from the metallic zero given by polished zinc and copper connected conductively with one another by water, and connected metallically with the two electrodes of an electroscope or electrometer. Kohlrausch, in 1851*, devised an apparatus for carrying out this kind of investigation systematically, and with a good approach to accuracy, by aid of a Dellman's electrometer and a Daniell's cell, as more definite and constant than a zinc-water-copper cell. This method of Kohlrausch's for measuring the Volta electromotive forces between dry metals "has been employed with modifications by Hankel, by Gerland, by Clifton, by Ayrton and Perry, by von Zahn, and by most other experimenters on the subject"†. About thirty-seven years ago, in repetitions of Volta's fundamental experiment proving contact electricity by electroscopic phenomena resulting from change of distance between parallel plates of zinc and copper, I found a null method for measuring electromotive forces due to metallic contact between dissimilar metals, in terms of the electromotive force of a Daniell's cell, which is represented diagrammatically in fig. 7, and in perspective in fig. 8. The two disks are protected against disturbing influences by a metal sheath. The lower disk is permanently insulated in a fixed position, and is kept connected with the insulated pair of quadrants of a quadrant electrometer. The upper disk is supported by a metal stem passing through a collar in the top of the sheath, so that it is kept always parallel to the lower disk and metallically connected to the sheath, while it can be lifted a few centimetres at pleasure from an adjustable lowest position in which its lower face is about half a millimetre or a millimetre above the upper face of the lower disk. A portion of the wire connecting the lower plate to the insulated quadrants of the electrometer is of polished platinum, and contact between this and a platinum-tipped wire connected to the slider of a potential divider is made and broken at pleasure. For certainty of obtaining good results it is necessary that these

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* Poggendorff's *Annalen*, vols. lxxv. p. 88; lxxxii. pp. 1 and 45; and lxxxviii. p. 465, 1851 and 1853.

† Prof. O. J. Lodge, "On the Seat of the Electromotive Forces in the Voltaic Cell," Brit. Assoc. Report, 1884, pp. 464–529.

contacts should be between clean and dry polished metals, because if the last connexion on breaking contact is through semi-moist dust, or oxide, or "dirt" (defined by Lord Palmerston to be matter in a wrong place), or if it is anything other than metallic, vitiating disturbance is produced.

§ 10. To make an experiment, first test the insulation with the upper plate held up in its highest position, and after that with it let down to its lowest position, in each case proceeding thus: Holding by hand the wire connected to the slider, run the slider to zero, make contact at P, observe on the screen the position of the spot of light from the electrometer mirror for the metallic zero, and then run the slider slowly to the top of its scale and break contact; the spot of light should remain steady, or at all events should not lose more than a very small percentage of its distance from metallic zero, in half a minute. Repeat the test with the cell reversed. If the test is satisfactory with the upper plate high, the insulation of the insulated quadrants in the electrometer and of the lower disk in the Volta-condenser is proved good. If after that the test is not satisfactory with the upper disk at its lowest, we infer that there are vitiating shreds between the two plates, and we must do what we can to remove them ; or, if necessary, we must alter the screw-stop at the top so as to increase the

Fig. 7.

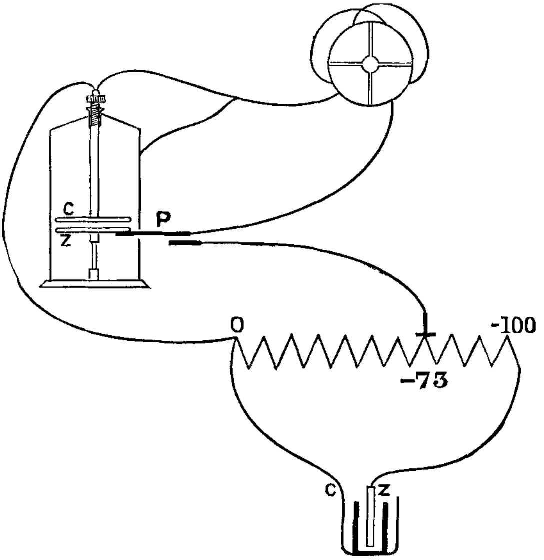
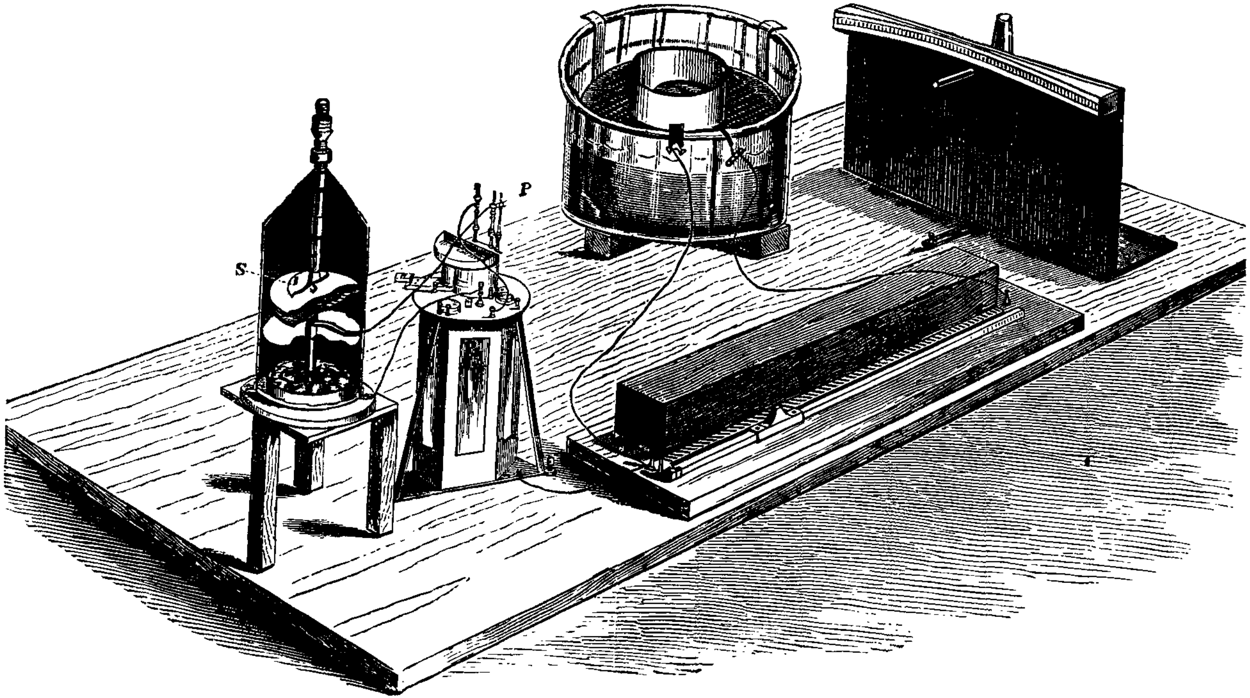


Fig. 8.



shortest distance between the plates sufficiently to prevent bridges of shred or dust between them, and so to give good insulation. The smaller we make the shortest distance with perfect enough insulation, the more sensitive is the apparatus for the measurement of contact electricity performed as follows :—

§ 11. Run the slider to zero; make and keep made the contact at P till the spot of light settles at the metallic zero; break contact at P, and lift the upper plate slightly. (If you lift it too far, the spot of light may fly out of range.) If the spot of light moves in the direction showing positive electricity on the insulated quadrants (as it does if the lower plate is zinc and the upper copper), connect the cell to make the slider negative (as shown in fig. 7). Repeat the experiment with the slider at different points on the scale, until you find that, with contact P broken, lifting the upper plate causes no motion of the spot of light. If the compensating action with the slider at the top of the range is insufficient, add a second cell; if it is still insufficient, add a third cell; if still insufficient, add a fourth[*].

§ 12. By this method I made an extended series of experiments in the years 1859–61, as stated in a short paper communicated to Section A of the British Association at its Swansea meeting in August 1880, which with additions published in 'Nature' for April 14, 1881, is appended to the present article.

