II. *The Contact Theory of Voltaic Action.*—Paper No. III.

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[Plates 4–5.]

I.

Up to the commencement of 1876 direct experiments on the difference of potentials of solids in contact with liquids had been made by Volta,[*] Sir Humphry Davy,[†] MM. Buff,[‡] Becquerel,[§] Péclet,[||] Pfaff,[¶] Sir William Thomson,[**] Hankel,[††] and Gerland,[‡‡] and of liquids in contact with liquids by Kohlrausch;[§§] but although extremely interesting they were all incomplete, for the following reasons:—

1. The earlier experiments were not carried out with apparatus susceptible of giving accurate results.

2. Owing to the incompleteness of the apparatus, assumptions had to be made not justified by the experiments.

3. *No direct* experiments had been performed to determine the difference of potential of two liquids in contact, with the exception of a few by Kohlrausch, using a method which appeared to us quite inadmissible as regards accuracy of result.

With regard to the objection No. 1, it is needless to do more than to remark that some of the earlier experimenters thought it permissible to touch a liquid under test with the fingers, or assumed without experiment that a piece of blotting-paper, previously soaked in a liquid, acted inductively on a distant metallic surface as a layer of the liquid would.

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[*] Volta, Gehler's Wörterbuch, Bd. iv., s. 616.

[†] Davy, Ann. de Chim., t. lxiii., p. 230, 1807.

[‡] Buff, Ann. d. Chim. u. Pharm., Bd. xlii., s. 5, 1842; u. Bd. xlv., s. 137, 1844.

[§] Becquerel, Ann. de Chim. et Phys., t. xxv., p. 405, 1824; Pogg. Ann., Bd. ii., s. 169.

[||] Péclet, Ann. de Chim. et Phys. [3], t. ii., p. 233; Arch. de l'El., t. i., p. 621, 1841.

[¶] Pfaff, Pogg. Ann., Bd. li., s. 110 und 197, 1840.

[**] Thomson, Proc. Lit. and Phil. Soc. of Manchester, Jan. 21, 1862: Papers on Elec. and Mag., § 400, p. 317.

[††] Hankel, Elektr. Untersuchungen, vi.; Abhandl. der Math.-Phys., Classe der Königl. Sächs. Gesellschaft, Bd. vii., s. 585, 1865.

[‡‡] Gerland, Pogg. Ann., Bd. cxxxiii., s. 513, 1868.

[§§] Kohlrausch, Pogg. Ann., Bd. lxxix., s. 200, 1850.

Regarding objection No. 2, great vagueness existed as to whether the contact difference of potentials between two substances, A and B, which we shall call for brevity $\overline{AB}$, was a constant depending only on the substances A and B and the temperature, or whether, one or both being a liquid, it was a variable dependent upon what other substance was in contact with either. Some writers regarded it as a variable;[*] Gerland[†] considered he had proved it constant when one or both of the substances was a solid. But, first, the agreement of the value of the electro-motive force of each of his cells with the algebraical sum of the separate differences of potential at the various surfaces of separation, which was the test of the accuracy of his theory, is so striking, and so much greater than polarisation, &c., usually allows one to obtain in experiments of such delicacy, that one cannot help feeling doubtful regarding his conclusions; secondly, his apparatus did not allow of his experimenting with two liquids in contact, consequently he could not legitimately draw any conclusion in this latter case. And although Kohlrausch had made some few experiments on the difference of potentials of liquids in contact, still, since he employed moist blotting-paper surfaces instead of the surfaces of the liquids themselves, we felt, for this reason if for no other, that his results did not carry the conviction the distinguished position of the experimenter might have led us to anticipate.

In fact, the inability of all experimenters to *measure directly* and *accurately* with their apparatus the contact difference of potentials of a solid and a liquid, and especially of *two liquids*, caused the whole theory of voltaic action to remain in a vague and incomplete state. It therefore appeared to us, in 1875, desirable to design an apparatus and carry out a series of experiments on this subject; and the results obtained during the following year will be found in our papers Nos. I. and II. (Proc. Roy. Soc., No. 186, 1878). Our method consisted in measuring directly the difference of potentials in volts at each separate contact of dissimilar substances in the ordinary galvanic cells, and then ascertaining whether the algebraical sum of all the contact differences of potential was or was not equal to the electro-motive force of the particular cell in question. The result obtained was that, within the limits of experiment, if $\overline{AB}$,[‡] $\overline{BC}$, $\overline{CD}$, &c., were separately measured (any one or more of the substances being solid or *liquid*), then if any number A, B, C, D . . . . K were joined together, and the electro-motive force of the combination $\overline{AK}$ measured, the following equation was found true:—

$$\overline{AK}=\overline{AB}+\overline{BC}+\overline{CD}+\ldots\ldots+\overline{JK}.$$

Which proved that each surface of separation produced its effect independently of any other.

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[*] F. Jenkin, Elec. and Mag., p. 44, 1873

[†] Gerland, Pogg. Ann., Bd. cxxxvii., s. 552, 1869.

[‡] $\overline{AB}$, as previously defined, being the difference of potentials between A and B in contact with one another, but neither in contact with any other conductor.