§ 13. Quite independently[†], M. H. Pellat found the same method, and made admirable use of it in a series of experiments described in theses presented to the Faculty of Sciences in Paris in 1881[‡], of which the results, accurate to

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[*] The only case hitherto tested by any experimenter, so far as known to me, in which more than two Daniell cells would be required for the compensation, is briges metallic sodium, guarded against oxide by glass, in Mr. Erskine-Murray's experiments (§ 18 below), showing volta-difference of 3·56 volts from his standard gold plate. For direct test this would require four Daniell cells on the potential divider. The greatest volta-difference of potentials observed by Pellat was 1·08 volts, for which a Daniell's cell would rather more than suffice. About 1862 I found considerably more than the electromotive force of a single Daniell's element required to compensate the Volta electromotive force between polished zinc and copper oxidized by heat to a dark purple or slate colour.

[†] *Ann de Chimie et de Physique*, vol. xxiv. (1881) p. 20, footnote.

[‡] *Thèses présentées à la Faculté des Sciences de Paris, pour obtenir le Grade de Docteur-ès-Sciences Physiques*, par M. H. Pellat, Professeur de Physique au Lycée Louis le Grand, No. 461, juin 22, 1881. See also *Journal de Physique* (1881), xvi. p. 68, and May 1880, "Différence de potentiel des couches électriques qui recouvrent deux métaux en contact."

a degree of minuteness unknown in previously published researches on the electrical effects of dry contacts between metals, constitute in many respects the most important and most interesting extension of our knowledge of contact electricity since the times of Volta and Pfaff. One of his results (I shall have to speak of others later) was that Pfaff was right in 1829 * when he described experiments in which he found no difference in the Volta-contact-electromotive force between zinc and copper, whether tested in dry or damp air, oxygen, nitrogen, hydrogen, carburetted hydrogen, or carbonic acid, so long as no visible chemical action occurred; and that De la Rive was not right when he "asserted that there was no Volta effect in the slightly rarefied air then known as vacuum"†. Pfaff experimented with varnished plates; Pellat arrived at the same conclusion with polished unvarnished plates of zinc and copper. He found slight variations of the Volta electromotive force due to the nature of the gas surrounding the plates, and to differences of its pressure, of which he says: "Ces variations sont très faibles, par rapport à la différence de potentiel totale.... Ces variations dans la différence de potentiel sont toujours en retard sur les changements de pression. Elles ne paraissent donc pas dépendre directement de celle-ci, mais bien des modifications qui en résultent dans la nature de la surface métallique, modifications qui mettent un certain temps à se produire." The smallest pressures for which Pellat made his experiments were from 3 to 4 or 5 centim. of mercury.

§ 14. The same method was used by Mr. J. T. Bottomley in an investigation by which he demonstrated with minute accuracy the equality of the Volta-contact-difference measured in a glass tube exhausted to less than $\frac{1}{523}$ millim. of mercury ‡ ($2\frac{1}{2}$ millionths of an atmosphere), and immediately after in the same tube filled with air to ordinary atmospheric pressure; and again exhausted and filled with hydrogen to atmospheric pressure three times in succession; and again exhausted and filled to atmospheric pressure with oxygen. In some cases the electrical test was repeated several times, while the gas was entering slowly. The actual apparatus which he used is before you, and in it I think you will see with interest the little Volta-condenser, with plates of zinc and copper a little larger than a shilling, the upper hung on

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* *Ann. de Chim.* 2nd series, vol xli. p. 236.

† Lodge, Brit. Assoc. Report, 1884, pp. 477–8.

‡ A very high exhaustion had been maintained for two days, and finally perfected by two and a half hours' working at the pump immediately before the electric testing experiment.

a spiral wire by a long hook carrying also a small globe of soft iron. Thus you see by aid of an external magnet I can lift and lower the upper plate without moving the vacuum tube, which, during the experiments, was kept in connexion with a Sprengel pump and phosphoric acid drying-tubes. Mr. Bottomley sums up thus :—" The result of my investigation, so far as it has gone, is that the Volta contact effect, so long as the plates are clean, is exactly the same in common air, in a high vacuum, in hydrogen at small and full pressure, and in oxygen. My apparatus, and the method of working during these experiments, was so sensitive that I should certainly have detected a variation of 1 per cent. in the value of the Volta contact effect, if such a variation had presented itself"*.

§ 15. With the same method further researches have been carried on by Mr. Erskine Murray, and important and interesting results obtained, within the last four years, in the Physical Laboratories of the Universities of Glasgow and Cambridge. He promises a paper for early communication to the Royal Society, and, from a partial copy of it which he has already given me, I am able to tell you of some of his results. Taking generally as standard a gilt brass disc which he found among the apparatus remaining from my experiments of 1859–61, he measured Volta-differences from it in terms of the modern standard *one volt*. These differences are what we may call the Volta-potentials of the different metallic surfaces, or surfaces of metallic oxides, iodides, &c., or metallic surfaces altered by cohesion to them of gases or vapours, or residues of liquids which had been used for washing them; if for simplicity we agree to call the Volta-potential of the gold, zero. As a rule he began each experiment by polishing the metal plate to be tested on clean glass-paper or emery-cloth, and then measured its difference of potential from the standard gold plate. After that the plate was subjected to some particular treatment, such as filing or burnishing ; or polishing on leather or paper ; or washing with water, or alcohol, or turpentine, and leaving it wet or drying it ; or heating it in air, or exposing it to steam or oxygen, or fumes of iodine or sulphuretted hydrogen ; or simply leaving it for some time under the influence of the atmosphere. The plate as altered by any of these processes was then measured for potential against the standard gold. Very interesting and instructive results were found ; only of one can I speak at present. Burnishing by rubbing it firmly with a rounded steel tool, or by rubbing two plates of the

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* Brit. Assoc. Report, 1885, pp 901–3.

same metal together, increased the potential in every case; that is to say made the metallic surface more positive if it was positive to begin with; or made it less negative or changed it from negative to positive, if it was negative to begin with. Thus:—

Zinc immediately after being scratched sharply by polishing on clean glass-paper was found	+ ·70 volt.
After being burnished with hard steel burnisher it was found	+ ·94 volt.
After being left to itself for 2 hours it was found	+ ·92 volt.
After further burnishing	+ 1·00 volt.
After still further burnishing	+ 1·02 volt.
It was then scratched by polishing on glass-paper, and its surface potential returned to its original value of . .	+ ·70 volt.

§ 16. This seems to me a most important result. It cannot be due to the removal of oxygen, or oxide, or of any other substance from the zinc. It demonstrates that change of arrangement of the molecules at the free surface, such as is produced by crushing them together, as it were, by the burnisher, affects the electric action between the outer surface of the zinc and the opposed parallel gold plate. It shows that the potential * in zinc (uniform throughout the homo-

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* There has been much of wordy warfare regarding potential in a metal, but none of the combatants has ever told what he means by the expression. In fact, the only definition of electric potential hitherto given has been for vacuum, or air, or other fluid insulator. Conceivable molecular theories of electricity within a solid or liquid conductor might admit the term potential at a point in the interior; but the function so called would vary excessively in intermolecular space, and must have a definite value for every point, whether of intermolecular space or within the volume of a molecule, or within the volume of an atom, if the atom occupies space. It would also vary intensely from point to point in the æther or air outside the metal at distances from the frontier small or moderate in comparison with the distance from molecule to molecule in the metal.

But when, setting aside our mental microscopic binocular which shows us atoms and molecules, we deal with the mathematical theory of equilibrium and motion of electricity through metals with outer surfaces bounded by æther or air or other insulating fluids or solids, we find it convenient to use a mathematical function of position called potential in the interior of each metal. This function must, for the case of equilibrium, fulfil the condition that it is of uniform value through each homogeneous portion of metal. Its value must, as a rule, change grageneous interior) increases from the interior through the thin surface-layer of a portion of its surface affected by the crushing of the burnisher, more by ·32 volt than through any thin surface-layer of portions of its surface left as polished and scratched by glass-paper. The difference of potentials of copper and zinc across an interface of contact between them is only about 2½ times the difference of potential thus proved to be produced between the homogeneous interior of the zinc and its free surface, by the burnishing. Pellat had found that polished metallic surfaces, seemingly clean and free from visible contamination of any kind, became more positive by rubbing them forcibly with emery-paper, zinc showing the greatest effect, which was ·23 volt. Murray's burnished surface of zinc actually *fell* ·32 volt when scratched by polishing on glass-paper.

§ 17. With two copper plates (*a*), (*b*) polished on emery and each compared with standard gold, Murray found	(*a*) — ·11 volt. (*b*) — ·06 volt.
They were then burnished by rubbing them forcibly together, and again tested separately ; he found	(*a*) — ·02 volt. (*b*) — ·02 volt.

Rises of Volta-potential of about the same amount were produced by burnishing with a steel burnisher copper plates which had been polished and scratched in various ways. Such experiments as those of Murray with burnishing ought to be repeated with hammering or crushing by a Bramah's press. Indeed Pellat * suggested that metals treated bodily "par le laminage ou le martelage" (rolling or hammering) might probably show Volta-electric properties of the same

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dually (or abruptly) with every gradual (or abrupt) change of quality of substance occupying space.

To illustrate the difficulty and complexity of expression with which I have struggled, and to justify if possible my ungainly resulting sentence in the text, consider the case of a crystal of pure metal: suppose, for example, an octahedron with truncated corners, all natural faces and facets. In all probability Volta-differences of potential would be found between the octahedronal and truncational faces. We might arbitrarily define the uniform interior potential as the potential of the air either near an octahedronal face or near a truncational face; or, still arbitrarily, we might define it as some convenient mean or average related to measurements of Volta-differences of potential between the different faces.

[*] *Ann. de Chimie et de Physique*, 1881, vol. xxiv. footnote on p. 83.

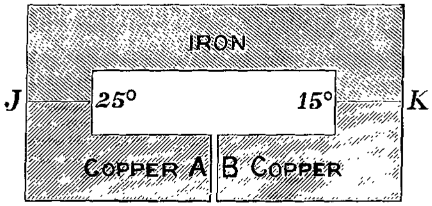
kind as, but more permanent than, those which he had found to be produced by violent scratching with emery-paper.

§ 18. It is interesting to remark that Murray's most highly burnished zinc differed from his emery-polished copper (*a*) by 1·13 volts. This is considerably greater, I believe, than the highest hitherto recorded Volta-difference between pure metallic surfaces of zinc and copper.

By far the greatest Volta-difference between two metallic surfaces hitherto measured is, I believe, 3·56 volts, which Murray, in another part of his work, found as the Volta-difference between bright sodium protected by glass and his standard gold. He had previously found a copper surface after exposure to iodine vapour to be —·34 relatively to his standard gold. The difference between this iodized surface and the bright metallic surface of sodium was therefore 3·90 volts: which is the highest dry Volta-electromotive force hitherto known.

§ 19. Seebeck's great discovery of thermoelectricity (1821) was a very important illustration and extension of the twenty years' earlier discovery of the contact electricity of dry metals by Volta. It proved independently of all disturbing conditions that the difference of potentials between two metals in contact varies with the temperature of the junction. Thus, for instance, in the copper-iron arrangement represented in fig. 9, with its hot junction at 25° and its cold at 15°, the electromotive force tends to produce current from copper to iron through hot, and its amount is ·00148 volt: that is to say, if the circuit is broken at A B the two opposed faces A, B, at equal temperatures, present a difference of electric potential of ·00148 volt, with B positive relatively to A. This is not too small a difference to be tested directly by the Volta-static method, worked by two exactly similar metal discs connected to A and B, when they are at their shortest distance from one another, and then disconnected from A and B, and separated and tested by connexion with a delicate quadrant

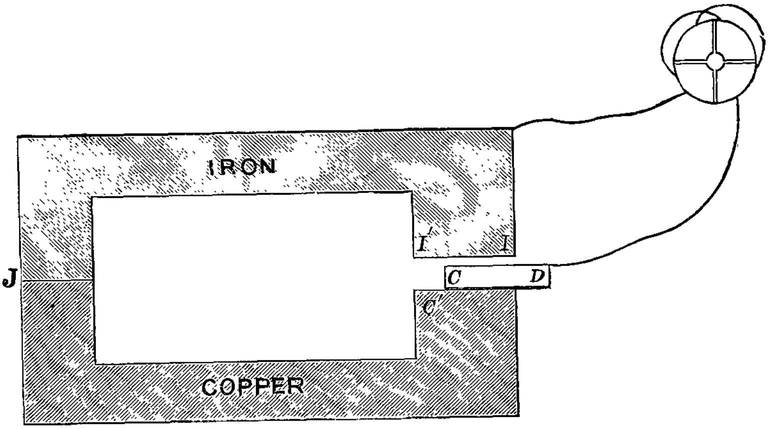
Fig. 9.



electrometer. But the test would be difficult, because of the difficulty of preparing the opposed surfaces of two equal and similar disks, so as to make them equal in their surface-Volta-potentials within one one-thousandth of a volt, or even to make their difference of potentials constant during the time of experiment within one one-thousandth of a volt. There would, however, be no interest in making the experiment in this way, because by the electromagnetic method we can with ease exhibit and measure with great accuracy the difference of potentials between A and B, by keeping them exactly at one temperature and connecting them by wires of any kind with brass or other terminals of a galvanometer of high enough resistance not to sensibly diminish the difference of potentials between A and B, provided all the connexions between metals of different quality except J and K are kept at one and the same temperature (or pairs of them, properly chosen, kept at equal temperatures).

§ 20. Suppose, now, instead of breaking a circuit of two metals at a place in one of the metals, as A B in copper in fig. 9, we break it at one of the junctions between the two metals, as at C′ C, I′ I, fig. 10. C D represents a movable slab of copper which (for §22 below) may be pushed in so as to be wholly opposite to I′ I, or at pleasure drawn out to any position, still resting on the copper below it as shown in the diagram. Calling zero the uniform potential over the surfaces C′ C D, the potential at I′ I would be about +·16 volt (according to Murray's results for emery-polished copper and

Fig. 10.



iron surfaces) if the temperature at J and throughout the system is uniform at about 15° C. Keeping now the temperature of C′ C, I′ I exactly at 15°, let the temperature of J be raised to 25°. The difference of potentials between C′ C and I′ I would be increased to ·16148 volt, supposing ·16000 to have been exactly the difference of potentials when the temperature of J was 15°. This difference of differences of potentials would be just perceptible on the most delicate quadrant electrometer connected as indicated in the diagram. Lastly, raise the temperature of C′ C and I′ I to exactly 25°, J being still kept at this temperature : the spot of light of the electrometer will return exactly to its metallic zero. But, would the Volta-difference of potentials between the surfaces C′ C, I′ I remain unchanged, or would it return exactly to its previous value of ·16000, or would it come to some other value ? We cannot answer this question without experiment. The proper method, of course, would be to use the metal-sheathed Volta-condenser and compensation (§ 9 above), and with it measure the Volta-differences between copper and iron at different temperatures, the same for the two metals in each case. The sheath and everything in it should, in each experiment, be kept at one and the same constant temperature. But it would probably be very difficult to get a decisive answer, because of the uncertainties and time-lags of changes in the Volta-potential of metallic surfaces with change of temperature, which, if we may judge from Pellat's and Murray's experiments on effects of temperature when the two metals are unequally heated, would probably also be found when the temperatures of the two metals, kept exactly equal, are raised or lowered at the same time.

§ 21. The thermoelectric difference between bismuth and antimony is about ten times that between copper and iron for temperature differences of ten or twenty degrees on the two sides of 20° C., and their Volta-contact difference is exceedingly small (according to Pellat, just one one-hundredth of a volt when both their surfaces are strongly scratched by rubbing with emery). It would be very interesting, and probably instructive, to find how much their Volta-contact difference varies with temperature by the method at present suggested. The great variations of Volta-surface potentials, found by Pellat and Murray, when one of the two metals is heated, may have been due to difference of temperatures between the two opposed plates with air between them ; and it is possible that no such large variation, or that large variation only due to changes of cohering gases, may be found when the two metals are kept at equal temperatures, and these temperatures are varied as in the experiment I am now suggesting.

§ 22. Peltier's admirable discovery (1834) of cold produced where an electric current crosses from bismuth to antimony, and heat where it crosses from antimony to bismuth, in a circuit of the two metals, with a current maintained through it by an independent electromotive force, is highly important in theory, or in attempts for theory, of the contact electricity of metals.