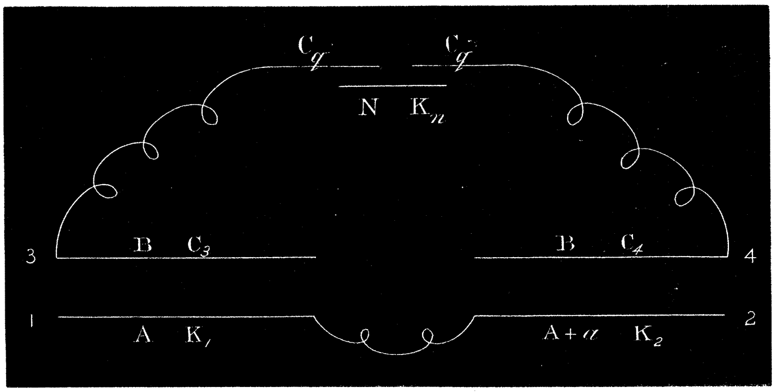
Since a preliminary notice of our first paper was communicated by Sir **William Thomson** to the British Association in 1876, Professor **Clifton** has published one "On the Difference of Potential produced by the Contact of Different Substances;"* but in spite of the exact workmanship of Professor **Clifton's** apparatus and the probable accuracy of the results attainable with it, it nevertheless possesses the same objection as the instrument employed by **Gerland**, namely, that it was not possible to measure directly with it the difference of potential of two liquids in contact. The results given by Professor **Clifton** are, as far as they go, generally in accord with those contained in our paper.

II.

The experiments of which the results form the subject of the present communication were made during 1877 and 1878, and the new apparatus employed, although generally the same in principle as that previously used, possessed many important modifications suggested by experience.

The method of measurement was as follows† :—Let 3 and 4 be two insulated gilt-brass plates connected with the electrodes of a delicate quadrant electrometer. Let 1 under 3 and 2 under 4 be the surfaces whose contact difference of potential is to be measured. 3 and 4 are first connected together and then insulated, but remain connected with their respective electrometer quadrants. Now, 1 and 2 are made to change places with one another, 1 being now under 4 and 2 under 3, then the deflection of the electrometer needle will give a measure of the difference of potentials between 1 and 2.

Fig. 1.



For before reversal let (fig. 1) the potential of the electrometer needle be N, of the induction plates and of the quadrants be B, of the substance 1 be A, and of the substance 2 be $A+\alpha$, so that α is what we desire to measure ;

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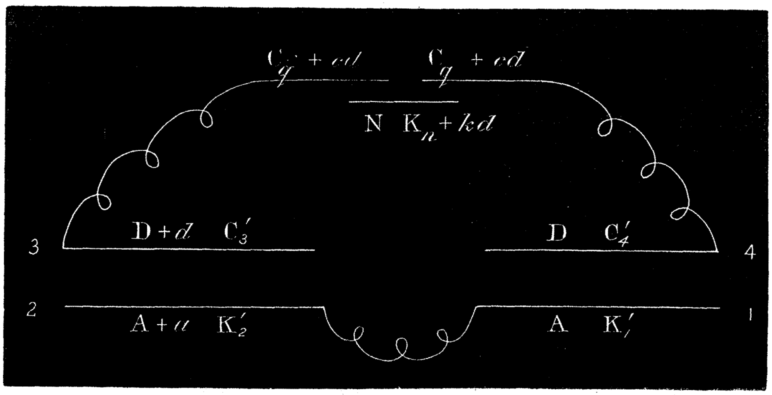
* Proc. Roy. Soc., 1877, vol. xxvi., p. 299.

† It need hardly be noticed that an *inductive* and not a *conductive* method of experimenting must necessarily be employed since the latter would introduce always unknown differences of potential.

Let the capacity of each pair of quadrants be C_q, of 3 be C_3, and of 4 be C_4;

Let the coefficient of induction of the electrometer needle on each pair of quadrants be K_n, of substance 1 on plate 3 be K_1, and of substance 2 on plate 4 be K_2.

Fig. 2.



Now on reversal (fig. 2) the needle will be deflected and the change of the capacity of each pair of electrometer quadrants, as well as the change of the coefficient of induction of the needle on each, will be proportional to the deflection, that is, proportional to d the difference of potentials now existing between the two sets of quadrants, therefore let the potential of 3 become $D+d$, and of 4 become D;

Let the capacity of each pair of quadrants become C_q+cd, and of 3 become C'_3, of 4 become C'_4;

Let the coefficient of induction of the electrometer needle on each pair of quadrants become K_n+kd, of substance 2 on plate 3 become K'_2, and of substance 1 on plate 4 become K'_1; then—

Before reversal, fig. 1,

$$\left.\begin{array}{l}\text{The charge in 3 and in}\\ \quad\text{the pair of attached}\\ \quad\text{quadrants}\end{array}\right\}=AK_1+BC_3+NK_n+BC_q$$

$$\left.\begin{array}{l}\text{The charge in 4 and in}\\ \quad\text{the pair of attached}\\ \quad\text{quadrants}\end{array}\right\}=(A+a)K_2+BC_4+NK_n+BC_q$$

After reversal, fig. 2,

$$\left.\begin{array}{l}\text{The charge in 3 and in}\\ \quad\text{the pair of attached}\\ \quad\text{quadrants}\end{array}\right\}=(A+a)K'_2+(D+d)C'_3+N(K_n+kd)+(D+d)(C_q+cd)$$

$$\left.\begin{array}{l}\text{The charge in 4 and in}\\ \quad\text{the pair of attached}\\ \quad\text{quadrants}\end{array}\right\}=AK'_1+DC'_4+N(K_n+kd)+D(C_q+cd)$$

This is the most general case, it only assumes the electrometer quadrants to be symmetrical with reference to the needle, but allows any amount of unsymmetry in our induction apparatus. In practice, the motion of the electrometer needle is usually in these experiments so small that we may neglect the change in the capacity of the quadrants, and in the coefficient of induction of the needle on them produced by this motion; consequently since the charge in the plate 3 and the attached pair of quadrants is not altered by the reversal

$$AK_1+BC_3+NK_n+BC_q=(A+a)K'_2+(D+d)C'_3+NK_n+(D+d)C_q,$$

similarly

$$AK'_1+DC'_4+NK_n+DC_q=(A+a)K_2+BC_4+NK_n+BC_q$$

$$\therefore aK_2=A(K'_1-K_2)+D(C'_4+C_q)-B(C_4+C_q)$$

$$d(C'_3-C_q)=A(K_1-K'_2)+B(C_3+C_q)-D(C'_3+C_q)$$

In order therefore that a, which is the difference of potentials we desire to measure, shall be proportional to d, the observed difference of potentials, it is necessary that

$$\text{either } C_3=C_4 \text{ or } B=0$$

$$\text{and either } C'_3=C'_4 \text{ or } D=0$$

$$\text{and either} \begin{cases} K_1=K'_2 \\ K'_1=K_2 \end{cases} \text{or } A=0$$