From an unsatisfactory * hypothetical application of Carnot's principle to the thermodynamics of thermoelectric currents I long ago inferred † that probably electricity crossing a contact between copper and iron in the direction from copper to iron would produce cold, and in the contrary direction heat when the temperature is below 280° C. (the thermoelectric neutral temperature of copper and iron ‡), and I verified this conclusion by experiment §. Hence we see, looking to fig. 10, if the movable copper plate CD is allowed to move inwards (in the position shown in the diagram it is pulled inwards by the Volta-electrifications of the opposed surfaces of iron and copper), cold will be produced at the junction J, all the metal being at one temperature to begin with; and if we draw out the copper plate CD, heat will be produced at J. The thermodynamics of this action ||, because it does not involve unequal temperatures in different parts of the metals concerned, is a proper subject for unqualified application of Carnot's law, and has nothing of the unsatisfactoriness of the thermodynamics of thermoelectric currents, which essentially involves dissipation of energy by conduction of heat through metals at different temperatures in different parts. At present we cannot enter further into thermodynamics than to remark that when the plate CD is drawn out, the heat produced at J is not the thermal equivalent of the work done by the drawing out of the copper plate, but in all probability is very much less than the thermal equivalent. Probably by far the greater part of the work spent in draw-

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* 'Mathematical and Physical Papers,' vol. i. art. xlviii. § 106, reprinted from 'Transactions of the Royal Society of Edinburgh,' May 1854.

† Ibid. § 116 (19).

‡ In a thermoelectric circuit of copper and iron the current is from copper to iron through hot when both junctions are below 280° C. It is from iron to copper through hot when both junctions are above 280° C.

§ 'Experimental Researches in Thermoelectricity,' Proc. R. S. May 1854; republished as art. li. in 'Mathematical and Physical Papers,' vol. i. (see pp. 464–465).

|| [March, 1898.] It has been given in a communication to the Royal Society of Edinburgh entitled 'The Thermodynamics of Volta-contact Electricity: Feb. 21, 1898.

ing out the plate against the electric attraction goes to storing up electrostatic energy, and but a small part of it is spent on heat produced at J; or on excess (positive or negative) of this Peltier heat above quasi-Peltier (positive or negative) absorptions of heat in the surface-layers of the opposed surfaces when experiencing changes of electrification.

§ 23. Returning to fig. 9; suppose, by electrodes connected to AB and an independent electromotive force, a current is kept flowing from copper to iron through one junction, and from iron to copper through the other; the Peltier heat produced where the current passes from iron to copper is manifestly not the thermal equivalent of the work done. In fact, if the two junctions be at equal temperatures, the amounts of Peltier heat produced and absorbed at the two junctions will be equal, and the work done by the independent electromotive force will be spent solely in the frictional generation of heat.

§ 24. Many recent writers *, overlooking the obvious principles of §§ 22, 23, have assumed that the Peltier evolution of heat is the thermal equivalent of electromotive force at the junction. And in consequence much confusion, in respect to Volta's contact electricity and its relation to thermoelectric currents, has largely clouded the views of teachers and students. We find over and over again the statement that thermoelectric electromotive force is very much smaller than the Volta-contact electromotive force of dry metals. The truth is, Volta-electromotive force is found between metals all of one temperature, and is reckoned in volts, or fractions of a volt, without reference to temperature. If it varies with temperature, its *variations* may be stated in fractions of a volt per degree. On the other hand, thermoelectric electromotive force depends essentially on difference of temperature, and is essentially to be reckoned *per degree*; as for example, in fraction of a volt per degree.

§ 25. Volta's second fundamental discovery, that is, his discovery (§ 5 above) that vitreous and resinous electricity flow away from zinc and copper to insulated metals connected

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* Perhaps following Clerk Maxwell, or perhaps independently. At all events we find the following in his splendid book of 1873: "Hence $J\Pi$ represents the electromotive contact force at the junction acting in the positive direction. . . . . 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 electromotive force must be sought for, not at the junction of the two metals, but at one or both of the surfaces which separate the metals from the air or other medium which forms the third element of the circuit."—'Treatise on Electricity and Magnetism,' vol. i. § 249.

with them (for example, the two electrodes of an insulated electrometer) when the two metals are separated after having been in metallic contact, makes it quite certain that there must be electric force in the air or æther in the neighbourhood of two opposed surfaces of different metals metallically connected. This conclusion I verified about thirty-six years ago by experiments described in a letter to Joule, of January 21, 1862, which he communicated to the Literary and Philosophical Society of Manchester, published in the 'Proceedings' of the Society and in 'Electrostatics and Magnetism' (§ 400) under the title of "A New Proof of Contact Electricity."

§ 26. Volta's second fundamental discovery also makes it certain that movable pieces of two metals, metallically connected, attract one another, except in the particular case when their free surfaces are Volta-electrically neutral to one another. This force, properly viewed, is a resultant of chemical affinity between thin surface-layers of the two metals. And the work done by it, when they are allowed to approach through any distance towards contact between any parts of the surfaces, is the dynamical equivalent of the portion of their heat of combination due to the approach towards complete chemical combination constituted by the diminution of distance between the two bodies. To fix the ideas, let the metals be two plane parallel plates of zinc and copper, with distance between them small in comparison with their diameters, and let us calculate the amount of the attractive force between them at any distance. Let V be the difference of potentials of the air or æther very near the two metallic frontiers, but at distances from these frontiers amounting at least to several times the distance from molecule to nearest molecule in either metal (see footnote on § 16 above). The electric force in air or æther between these surfaces will be V/D, if D denotes the distance between them. Hence (our molecular microscopic binocular set aside) if ρ is the electric density of either of the opposed surfaces, A the area of either of the two, and P the attraction between them, we have

$$\frac{V}{D}=4\pi\rho, \quad P=\frac{1}{2}\rho\frac{V}{D}A.$$

Hence

$$P=\frac{V^2A}{8\pi D^2}.$$

Hence the work done by electric attraction in letting them come from any greater distance asunder D′ to any smaller distance D is

$$\frac{V^2A}{8\pi}\left(\frac{1}{D}-\frac{1}{D'}\right), \text{ or approximately, } \frac{V^2A}{8\pi D},$$

if D is very small in comparison with D′.

§ 27. For clean sand-papered copper and zinc* we may take V as $\frac{3}{4}$ of a volt C.G.S. electromagnetic, or $\frac{1}{400}$ C.G.S. electrostatic.

Let now A be 1 sq. centim. and D ·001 of a centim. We find P equal to ·249 dyne, and the work done by attraction to this distance from any much greater distance is ·000249. This is sufficient to heat $5{\cdot}9\times10^{-12}$ grammes of water 1°.

The table on the next page shows corresponding calculated results for various distances ranging from 1/100 of a centim. to $1/10^{10}$ of a centim.

Columns 5 and 6 are introduced to illustrate the relation between the electric attraction we are considering and chemical affinity as manifested by heat of combination. The "brass" referred to is an alloy of equal parts of zinc and copper, assumed to be of specific gravity 8 and specific heat ·093.

§ 28. It would be exceedingly difficult, if indeed possible at all, to show by direct experiment, at any distance whatever, the force of attraction between the disks; as we see from the table, at a distance of 1/100 of a centim. it amounts to only 1/400 of a milligramme-heaviness; and to only $2\frac{1}{2}$ grammes-heaviness at the distance 10^{-5} of a centimetre, which is about $\frac{1}{6}$ of the wave-length of ordinary yellow light. At the distances 10^{-7}, 10^{-8}, 10^{-9} of a centimetre the calculated forces of attraction are 25 kilogrammes, $2\frac{1}{2}$ tons†, and 250 tons. This last force is 2 or 3 times the breaking-weight per square centim. of the strongest steel (pianoforte wire), 6 times that of copper,

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* Pellat's measured values range from ·63 to ·92, according to the physical condition left by less or more violent scrubbing with emery-paper. The mean of these numbers is ·77. Murray's range was still wider, from ·63 volt to 1·13, the smallest being for copper burnished, opposed to zinc scratched and polished with glass-paper; and the largest, copper polished merely with emery-paper, opposed to zinc polished and burnished.

† The metrical ton is about 2 per cent. less than (·984 of) the British ton in general use through the British empire for a good many years before 1890, but destined, let us hope, to be rarely if ever used after the 19th century, when the French metrical system becomes generally adopted through the whole world.

Metallically connected Parallel Discs of Zinc and Copper, each of 1 square centim. area attracting one another.