Now the conditions on the left hand side mean perfect symmetry of our induction apparatus before and after reversal. But as this, at any rate in Japan, is practically unattainable, it is desirable to make B, D, and A each nought. B can be made nought and also D very small by not merely connecting plates 3 and 4 together at the commencement of each experiment, but also with the outside of the electrometer or the earth, and we can also make A small by connecting either substance 1 or 2 also with the earth. Such connexions were always made in the following experiments.

In order to rotate the lower substances 1 and 2, it is necessary, if one or both of them be a liquid, to first increase the distance between 1 and 2 and between 3 and 4, in order that 3 and 4 may not strike against the sides of the vessels containing the liquids. In our former apparatus this was done by the table carrying 1 and 2 being supported and capable of revolution on a central leg, which itself was movable up and down (Proc. Roy. Soc., No. 186, vol. xxvii., pl. 7). But when the two substances of which it was desired to measure the difference of potentials were, say, a vessel of mercury and a comparatively thin plate of metal, the difference of weight on the two sides made it almost impossible with this method to obtain sufficient parallelism of the surfaces 1, 2, and 3, 4; so that our former experiments were necessarily confined to pairs of substances not having a great difference in weight. But, as it was obviously desirable that the present investigation should not be thus limited, it became necessary to construct a new apparatus, of which the end elevation is shown in Plate 5, and the side elevation in Plate 4.

Again, in the old apparatus it was necessary to open the metal cover enclosing the whole apparatus in order to lower, rotate, and raise plates 1 and 2. Now we consider that, although theoretically there was no objection to opening this case, provided it was shut again to screen the apparatus from exterior electrical induction before a reading was made, still that, as it introduced a possibility of the plates 3 and 4 being touched during an experiment, this opening was objectionable. In the present arrangement, the table A B, which carries the levelling screws *l l* for supporting the substances of which the contact differences of potential are to be measured (in our figure a liquid, L, and a solid plate, P, about 530 square centimetres in area), runs with three wheels, W, on a circular very rigid metallic horizontal railway, R; and to avoid lateral motion the table is kept centred by a stout iron pin, M, turning in a brass socket, S. The necessary vertical motion is produced in this apparatus by the plates 3 and 4, which are attached to the upper framework with an arrangement similar to that employed with a parallel ruler, being raised or lowered by a vertical brass rod, *r r*, capable of rotation, so as to allow of the pin, *p p*, passing through the slot, *s s* (shown in plan below), or being stopped by it when the rod is required to remain raised. The plates 3 and 4, which are each about 300 square centimetres in area, are supported by chemically clean glass rods, G, kept artificially dry by pumice-stone soaked in sulphuric acid, and resting in the leaden cups, U, sliding into the brass cylindrical tubes, B, with bayonet joints. These leaden cups may be lowered by handles, *h*, so as to rest on the brass plates 3 and 4 when the instrument is not in use, thus preventing access to B of the external air. The permanent adjustment for coincidence of the plane surfaces of the brass plates is effected by means of three screws, *w*, in each of the brass caps, C. Temporary adjustment of the horizontality of the brass plates is effected by means of a spirit level and the three large levelling screws, K, which support the whole apparatus, and the positions of which are fixed by hole, slot, and plane.

T T are strips of brass soldered to the induction plates 3 and 4, and connected by means of clips to fine platinum wires leading to the insulated electrodes of the quadrant electrometer, and to the insulated terminals of a highly insulated short circuit key, not shown in the drawing.

In addition to the whole framework being made very stout and of cherry-wood, one of the Japanese woods that warps least, it was further strengthened by various cross tie-pieces, as shown in the drawings.

The whole apparatus, including the short circuit key and electrometer, was, to avoid induction from outside, enclosed in a large zinc case connected with the earth, and was not opened at all during one complete experiment, consisting of some ten short circuitings of the upper plates, reversals of the table A B, and corresponding readings to the right and left of the electrometer needle.

We shall now describe a complete operation to obtain the contact difference of potentials, between a metal and liquid, for example. Suppose the permanent adjustments to have been made, and the gilt plates 3 and 4 to be quite bright. The plate P is cleaned with emery paper that has touched *no other metal*, and all traces of the emery removed by means of a clean cloth; it is then placed on the three levelling screws, *l*, and fixed in position by hole, slot, and plane. The porcelain dish containing the liquid is laid in a metal one just fitting it, and on the base of which is a hole, slot, and plane; this is now laid on the other levelling screws, *l*.

The rod, *r r*, is then lowered until the disk, *d d*, rests on a brass plate let into the top of the wooden framework at the top of the instrument—that is, until the induction plates 3 and 4 are in their lowest position. The levelling screws, *l l*, are now raised until a small metal ball, of a diameter of 8 millims., is in contact at three fixed points with the plate 4 and the plate P, or until when in contact with the plate 3 it and its reflection in the liquid L appear to meet. To avoid any harm arising from possible contact of the liquid with this gauge ball, it was made of a material not acted on by the particular liquid under experiment.

Before proceeding further, each pair of quadrants is in succession put to earth, the other pair remaining insulated in order to test for any possible leakage from the needles to the quadrants. Each pair of quadrants is now charged with a battery, the other pair being connected with the earth, in order to test for any leakage along the glass rods G, the small glass rods supporting the quadrants in the electrometer, or along the paraffined ebonite pillars of the short circuiting key. It having thus been ascertained that there is no leakage, the strip of metal which has been cut from the same sheet of metal as P itself, and temporarily attached to it by a binding screw soldered to P, is made quite bright with emery paper and a cloth, and its end dipped into the liquid L, as shown in Plate 4. The zinc case is then closed up, plates 3 and 4 connected together, and with the earth, by means of a key (the handle of which was a long thin ebonite rod projecting through the zinc case), and the electrometer reading taken. 3 and 4 are then insulated from one another, and from the earth, and raised by means of the rod, *r r*, projecting above through the zinc case; the table A B turned from below by means of a handle passing through the base of the instrument; 3 and 4 then lowered into exactly their former position, ensured by the parallel motion of the supporting beam and by the limiting stop, *d d*. The reading of the electrometer is now taken. Again short circuit, insulate, raise, reverse, and lower, and take a new electrometer reading, &c.

Some ten readings having been thus obtained, a fresh set of experiments is always made with the same two substances in the following way in order to compensate for the error introduced by defects in parallelism of the apparatus affecting the result obtained from two rigid surfaces (as that of copper and zinc), differently from the result found with one or with two liquid surfaces under test. Instead of commencing, as before, with the liquid L under 3 and the plate P under 4, we start with the plate under 3 and the liquid under 4, and readjust, by means of the levelling screws *l*, the heights of the surfaces, until their distance from the plates 3 and 4 is, as before, 8 millims. We then short circuit, insulate, raise, reverse, and lower, and take exactly as many readings as before; and the mean of the two sets of readings, obtained with the two modes of levelling, is regarded as the result of the particular experiment.

III.

The results we have already obtained in this present investigation group themselves under three heads:—

1st. The contact difference of potentials of metals and liquids at the same temperature.

2nd. The contact difference of potentials of metals and liquids when one of the substances is at a different temperature from the other in contact with it; for example, mercury at 20° C. in contact with mercury at 40° C.

3rd. The contact difference of potentials of carbon and of platinum with water, and with weak and strong sulphuric acid.

But those contained under head No. 1 are alone contained in the present investigation. The remainder of our completed experiments we desire to have the honour of submitting on a subsequent occasion to the Royal Society.

A fourth very important division of the subject, namely, the measurement of the contact difference of potential of substances in other gases than air, it has been our intention for some time to take in hand; but, although we commenced the working drawings of the apparatus necessary for that investigation at the beginning of 1877, we have not yet had an opportunity of constructing it.

The numbers which follow in the accompanying tables are those to which alone we attach importance, but it need hardly be said that, in such delicate experiments as the present, much time has to be spent in obtaining measurements which are afterwards found out to be wrong for a variety of reasons. All such we have not included in the following tables; and this therefore explains why, in some cases, one measurement only is apparently the result of a whole day's work.

In our previous papers Nos. I. and II. we used as our standard electro-motive force that of a LATIMER CLARK's standard mercurous-sulphate cell, since that was the most constant galvanic cell known to us; and we found experimentally, as Sir WILLIAM THOMSON previously ascertained, that zinc had to copper a contact difference of potentials 0·75 volt. Now, although Mr. LATIMER CLARK's cell is a very constant element, the difference of potentials of zinc and copper is even more constant; we have, therefore, in the present investigation compared all our measurements with this standard, which we have taken to be equal to 0·75 volt.

Date.	The following—	Has to the following—	At— ° C.	A contact difference of potentials, in volts.	Remarks.
30/1/78	Zinc sulphate, sp. gr. 1·125, at 16°·9 C.	Copper sulphate, sp. gr. 1·087, at 16°·6 C.	16·6	+ 0·090	Each of the numbers in the preceding column is the average of about ten observations.
	Copper	,, ,,	17	+ 0·103	
	Zinc	Zinc sulphate, sp. gr. 1·125, at 16°·9 C.	17	− 0·238	
8/2/78	Copper	Distilled water	..	+ 0·269	
11/2/78	Zinc	,, ,,	13·5	+ 0·088	
	Zinc sulphate, saturated at 15°·3 C.	,, ,,	13·5	+ 0·120	
	Zinc	,, ,,	13·5	+ 0·156	
	Copper	,, ,,	16	+ 0·100	
12/2/78 10 A.M.	Copper sulphate, saturated at 15° C.	,, ,,	13	+ 0·044	The contact difference of potentials of saturated copper sulphate with distilled water was here measured several times on different occasions, as a test of the efficiency of our method of measuring the difference of potentials of *two liquids in contact.* The comparative constancy of the numbers obtained on the different occasions, 0·044, 0·052, 0·040, 0·040, 0·041 volt (each being the mean of some ten observations), proves that our method is practically accurate.
	Zinc sulphate, saturated at 15°·3 C.	,, ,,	14·5	+ 0·190	
11 A.M.	Copper sulphate, saturated at 15° C.	,, ,,	14·6	+ 0·052	
3.15 P.M.	,, ,,	,, ,,	16	+ 0·040	
7.35 P.M.	,, ,,	,, ,,	15	+ 0·040	
15/2/78	Copper sulphate, saturated at 15° C.	,, ,,	16	+ 0·041	
18/2/78	Zinc sulphate, saturated at 15°·3 C.	Copper sulphate, saturated at 15° C.	14	+ 0·090	
	,, ,,	Distilled water	15·5	+ 0·184	
19/2/78	Copper	Copper sulphate, saturated at 15° C.	15·6	+ 0·070	
	,,	Distilled water	16	+ 0·150	
	Zinc	,, ,,	17·4	− 0·105	
	,,	Zinc sulphate, saturated at 17° C.	17	− 0·457	
	Copper	Tin	17	− 0·456	
19/2/78	,,	Lead	18	− 0·542	
	Lead	Zinc	18·7	− 0·210	
	Zinc	Tin	19	+ 0·281	
	Copper	Iron	18	− 0·146	
20/2/78	Lead	Tin	17·8	+ 0·099	
21/2/78	Iron	Water	13	+ 0·148	
	Platinum	,,	14	+ 0·310	
	,,	Nitric acid	17	+ 0·672	Difficult to measure in consequence of the film which condensed on the gilt induction plates.
	Zinc	Distilled water with a slight trace of sulphuric acid.	17	− 0·241	
	,,	Distilled water with about $\frac{1}{5}$ per cent. of sulphuric acid.	18	− 0·289	
	,,	Distilled water with about $\frac{1}{3}$ per cent. of sulphuric acid.	19	− 0·312	
	,,	1 of sulphuric acid and 20 of distilled water by weight.	18·8	− 0·344	The value slowly increased from the formation of a salt on the surface of the zinc.
	,,	1 of sulphuric acid and 30 of distilled water by weight.	19	− 0·344	The zinc slowly blackened, but not so quickly as before.
22/2/78	,,	Solution sea-salt, sp. gr. 1·18, at 20°·5 C.	19	− 0·506	
23/2/78	Copper	,, ,,	15	− 0·475	
25/2/78	Lead	Distilled water	17	+ 0·184	
	,,	Strong sulphuric acid	17·8	+ 0·720	
26/2/78	Zinc	Sal-ammoniac, saturated at 15°·5 C.	14	− 0·637	
	Copper	,, ,,	15	− 0·396	
	,,	Strong sulphuric acid	17	+ 1·056	
	Lead	,, ,,	18	+ 0·720	
	Platinum	,, ,,	18	+ 1·424	
	,,	Lead	18	− 0·771	
27/2/78	Copper	Platinum	15	+ 0·238	
	Platinum	Zinc	16·4	− 0·981	
	,,	Iron	17	− 0·369	
	,,	Tin	17	− 0·690	