1. Distance between plates. D.	2. Force of attraction in dynes *. P.	3. Work in ergs *. W.	4. Equivalent of W in heat-units (gramme-water-1° Cent.). H.	5. (See § 27.) Heat-units per gramme of brass disc of thickness D and area 1 sq. cm. $H \div 8D$.	6. (See § 27.) Rise of temperature produced by giving H to copper and zinc discs of thickness $\frac{1}{2}$ D, or to brass disc of thickness D and area 1 sq. cm. if specific heat constant at ·093. $H \div (8 \times D \times \cdot 093)$.
10^{-2} of centimetre.	$10^{-4} \times 25$ of dyne.	$10^{-4} \times \cdot 25$ of erg.	$10^{-12} \times \cdot 59$ of heat-unit.		
10^{-3} ,,	$10^{-2} \times 25$,,	$10^{-3} \times \cdot 25$,,	$10^{-11} \times \cdot 59$,,		
10^{-4} ,,	25 dynes.	$10^{-2} \times \cdot 25$,,	$10^{-10} \times \cdot 59$,,		
10^{-5} ,,	$10^{2} \times 25$,,	$10^{-1} \times \cdot 25$,,	$10^{-9} \times \cdot 59$,,		
10^{-6} ,,	$10^{4} \times 25$,,	·25 ,,	$10^{-8} \times \cdot 59$,,	·00074	0·079°
10^{-7} ,,	$10^{6} \times 25$,,	$10 \times \cdot 25$ ergs.	$10^{-7} \times \cdot 59$,,	·074	·79°
10^{-8} ,,	$10^{8} \times 25$,,	$10^{2} \times \cdot 25$,,	$10^{-6} \times \cdot 59$,,	7·4	79°
10^{-9} ,,	$10^{10} \times 25$,,	$10^{3} \times \cdot 25$,,	$10^{-5} \times \cdot 59$,,	740	7,900°
10^{-10} ,,	$10^{12} \times 25$,,	$10^{4} \times \cdot 25$,,	$10^{-4} \times \cdot 5$,,	74,000	790,000°

* The dyne is ·981 of a milligramme heaviness in the latitude of Greenwich. For approximate estimate it may be taken as 2 per cent. less than 1 milligramme heaviness in any latitude. The erg is the work done by a force of 1 dyne acting through the space of 1 centimetre.

15 times that of zinc. We are therefore quite sure that the increase of attraction according to the inverse square of the distance is not continued to such small distances as 10^{-9} of a centimetre; and at distances less than this the electric attraction merges into molecular force between the two metals.

§ 29. Consider, now, a large number of discs of zinc and copper, each of 1 square centim. area and thickness D, and polished on both sides. On one side of each disc attach three very small columns, of length D, of glass or other insulating material, and place one disc on top of the insulators of another, zinc and copper alternately, so as to make a dry insulated pile of the metal discs separated by air spaces each equal to the thickness D. If in the building of this pile each disc is kept metallically connected with the one over which it is placed while it is being brought into its position, work will be done upon it by electric attraction to the amount shown in column 3, and the total work of electric attraction during the building of the pile will be the amount shown in column 3 multiplied by one less than the number of discs.

But if each disc, after being metallically connected with the one on which it is to be placed till it comes within some considerable distance—say 300 D, for example, from the disc over which it is to rest—is then disconnected and kept insulated while carried to its position in the pile, no work will be done on it by electric attraction. And if now, lastly, metallic connexion is made between all the discs of the pile, currents pass from each copper to each zinc disc, and heat is generated to an amount equal to that shown in column 4, multiplied by one less than the number of discs; and if this heat is allowed to become uniformly diffused through the metals, they rise in temperature to the extent shown in column 6.

All these statements assume that the electric attraction increases according to the inverse square of the distance between opposed faces of zinc and copper. We have already (§ 28) seen that this assumption cannot be extended to such small distances as 10^{-9} of a centimetre. We have now further proof of this conclusion beyond the possibility of doubt, because the large numbers in columns 5 and 6 for 10^{-9} are enormously greater than any rational estimate we can conceive for the heat of combination of equal parts of zinc and copper per gramme of the brass formed. (See § 32 below.)

§ 30. When, on a Friday evening in February 1883—fourteen years ago—quoting from an article which had been published in Nature* in 1879, I first brought these views before the Royal Institution, we had no knowledge of the amount of heat of combination of zinc and copper, nor indeed of any other two metals. It appeared probable to us, from Volta's discovery of contact electricity between dry metals, that there must be some heat of combination; but I could then only express keenly-felt discontent with our ignorance of its amount. Now, however, after twenty-seven years' endurance, I am happily relieved since yesterday by Professor Roberts-Austen, who most kindly undertook to help me in my preparations for this evening, with an investigation on the heat of combination of copper and zinc, by which he has found that the melting together of 30 per cent. of zinc with 70 per cent. of copper generates about 36 heat-units (gramme-water-Cent.) per gramme of the brass formed. I am sure you will all join with me in hearty thanks to him, both for this result and for his further great kindness in letting us now see a very beautiful experiment, demonstrating a large amount of heat of combination between aluminium and copper, in illustration of his mode of experimenting with zinc and copper, which could not be so conveniently put before you because of the dense white fumes inevitable when zinc is melted in the open air.

[Experiment: A piece of solid aluminium dropped into melted copper: large rise of temperature proved by thermo-electric test. Result seen by all in large deflexion of spot of light reflected from mirror of galvanometer.]

§ 31. Another method of investigating the heat of combination of metals, which I have long had in my mind, is to compare the heat evolved by the solution of an alloy in an acid with the sum of the heats of combination of its two constituents in mixed powders. The former quantity must be less than the latter by exactly the amount of the heat of combination. This investigation was undertaken a month ago by Mr. Galt in the Physical Laboratory of the University of Glasgow, and he has already obtained promising results; but many experimental difficulties, as was to be expected, have presented themselves, and must be overcome before trustworthy results can be obtained.

[*Added Feb.* 1898.—By dissolving a gramme of a powdered alloy, and again a gramme of mixed powders of the two metals in the same proportion, in dilute nitric acid, Mr. Galt has now obtained approximate determinations of heats of

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* 'Nature,' vol. i. p. 551, "On the Size of Atoms."

combination for four different alloys, as shown in the following table*:—

No.	Alloy.	Heat of combination per gramme of alloy in gramme-water-Cent. thermal units.
I.	...... { 48 per cent. zinc 52 „ copper } ...... (Approximately chemical combining proportions*.)	77
II.	...... { 30 per cent. zinc 70 „ copper }	34·6
III.	... { 76·7 per cent. silver 23·3 „ copper } ... (Approximately chemical combining proportions*.)	18
IV.	... { 51·6 per cent. silver 48·4 „ copper } ...	7

* The combining proportions are—
(i.) 50·8 zinc with 49·2 copper,
and (ii.) 77·4 silver with 22·6 copper.

The composition stated for the alloy in each case is the result of chemical analysis. No. I. was intended to be equal parts of zinc and copper (as being approximately the chemically combining proportions); but the alloy, which resulted from melting together equal parts, was found to have 4 per cent. more copper than zinc, there having no doubt been considerable loss of the melted zinc by evaporation. No. III. turned out on analysis to be, as intended, very nearly in the chemically combining proportions of silver and copper. No. IV. was intended to be equal parts of silver and copper, but analysis showed the deviation from equality stated in the table. The proportions of No. II. were chosen for the sake of comparison with Professor Roberts-Austen's result (§ 30), and the agreement (34·6 and 36) is much closer than could have been expected, considering the great difference of the two methods and the great difficulties in the way of obtaining exact results which each method presents.

From a chemical point of view it is interesting to see, from Mr. Galt's results, how much more, both in the case of copper and zinc, and copper and silver, the heat of combination is, when the proportions are approximately the chemically combining proportions, than when they differ from these proportions to the extents found in Alloys II. and IV. Mr. Galt

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* [*May*, 1898.—Later experiments with more carefully purified metals have given somewhat different numbers for column 3.—K.]

intends, in continuance of his investigation, to determine as accurately as he can the heats of combination of many different alloys of zinc and copper and of silver and copper, and so to find whether or not it is greatest when the proportions are exactly the chemically "combining proportions." He hopes also to make similar experiments with bismuth and antimony, using *aqua regia* as solvent.]