Date.	The following—	Has to the following—	At—	A contact difference of potentials, in volts.	Remarks.
			° C.		
28/2/78	Copper	Alum, saturated at 16°·5 C.	15	−0·243	Each of the numbers in the preceding column is the average of about ten observations.
	Zinc	,, ,,	17·8	−0·536	
	Lead	Sal-ammoniac, saturated at 17° C.	18	−0·189	
	Iron	,, ,,	18	−0·652	
	Lead	1 of sulphuric acid, 5 of distilled water.	17	−0·120	
1/3/78	,,	Distilled water	17	+0·167	
	,,	Alum, saturated at 16°·5 C.	16	−0·139	
	Iron	,, ,,	16	−0·653	
4/3/78	Lead	Distilled water	15·5	+0·163	
	,,	Solution sea-salt, saturated at 17° C.	17	−0·267	
	Iron	,, ,,	18	−0·605	
	Zinc	,, ,,	15·4	−0·624	
	Copper	,, ,,	16	−0·524	
5/3/78	Lead	Alum, saturated at 16°·5 C.	16	−0·139	
	Iron	,, ,,	16	−0·653	
6/3/78	,,	Mercury	19·4	+0·501	
	Copper	,,	19	+0·378	
7/3/78	,,	Brass	19	−0·151	
	Zinc	,,	18	+0·679	
	Iron	,,	19	+0·064	
	Lead	,,	18·5	+0·472	
	Tin	,,	18·5	+0·372	
	Platinum	,,	18·6	−0·287	
	,,	Solution sea-salt, saturated at 17° C.	18	−0·856	
	Tin	,, ,,	17·8	−0·304	
	,,	Sal-ammoniac, saturated at 15°·5 C.	18	−0·364	
8/3/78	Platinum	,, ,,	17	+0·057	
	,,	Alum, saturated at 16°·5 C.	17	+0·246	
	Tin	,, ,,	17	−0·225	
9/3/78	,,	Distilled water	14·5	+0·177	
	Iron	Mercury	16	+0·503	
	Lead	,,	15	+1·00 rapidly diminishing to 0	
11/3/78	Tin	1 of distilled water, 5 of sulphuric acid by weight.	16	−0·256	
	Brass	,, ,,	15	+0·016	
	,,	Distilled water	14	+0·207	
	,,	Solution sea-salt, saturated	14·5	−0·435	
	,,	Alum, saturated	14·5	−0·014	
	,,	Sal-ammoniac, saturated	14	−0·335	
12/3/78	Tin	Distilled water	16	+0·177	
	Platinum	Mercury	17	+0·204	

Here a number of apparently very discordant results were obtained when experimenting with mercury. The explanation at length was found to be due to the apparent contact difference of potentials between a metal and mercury as measured inductively, varying much with small alterations of temperature. Now as the mercury was redistilled in the laboratory between every two experiments to remove all traces of impurities, probably in some cases it had not become perfectly cold before a new experiment was made, and hence the apparent irregularities in the results. As, however, this investigation forms the subject of a future paper, it is unnecessary to say more now than to remark that in all the results mentioned in this communication, the mercury was not used until its temperature had become approximately that of the air.

13/3/78	Platinum	Mercury	16	+0·129	
	Copper	,,	16	+0·316	
14/3/78	,,	,,	15	+0·254	
	,,	Very clean mercury	15	+0·312	
15/3/78	Zinc	Saturated zinc sulphate	16	−0·420	
	Saturated zinc sulphate	Saturated copper sulphate	16	+0·095	
	Zinc	1 of distilled water, 3 of saturated zinc sulphate.	16	−0·444	

Date.	The following—	Has to the following—	At— ° C.	A contact difference of potentials, in volts.	Remarks.
15/3/78 .	Saturated copper sulphate .	1 of distilled water with 3 of saturated solution of zinc sulphate.	16	−0·102	Each of the numbers in the preceding column is the average of about ten observations.
	„ „	1 of distilled water with 1 of saturated solution of zinc sulphate.	16	−0·093	
	Zinc	Saturated zinc sulphate . .	16	−0·440	
	Copper.	Alum, saturated	15	−0·109	
As a small leakage was now observed between the needle of the electrometer and the quadrants this instrument was taken to pieces and cleaned.					
18/3/78 .	Copper.	Mercury	13·5	+0·351	
19/3/78 .	Iron	„	13·5	+0·473	
	Copper.	Alum, saturated	15	−0·145	
	Platinum	Strong sulphuric acid . .	15	+1·587	
	Lead	„ „	14·5	+1·252	
	Copper.	„ „	15	+1·170	
20/3/78 .	Platinum.	Mercury	15·5	+0·198	
	Brass	Distilled water	15	+0·256	
26/3/78 .	„	Sal-ammoniac, saturated at 15°·5 C.	17	−0·361	From the 26th March to the 8th April occupied with experiments on the contact difference of potentials of hot and cold mercury.
8/4/78 .	„	Zinc	15·7	−0·697	

IV.

We now endeavoured to measure the contact differences of potential of each pair of constituents in a LATIMER CLARK'S mercurous sulphate cell. First we tried mercury and mercurous sulphate paste, the mercury being put into one of our porcelain dishes and the mercurous sulphate paste into the other, the connexion between the two being made by a small glass siphon filled with the mercurous sulphate paste and the earth connexion by a platinum wire dipping into the paste in the porcelain dish. Many days were spent unsuccessfully at this experiment, and at similar ones which follow, on account of the thin layer of water which floated on the top of the mercurous sulphate, even after great care had been taken to remove it with a pipette. Often, therefore, instead of measuring the contact difference of potentials between a substance A and the mercurous sulphate paste, we obtained that of A with the paste plus that of the paste with water. At length, however, we obtained the following, each number given being, as usual, the mean of many experiments. Very great care was taken to have the materials chemically pure, the mercury being frequently redistilled; also to prevent any discrepancies in these results being caused by any possible electrification of the porcelain vessels themselves, they were thoroughly de-electrified after cleaning and before using.

It may be noticed that this difficulty experienced by the thin layer of water which floated on the mercurous sulphate paste is a very good example of the inaccuracies that must have been introduced by former experimenters using a moist blotting paper surface instead of the surface of a liquid itself. (See page 15, "Reasons for Incompleteness of Early Experimenters.")

Date.	The following—	Has to the following—	At—	A contact difference of potentials, in volts.	Remarks.
			°C.		
12/4/78 .	Mercury	Mercurous sulphate paste	15	−0·092	Connexion between the mercury and the paste made by a small glass siphon tube filled with the paste. Connexion with the earth made by a platinum wire dipping in the paste in the last four, and with an iron wire dipping into the mercury in the first case.
23/4/78 .	”	” ”	17	+0·405	
	”	” ”	17	+0·420	
24/4/78 .	”	” ”	19	+0·360	
25/4/78 .	”	” ”	17	+0·470	
13/4/78 .	Saturated solution zinc sulphate	” ”	16	+0·103	Connexion between the liquid and the paste formed by a tube filled with the paste, but neither were connected with the earth.
	” ”	” ”	17	+0·106	Zinc sulphate solution connected with the earth by a platinum wire, the connexion with the paste remaining as before.
23/4/78 .	” ”	” ”	18	+0·740	” ” ”
24/4/78 .	” ”	” ”	18	+0·900	” ” ”
	” ”	” ”	18	+0·720	” ” ”
27/4/78 .	” ”	” ”	19	+0·100	Connexion between the liquid and the paste formed by a very clean cotton wick previously soaked in the saturated solution of pure zinc sulphate. Connexion with the earth made by a platinum wire dipping into the porcelain vessels containing the zinc sulphate.
	” ”	” ”	19	+0·080	
	” ”	” ”	19	+0·120	
		” ”	19	+0·090	

In order to ascertain whether the high or the low value for the constant difference of potentials of zinc sulphate with mercurous sulphate was correct, an *incomplete* cell of zinc sulphate solution, mercurous sulphate paste, and mercury was formed, and the electro-motive force measured, the arrangement employed consisting of the zinc sulphate solution being put in one of the porcelain dishes, and in the other the mercury, the two being connected with a small beaker containing mercurous sulphate paste, and which did not act inductively on the induction plates. The connexion between the zinc sulphate and the mercurous sulphate was made by a clean cotton wick previously soaked in a saturated solution of the former, and the connexion between the mercury and the paste in the beaker by a small glass siphon tube filled with the latter. Earth connexion in the first experiment recorded was made by a platinum wire dipping into the mercury, afterwards by a platinum wire dipping into the zinc sulphate instead of into the mercury.

SATURATED zinc sulphate and mercury connected by mercurous sulphate paste.

Date.	Temperature.	Difference of potentials in volts.
24/4/78	18°	+0·725
25/4/78	17°	−0·330
27/4/78	19°	+0·770

Now the mean of the low set of values obtained previously with zinc sulphate and mercurous sulphate is +0·100, and of the high values +0·787; the mean of the values previously obtained with mercury and mercurous sulphate is +0·414, and a single value −0·092. In order to obtain the electro-motive force of the incomplete cell we must subtract the two latter from the two former, giving us

−0·314 or +0·879,

which are practically equal to the extreme values obtained directly for the electro-motive force of the incomplete cell. It therefore seems to be tolerably certain that the variable results obtained when experimenting with mercurous sulphate paste are due to the uncertainty of the nature of the bounding surface.