[§ 32. *February*, 1898.—Looking now to column 5 of the table of § 27, we see from Professor Roberts-Austen's result, 36 thermal units, for the heat of combination of 30 per cent. copper with 70 per cent. zinc, and from Galt's 77 thermal units for equal parts of copper and zinc, that the law of electric action on which the calculations of the tables are founded is utterly disproved for discs of metal of one one-thousand-millionth of a centimetre thickness, with air or æther spaces between them of the same thickness, but is not disproved for thicknesses of one one-hundred-millionth of a centimetre.

Consider now our ideal insulated pile (§ 29) of discs 10^{-8} of a centimetre thick, with air or æther spaces of the same thickness between them. Suddenly establish metallic connexion between all the discs. The consequent electric currents will generate 7·4 thermal units, and heat the disks by 79° C. Take again the insulated column with thicknesses and distances of 10^{-8} of a centimetre; remove the ideal glass separators and diminish the distance to 10^{-9} of a centimetre (the thicknesses of discs being still 10^{-8} of a centimetre). Now, with these smaller distances between two opposed areas, make metallic contact throughout the column by bending the corners (the discs for convenience being now supposed square): 74 thermal units will be immediately generated, and the discs will rise 790° in temperature, and we have a column of hot brass—perhaps solid, perhaps liquid. This last statement assumes that the law of electric action, on which the table is founded, holds for discs 10^{-8} of a centimetre thick, with æther or air spaces between them of 10^{-9} of a centimetre. In reality it is probable that the law of electric action for discs 10^{-8} of a centimentre thick, begins to merge into more complicated results of intermolecular forces, before the distance is as small as 10^{-8} of a centimetre.

Resuming our mental molecular microscopic binocular (§ 16, footnote), we cannot avoid seeing molecular structures beginning to be perceptible at distances of the hundred-millionth of a centimetre, and we may consider it as highly probable that the distance from any point in a molecule of copper or zinc to the nearest corresponding point of another molecule is less than one one-hundred-millionth, and greater than one one-thousand-millionth of a centimetre.]

§ 33. In all that precedes I have, by frequent repetition of the phrase "air or æther," carefully kept in view the truth that the *dry* Volta contact-electricity of metals is, in the main, independent of the character of the insulating medium occupying space around and between the metals concerned in each experiment, and depends essentially on the chemical and physical conditions of molecules of matter in the thin surface stratum between the interior homogeneous metal and the external space, occupied by æther and dry or moist atmospheric air or any gas or vapour which does not violently attack the metal: or by æther with vapours only of mercury and glass and platinum and steel and vaseline (caulking the glass-stopcocks), as in Bottomley's experiments (§ 14 above).

This truth has always seemed to me convincingly demonstrated by Volta's own experiments, and I have never felt that that conviction needed further foundation; though of course I have not considered quite needless or uninstructive Pfaff's and my own and Pellat's repetitions and verifications, in different gases at different pressures, and Bottomley's extension of the demonstration to vacuum of $2\frac{1}{2}$ millionths of an atmosphere. I am now much interested to see by Professor Oliver Lodge's report, already referred to (§ 4 above), that in the Bakerian Lecture to the Royal Society in 1806 *, Sir Humphry Davy, who had had contemporaneous knowledge of Volta's first and second discoveries, expressed himself thus clearly as to the validity of the second: "Before the experiments of M. Volta on the electricity excited by mere contact of metals were published, I had to a certain extent adopted this opinion," an opinion of Fabroni's; "but the new fact immediately proved that another power must necessarily be concerned, for it was not possible to refer the electricity exhibited by the opposition of metallic surfaces to any chemical alterations, particularly as the effect is more distinct in a dry atmosphere, in which even the most oxidizable metals do not change, than in a moist one, in which many metals undergo oxidation."

§ 34. It is curious to find, thirty or forty years later, De la Rive explaining away Volta's second discovery by moisture in the atmosphere! Fifty-one years ago, when I first learned Volta's second discovery, by buying, in Paris, apparatus by which it has ever since been shown in the ordinary lectures of my class in the University of Glasgow, I was warned that De la Rive had found it wrong, and had proved it to be due

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* Phil. Trans. 1807.

to oxidation of the zinc by moisture from the air. I soon tested the value of this warning by the experiments of § 5 above, and a considerable variety of equivalent experiments, in one of which (real or ideal, I cannot remember which), a varnished zinc disc, scratched in places and moistened, sometimes on the scratched parts and sometimes where the varnish was complete, was tested in the usual manner by separating from contact with an unvarnished or varnished copper disc, with or without metallic connexion when the discs were at their nearest.

[§ § 35–40 *are added in February* 1898.]

§ 35. Within the last eighteen or twenty years there has been a tendency among some writers to fall back upon De la Rive's old hypothesis, of which there are signs in expressions quoted by Professor Oliver Lodge in his great and valuable report of 1884, and in some statements also of Professor Lodge's own views.

In what is virtually a continuation of this report in the Phil. Mag. a year later*, we find the following with reference to writings of Helmholtz and myself on the contact-electricity of metals :—" Both these contact theories, in explaining the Volta effect, ignore the existence of the oxidizing medium surrounding the metals. My view explains the whole effect as the result of this oxygen bath, and of the chemical strain by it set up." With views seemingly unchanged, he returned to the subject at the end of 1897 with the following statement in the printed syllabus of his " Six Lectures adapted to a Juvenile Auditory, on the Principles of the Electric Telegraph" (Royal Institution, December 28, 1897, January 8, 1898) :—

" Chemical method of producing a current—Voltaic cell—Two differently oxidizable metals immersed in an oxidizing liquid and connected by a wire can maintain an electric current, through the liquid and through the wire, so long as the circuit is closed. [The same two metals immersed in a potentially oxidizing gas and connected by a wire, can maintain an electric force or voltaic difference of potential in the space between them.]

" N.B.—No one need try too hard to understand sentences in brackets."

And lastly, after some correspondence which passed between us in December, I have to-day (Feb. 14) received from him

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* Prof. O. Lodge " On the Seat of the Electromotive Force in a Voltaic Cell," Phil. Mag. October 1885, p. 383.

a "slightly amplified statement made in order to concentrate the differences," which he kindly gives me for publication as a supplement to the shorter statement from the syllabus.

Amplification, February, 1898.

"There is a true contact-force at a zinc-copper junction*, "which on a simple and natural hypothesis (equivalent to "taking an integration-constant as zero) can be measured "thermoelectrically† and is about $\frac{1}{3}$ millivolt at 10° C.

"A voltaic force, more than a thousand times larger†, "exists at the junction of the metals with the medium surrounding "them; and in an ordinary case is calculable as the "difference of oxidation-energies of zinc and copper; but it "has nothing to do with the heat of formation of brass.

"*References*:—

"Phil. Mag. [5]:
"vol. xix. pp. 360 and 363, brass and atoms, pp. 487 and 494,
"summary;
"vol. xxi. pp. 270 and 275, thermoelectric argument;
"vol. xxii. p. 71, Ostwald experiment;
"August 1878, Brown experiment."

§ 36. With respect to the first of the two paragraphs of this last statement and the first two lines of the second, the wrongness of the view there set forth is pointed out in § 24 above. With respect to the last clause of the second paragraph and the statement quoted from the syllabus, I would ask any reader to answer these questions:—

(i.) What would be the efficacy of the supposed oxygen bath in the experiments of § 2 above with varnished plates of zinc and copper? or in Erskine Murray's experiment, described in his paper communicated last August to the Royal Society, in which metallic surfaces, scraped under melted paraffin so as to remove condensed oxygen or nitrogen from them, and leave fresh metallic surfaces in contact with a hydro-carbon, are subjected to the Voltaic experiment? or in Pfaff's and my own and Pellat's experiments with different gases, at ordinary and at low pressures, substituted for air? or in Bottomley's high vacuum and hydrogen and oxygen experiments (§ 14 above)?

(ii.) What would be the result of Volta's primary experiment, shown at the commencement of my lecture (§ 1 above),

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* See footnote on § 16 above. K. Feb. 14, 1898.

† See § 24 above. K. Feb. 14, 1898.

if it had been performed in some locality of the universe a thousand kilometres away from any place where there is oxygen? The insulators may be supposed to be made of rock-salt or solid paraffin, so that there may be no oxygen in any part of the apparatus. This I say because I understand that some anti-Voltaists have explained Bottomley's experiments by the presence of vapour of silica from the glass, supplying the supposedly needful oxygen!

§ 37. The anti-Voltaists seem to have a superstitious veneration for oxygen. Oxygen is entitled to respect because it constitutes 50 per cent. of all the chemical elements in the earth's crust; but this gives it no title for credit as coefficient with zinc and copper in the dry Volta experiment, when there is none of it there. Oxygen has more affinity for zinc than for copper; so has chlorine and so has iodine. It is partially true that different metals—gold, silver, platinum, copper, iron, nickel, bismuth, antimony, tin, lead, zinc, aluminium, sodium—are for dry Volta contact-electricity in the order of their affinities for oxygen; but it is probably quite as nearly true that they are in the order of their affinities for sulphur, or for oxy-sulphion (SO_4) or for phosphorus or for chlorine or for bromine. It may or may not be true that metals can be unambiguously arranged in order of their affinities for any of these named substances; it is certainly true that they cannot be *definitely and surely* arranged in respect to their dry Volta contact-electricity. Murray's burnishing, performed on a metal which has been treated with Pellat's washing with alcohol and subsequent scratching and polishing with emery, alters the Volta quality of its surface far more than enough to change it from below to above several metals polished only by emery; and, in fact, Pellat had discovered large differences due to molecular condition without chemical difference, before Murray extended this fundamental discovery by finding the effect of burnishing.

§ 38. Returning to Professor Lodge's supposed oxygen bath (§ 35); if it exists between the zinc and copper plates, it diminishes or annuls or reverses the phenomenon, to explain which he invokes its presence (see § 5 above).

§ 39. Many years ago I found that ice, or hot glass, pressed on opposite sides by polished zinc and copper, produced deviations from the metallic zero of the quadrants of an electrometer metallically connected with them in the same direction as if there had been water in place of the ice or hot glass. From this I inferred that ice and hot glass, both of which had been previously known to have notable electric conductivity, acted as electrolytic conductors.

Experiments made by Maclean and Goto in the Physical Laboratory of the University of Glasgow in 1890[*], proved that polished zinc and polished copper, with fumes passing up between them from the flame of a spirit-lamp 30 centimetres below, gave, when metallically connected to the quadrants of an electrometer, deviations from the metallic zero in the same direction, and of nearly the same amount, as if cold water had been in place of the flame. This proved that flame acted as an electrolytic conductor. They also found that hot air from a large red-hot soldering bolt, put in the place of the spirit-lamp, had no such effect; nor had breathing upon the plates, nor the vapour of hot water, any effect of the kind. In fact hot air, and either cloudy or clear steam, act as very excellent insulators; but there is some wonderful agency in fumes from a flame, remaining even in cooled fumes, in virtue of which the electric effect on zinc and copper is nearly the same as if continuous water, instead of fumes, were between the plates and in contact with both[†].

A similar conclusion in respect to air traversed by ultra-violet light was proved by Righi[‡], Hallwachs[§], Elster and Geitel[||], Branly[¶]. The same was proved for ordinary atmospheric air, with Röntgen rays traversing it between plates of zinc and copper, by Mr. Erskine Murray, in an experiment suggested by Professor J. J. Thomson, and carried out in the Cavendish Laboratory of the University of Cambridge[**].

§ 40. The substitution for ordinary air between zinc and copper, of ice or hot glass, or of air or gas modified by flame or by ultra-violet rays, or by Röntgen rays, or by uranium (§§ 41, 42 below), gives us, no doubt, what would to some degree fulfil Professor Lodge's idea of a "potentially-oxidizing" gas, and each one of the six fails wholly or partially to "maintain electric force or voltaic difference of potential in the space between them." In fact, Professor Lodge's bracketed sentence, so far as it can be understood, would be nearer the truth if in it "cannot" were substituted for "can." I hope no reader will consider this sentence too short or sharp. I am quite sure that Professor Lodge will approve of its tone, because in his letter to me of the 14th, he says, "In case of divergence of view it is best to have both aspects stated as

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[*] Phil. Mag. Aug. 1890.

[†] Kelvin and Maclean, R.S.E., 1897.

[‡] *Rend. R. Acc. dei Lincei,* 1888, 1889.

[§] Wiedemann's *Annalen,* xxxiv. (1888).

[||] *Ibid.* xxxviii., xli. (1888).

[¶] *Comptes Rendus,* 1888, 1890.

[**] Proc. R. S. March 1896.

crisply and distinctly as possible, so as to emphasise the difference." I wish I could also feel sure that he will agree with it, but I am afraid I cannot, because in the same letter he says, "I am still unrepentant."

Continuation of Lecture of May 24, 1897.

§ 41. In conclusion, I bring before you one of the most wonderful discoveries of the century now approaching its conclusion, made by the third of three great men, Antoine Becquerel, Edmond Becquerel, Henri Becquerel—father, son, and grandson—who by their inventive genius and persevering labour have worthily contributed to the total of the scientific work of their time; a total which has rendered the nineteenth century more memorable than any one of all the twenty-three centuries of scientific history which preceded it, excepting the seventeeth century of the Christian era.

You see this little box which I hold in my right hand, just as I received it three months ago from my friend Professor Moissan, who will be here this day week to show you his isolation of fluorine. It induces electric conductivity in the air all round it. If I were to show you an experiment proving this, you might say it is witchcraft. But here is the witch. You see, when I open the box, a piece of uranium of about the size of a watch. This production of electric conductance in air is only one of many marvels of the "uranium rays" discovered a year ago by Henri Becquerel, of no other of which can I now speak to you, except that the wood and paper of this box, and my hand, are to some degree transparent for them.

I now take the uranium out of its box and lay it on this horizontal copper plate, fixed to the insulated electrode of the electrometer. I fix a zinc plate, supported by a metal stem which is in metallic connexion with the sheath of the electrometer, horizontally over the copper plate at a distance of about one centimetre from the top of the uranium. Look at the spot of light; it has already settled to very nearly the position which you remember it took when we had a water-arc between the copper and zinc plates, connected as now, copper to insulated quadrants and zinc to the sheath. I now lift the uranium, insulating it from the copper plate by three very small pieces of solid paraffin, so as to touch neither plate, or, again, to touch the zinc but not the copper. This change makes but little difference to the spot of light. I tilt the uranium now to touch the zinc above and the copper below; the spot of light comes to the metallic zero as nearly as you can see. I leave it to itself now, resting on its paraffin supports and not touching the zinc, and the spot of light goes back to where it was ; showing about three-quarters of a volt positive.

§ 42. I now take this copper wire, which is metallically connected with the zinc plate and the sheath of the electrometer, and bring it to touch the under side of the copper shelf on which the uranium is supported by its paraffin insulators. Instantly the spot of light moves towards the metallic zero, and after a few vibrations settles there. I break the contact ; instantly the spot of light begins to return to its previous position, where it settles again in less than half a minute. You see, therefore, that if I re-make and keep made the metallic contact between the zinc and copper plates, a current is continuously maintained through the connecting wire, by which heat is generated and radiated away, or carried away by the air, as long as the contact is kept made. What is the source of the energy thus produced ? If we took away the uranium, and sent cool fumes from a spirit-lamp, or shed Röntgen rays or ultra-violet light, between the zinc and copper, the results of breaking and making contact would be just what you see with uranium. So would they be—you have already, in fact, seen them (§ 5)—without either Röntgen rays or ultra-violet light, but with the copper and zinc a little closer together and with a drop of water between them : and so would they be with dry ice, or with hot glass, between and touched by the zinc and copper. In each of these six cases we have a source of energy ; the well-known electro-chemical energy given by the oxidation of zinc in the last-mentioned three cases ; and the energy drawn upon by the cooled fumes, or by the Röntgen rays or ultra-violet light, acting in some hitherto unexplained manner, in the three other cases. We may conjecture evaporations of metals ; we have but little confidence in the probability of the idea. Or does it depend on metallic carbides mixed among the metallic uranium ? I venture on no hypothesis. M. Becquerel has given irrefragable proof of the truth of his discovery of radiation from uranium of something which we must admit to be of the same species as light, and which may be compared with phosphorescence. When the energy drawn upon by this light is known, then, no doubt, the *quasi* electrolytic phenomena, induced by uranium in air *, which you have

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* Experiments made in the Physical Laboratory of the University of Glasgow [§ 33 of Kelvin, Beattie, and Smolan, Proc. R. S. E. ; also 'Nature,' March 11, 1897, and Phil. Mag. March 1898] show this electrolytic conductivity to be produced by uranium to nearly the same amount

seen, will be explained by the same dynamical and chemical principles as those of the previously known electrolytic action of cooled fumes from a spirit-lamp, and of air traversed by Röntgen rays or ultra-violet light.