The mercurous sulphate paste and the saturated zinc sulphate solution were now boiled together, as is done in preparing Mr. Latimer Clark's constant element. Using this mixture in one porcelain vessel and mercury in the other, and joining them with a small glass siphon filled with the mixture, we obtained

		Volts.	Mean of.
9/5/78	Mercury has to Mixture, 22° C.	−0·210	10
11/5/78	„ „ „	+0·072	10

Wetting the surface of the mixture with a little saturated zinc sulphate solution brings up the answer to +0·340, the latter being the mean of ten observations all giving nearly equal results. The following contact difference of potentials was now measured.

		Volts.
11/5/78	Amalgamated zinc has to Mixture	−0·840
	„ „ „	−0·930
	„ „ „	−0·740

A little saturated zinc sulphate solution being poured over the mixture and taken out again carefully with a pipette altered the result to +0·520.

The following incomplete cell consisting of mercury and amalgamated zinc joined by the mixture of saturated zinc sulphate and mercurous sulphate paste previously referred to was now made, and the mean electro-motive force was found to be about +0·200 volt, the mercury being positive to the amalgamated zinc; this is roughly equal to the first value obtained with mercury and the mixture added to the last value obtained with the mixture and amalgamated zinc.

It was found that

			Volts.
26/4/78	Amalgamated zinc had to Copper	18° C.	+0·894

From which it follows that

Amalgamated zinc had to Platinum „ =+1·125

Therefore the electro-motive force of a LATIMER CLARK'S cell should be

$$\begin{array}{lr} & \text{Volts.} \\ \overline{(\text{Platinum, Mercury})} & =+0\cdot156 \\ \overline{(\text{Mercury, Mixture, Amalgamated zinc})} & =+0\cdot200 \\ \overline{(\text{Amalgamated zinc, Platinum})} & =+1\cdot125 \\ \hline & 1\cdot481 \end{array}$$

The real value of the electro-motive force of the cell being about 1·46 volts.

Date.	The following—	Has to the following—	At—	A contact difference of potentials, in volts.	Remarks.
			° C.		
26/4/78 .	Amalgamated zinc	Copper	18	+ 0·894	
	„ „	Tin	18	+ 0·463	
	„ „	1 of sulphuric acid with 5 of distilled water by weight.	18	− 0·429	
	„ „	„ „		− 0·431	
	„ „	1 of sulphuric acid with 10 of distilled water by volume.	18	− 0·358	Wiping the zinc surface increases the reading, showing that the half-liquid surface of the amalgam introduces some indefiniteness.
	„ „	„ „	18	− 0·424	
	„ „	Distilled water . . .	18	+ 0·090	Readings go down rapidly, but wiping the strip of amalgamated zinc dipping into the water brings them up again.
	„ „	Strong sulphuric acid .	18	+ 0·848	As the zinc was rapidly acted on slightly by the strong sulphuric acid, it required re-amalgamating after every few observations.
27/4/78 .	„ „	Saturated zinc sulphate	19	− 0·284	No falling off in the readings.
The induction plates were now regilt.					
12/5/78 .	Carbon	Zinc	21·5	− 0·045	
	„	Copper	21·5	− 0·370	
	„	Lead	21·5	− 0·858	
	„	Mercury	21·5	+ 0·092	
	Platinum . . .	„	21·5	− 0·143	
15/5/78 .	Carbon	Zinc	22	− 1·143	Carbon slightly warm, having been washed and dried by heating.
The experiments of carbon with liquids constitute a separate paper.					
21/5/78 .	Distilled water .	Sulphuric acid . . .		+ 1·319 rising to + 1·600	

The connexion between the liquids was made by a glass rod dipped previously into distilled water, and the legs of which rested one in each of the porcelain dishes. During each of the experiments the readings gradually rose, but if the glass rods were taken out, redipped in distilled water, and replaced, they returned to their original value. In case this might be due to the drying up of the film of water on the surface of the connecting glass rod, the connexion between the liquids after the next experiment was made in the following way. In addition to the wetted glass rod, the legs of which dipped into the two porcelain dishes, there were twisted round it a few clean cotton threads, which had been previously soaked in distilled water or in the non-acid liquid employed, alum, copper sulphate, &c. The threads were of such a length that one of their ends dipped into the dish containing the non-acid liquid, while the other descended nearly, but not quite, to the acid.

Date.	The following—	Has to the following—	At—	A contact difference of potential, in volts.	Remarks.
			° C.		
21/5/78 .	Sulphuric acid . .	Saturated zinc sulphate		−1·699	After long delay goes up slightly.
22/5/78 .	Distilled water .	Sulphuric acid ,, . .	22	+1·278 rising slightly	
	Saturated solution alum.	,, ,, . . .	22	+1·458	
	Saturated solution copper sulphate	,, ,, . . .	22	+1·269	Increased a very little in two hours.

V.

As a test of the accuracy of the measurements we may see how nearly for any three metals A, B, C, the sum

$$\overline{AB}+\overline{BC}+\overline{CA}$$

equals nought, as it ought to, since it is well known that in any compound metallic circuit at uniform temperature there is no electro-motive force. In order that the test may be the more rigid we will employ only the measured contact differences of potential, and not the calculated ones or those marked with an asterisk in the table of contact differences of potential of solids with solids,

			Volts.	Sum.
1.	$\overline{(\text{Copper, Lead})}+\overline{(\text{Lead, Platinum})}$	=	+0·229	
	$\overline{(\text{Platinum, Copper})}$	=	−0·238	−0·009
2.	$\overline{(\text{Copper, Zinc})}+\overline{(\text{Zinc, Lead})}$	=	−0·540	
	$\overline{(\text{Lead, Copper})}$	=	+0·542	+0·002
3.	$\overline{(\text{Iron, Brass})}+\overline{(\text{Brass, Copper})}$	=	+0·151	
	$\overline{(\text{Copper, Iron})}$	=	−0·146	+0·005
4.	$\overline{(\text{Zinc, Platinum})}+\overline{(\text{Platinum, Copper})}$	=	+0·743	
	$\overline{(\text{Copper, Zinc})}$	=	−0·750	−0·007
5.	$\overline{(\text{Zinc, Platinum})}+\overline{(\text{Platinum, Lead})}$	=	+0·210	
	$\overline{(\text{Lead, Zinc})}$	=	−0·210	0·000
6.	$\overline{(\text{Iron, Copper})}+\overline{(\text{Copper, Brass})}$	=	+0·059	
	$\overline{(\text{Brass, Iron})}$		−0·064	−0·005

Now if it be remembered that the various experiments with the different metals, although made at an average temperature of 18° C., were, as mentioned in the various tables, made at somewhat different temperatures the one from the other, it will be seen that the previous six sums cannot be absolutely nought. We may therefore regard them as sufficiently small to prove a considerable amount of accuracy in the experiments.