APPENDIX *.

On a Method of Measuring Contact Electricity.

IN my reprint of papers on Electrostatics and Magnetism (§ 400, of original date, January 1862) I described briefly this method, in connexion with a new physical principle, for exhibiting contact electricity by means of copper and zinc quadrants substituted for the uniform brass quadrants of my quadrant electrometer. In an extensive series of experiments which I made in the years 1859–61, I had used the same method, but with movable disks for the contact electricity, after the method of Volta, and my own quadrant electrometer substituted for the gold-leaf electroscope by which Volta himself obtained his electric indications.

I was on the point of transmitting to the Royal Society a paper which I had written describing these experiments, and which I still have in manuscript, when I found a paper by Hankel in Poggendorf's *Annalen* for January, 1862, in which results altogether in accordance with my own were given, and I withheld my paper till I might be able not merely to describe a new method, but if possible add something to the available information regarding the properties of matter to be found in Hankel's paper. I have made many experiments from time to time since 1861 by the same method, but have obtained results merely confirmatory of what had been published by Pfaff in 1820 or 1821, showing the phenomena of contact electricity to be independent of the surrounding gas, and agreeing in the main with the numerical values of the contact differences of different metals which Hankel had published ; and I have therefore hitherto published nothing except the slight statements regarding contact electricity which appear in my 'Electrostatics and Magnetism.' As interest has been recently revived in the subject

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in common air, oxygen, and carbonic acid; and to about one-third of the same amount in hydrogen, at ordinary atmospheric pressure; but only to about $\frac{1}{100}$ of this amount in each of these four gases at pressures of two or three millimetres. There seems every reason to believe that it would be non-existent in high vacuum, such as that reached by Bottomley in his Volta-contact experiments (§ 14 above).

* First published in the British Association, Swansea meeting, August 1880, and 'Nature,' April 4, 1881.

of contact electricity, the following description of my method may possibly prove useful to experimenters. The same method has been used to very good effect, but with a Bohnenberger electroscope instead of my quadrant electrometer, in researches on contact electricity by M. H. Pellat, described in the *Journal de Physique* for May 1880.

The apparatus used in these experiments was designed to secure the following conditions :—To support, within a metallic sheath, two circular discs of metal about four inches in diameter in such a way that the opposing surfaces should be exactly parallel to each other and approximately horizontal, and that the distance between them might be varied at pleasure from a shortest distance of about one-fiftieth of an inch to about a quarter or half an inch. This part of the apparatus I have called a "Volta-condenser." The lower plate, which was the insulated one, was fixed on a glass stem rising from the centre of a cast-iron sole plate. The upper plate was suspended by a chain to the lower end of a brass rod sliding through a steadying socket in the upper part of the sheath. An adjustable screw on this stem prevents the upper plate from being let down to nearer than about one-fiftieth of an inch, or whatever shortest distance may be wanted in any particular case. A stout brass flange fixed to the lower end of this rod bears three screws, one of which S is shown in the drawing, by which the upper plate can be adjusted to parallelism to the lower plate. The other apparatus used consisted of a quadrant electrometer, and in my original experiments an ordinary Daniell's cell, in my later ones a gravity Daniell's cell of the form which I described in 'Proc. R. S.,' 1871 (pp. 253–259), with a divider by which any integral number of per cents. from 0 to 100 of the electromotive force of the cell could be established between any two mutually insulated homogeneous metals in the apparatus.

Connexions.—The insulated plate was connected by a brass wire passing through the case of the Volta-condenser to the electrode of the insulated pair of quadrants. The upper plate was connected to the metal sheath of the Volta-condenser, and to the metal case of the electrometer, one pair of quadrants of which were also connected to the case. One of the two terminals of the divider, connected to the poles of the cell, was connected to the case of the electrometer. To the third terminal (the bar carrying the slider) was attached one of the contact wires, which was a length of copper wire having soldered to its outer end a short piece of platinum. The other contact surface was a similar short piece of platinum fixed to the insulated electrode of the electrometer. Hence it will be seen that metallic connexion between the two plates was effected by putting the divider at zero and bringing into contact the two pieces of platinum wire.

Order of Experiment.—The sliding piece of the divider was put to zero, and contact made and broken, and the upper plate raised: then the deflexion of the spot of light was observed. These operations were repeated with the sliding piece at different numbers on the divider scale, until one was found at which the make-break and separation caused no perceptible deflexion. The number thus found on the divider scale was the percentage of the electromotive force of the Daniell cell, which was equal to the contact electric difference of the plates in the Volta-condenser.

[*Addendum*, November 23, 1880.—Since the communication of this paper to the British Association, I have found that a dry platinum disc, kept for some time in dry hydrogen gas, and then put into its position in dry atmospheric air in the apparatus for contact electricity, becomes positive to another platinum disc which had not been so treated, but had simply been left undisturbed in the apparatus. The positive quality thus produced by the hydrogen diminishes gradually, and becomes insensible after two or three days.]

P.S.—On December 24, 1880, one of two platinum plates in the Volta-condenser was taken out; placed in dried oxygen gas for forty-five minutes; taken out, carried by hand, and replaced in the Volta-condenser at 12.30 on that day. It was then found to be negative to the platinum plate which had been left undisturbed. The amount of the difference was about ·33 of a volt. The plates were left undisturbed for seventeen minutes in the condenser, and were then tested again, and the difference was found to have fallen to ·29 of a volt. At noon on the 25th they were again tested, and the difference found to be ·18. The differences had been tested from time to time since that day, the plates having been left in the condenser undisturbed in the intervals. The following table shows the whole series of these results:—

Time.	Electric difference between surfaces of a platinum plate in natural condition, and a platinum plate after 45 minutes' exposure to dry oxygen gas.
Dec 24, 12.30 p.m.	·33 of a volt.
24, 12.47 p.m.	·29 ”
25, noon	·18 ”
27, noon	·116 ”
28, 11.20 a.m.	·097 ”
31, noon	·047 ”
Jan. 4, 11.0 a.m.	·042 ”
11, 11.40 a.m.	·020 ”

Mr. Rennie, by whom these experiments were made during the recent Christmas holidays, had previously experimented on a platinum plate which had been made the positive pole in an electrolytic cell with an electromotive force of one volt, tending to decompose water acidulated with sulphuric acid; the other pole being a piece of platinum wire. After the plate had been one hour under this influence in the electrolytic cell he removed it, and dried it by lightly rubbing it with a piece of linen cloth. He then placed it in the Volta-condenser, and found it to be negative to a platinum plate in ordinary condition; the difference observed was ·27 of a volt. This experiment was made on October 21; and on November 8 it was found that the difference had fallen from ·27 to ·07. Mr. Rennie also made similar experiments with the platinum disc made the negative pole in an electrolytic cell, and found that this rendered the platinum positive to undisturbed platinum to a degree equal to about ·04 of a volt. The effect of soaking the platinum plate in dry hydrogen gas, alluded to in my first postscript, which also was observed by Mr. Rennie, was found to be about ·11 of a volt. Thus in the case of polarization by hydrogen, as well as in the case of polarization by oxygen, the effect of exposure to the dry gas was considerably greater than the effect of electro-plating the platinum with the gas by the electromotive force of one volt.

[K.]

VI. *On the Ratio of the Velocities of the Two Ions produced in Gases by Röntgen Radiation; and on some Related Phenomena.*

By JOHN ZELENY, *B.Sc., Assistant Professor of Physics, University of Minnesota**.

IT is the object of this paper to show that the positive and negative ions, which take part in the conduction of gases exposed to Röntgen rays, move with different velocities when in the same electric field; to determine the ratio of these velocities in several gases; and to consider various phenomena which are consequences of or are affected by the difference in the two values.

The subject matter will be treated under the following sub-divisions:—

§ 1. The method for determining the ratio of the two velocities.
§ 2. The apparatus used.
§ 3. The form of tube used for constancy of radiation.

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* Communicated by Professor J. J. Thomson.