The numbers given in the two large tables for the contact differences of potential of solids with solids, solids with liquids, and liquids with liquids might be employed to build up the electro-motive forces of well known one and two fluid galvanic cells. As however the summation law referred to at the commencement of this paper may be considered as having been established in our two previous papers on the contact theory of voltaic action, it is not necessary in the present instance to take further examples of it.

In all our experiments two air contacts enter into our measurements, and the summation law gives no indication of the value of the contact difference of potentials at these air contacts. For example, suppose it be desired to measure the difference of potentials between two substances A and B in contact, either or both of which may be solid or liquid, then in reality what we measure is

$$\overline{(\mathrm{Air,\ A})}+\overline{\mathrm{AB}}+\overline{(\mathrm{B,\ Air})}.$$

If now we measure by the inductive method the difference of potentials between B and C in contact, then what we really obtain is

$$\overline{(\mathrm{Air,\ B})}+\overline{\mathrm{BC}}+\overline{(\mathrm{C,\ Air})},$$

and the sum of these two we have proved in all cases to be equal to what is obtained if A and C be joined by B and the difference of potentials between A and C measured. What really we have proved is therefore that

$$\overline{(\mathrm{Air,\ A})}+\overline{\mathrm{AB}}+\overline{(\mathrm{B,\ Air})}+\overline{(\mathrm{Air,\ B})}+\overline{\mathrm{BC}}+\overline{(\mathrm{C,\ Air})}=\overline{(\mathrm{Air,\ A})}+\overline{\mathrm{AB}}+\overline{\mathrm{BC}}+\overline{(\mathrm{C,\ Air})}.$$

And this would be the case whatever the values of the difference of potentials at the air contacts, provided they remained constant, so that

$$\overline{(\mathrm{B,\ Air})}=-\overline{(\mathrm{Air,\ B})}.$$

One way, and the way we hope shortly to employ, to enable us to determine the electro-motive force of contact, in volts, of a substance and a gas is by repeating all these exact contact experiments in different gases, for if we measure by our inductive method the contact difference of potentials of A and B in a gas G then we shall obtain

$$\overline{\mathrm{GA}}+\overline{\mathrm{AB}}+\overline{\mathrm{BG}},$$

and the difference between this and the result of the first measurement will be

$$(\overline{\text{Air, A}})+(\overline{\text{B, Air}})-\overline{\text{GA}}-\overline{\text{BG}}.$$

Consequently, if such experiments be made and the exact electro-motive forces of contact measured in a number of gases, we shall ascertain whether the contact difference of potentials of a substance and a gas differs much with different gases. Qualitative experiments in this direction have already been made with very interesting results by Mr. Brown, of Belfast, but his experiments differ from ours in not being quantitative.

If the gas measurements such as we have indicated be extended to a good Crookes' vacuum we may then possibly approximate to the real value of $\overline{\text{AB}}$, a contact difference of potentials of A with B, the value that we should obtain by a measurement of the Peltier effect. It is therefore our purpose to extend these quantitative measurements not only to other gases than air but to a Crookes' vacuum, as well as to measure the Peltier effects for a number of contacts of dissimilar substances.

We have to thank two of the students of telegraphic engineering at the Imperial College of Engineering, Japan, Messrs. T. Iwata and N. Nakayama, for considerable assistance rendered us in the carrying out of this somewhat laborious investigation.

MEAN contact differences of potential in volts; solids with liquids, and liquids with liquids.

		Carbon.	Copper.	Iron.	Lead.	Platinum.	Tin.	Zinc.	Amalgamated zinc.	Brass.	Mercury.	Distilled water.	Alum solution, saturated at 15° C.	Copper sulphate solution, saturated at 15° C.	Zinc sulphate solution, saturated at 15°·3 C.	Zinc sulphate solution; specific gravity, 1·125 at 16°·9 C.	1 distilled water, 3 saturated solution zinc sulphate.	Strong nitric acid.
	Mercury	·092	·308	·502	..	·156	..	..	..	..	..	..	..	..	..	..	..	..
	Distilled water	·01 to ·17*	·269 to ·100	·148	·171	·285 to ·345	·177	−·105 to +·156	·100	·231	..	..	..	+·043	·164	..	..	..
Solutions.	Alum, saturated at 16°·5 C.	..	−·127	−·653	−·139	·246	−·225	−·536	..	−·014	..	..	..	..	..	..	..	..
	Copper sulphate, saturated at 15° C. . . .	..	·070	..	..	..	..	..	..	..	..	−·043	..	..	·095	..	·102	..
	Copper sulphate solution; specific gravity, 1·087 at 16°·6 C. .	..	·103	..	..	..	..	..	..	..	..	..	..	..	..	·090	..	..
	Sea salt; specific gravity, 1·18 at 20°·5 C. . .	..	−·475	−·605	−·267	−·856	−·334	−·565	..	−·435	..	..	..	..	..	..	..	..
	Sal ammoniac, saturated at 15°·5 C. . . .	..	−·396	−·652	−·189	·057	−·364	−·637	..	−·348	..	..	..	..	..	..	..	..
	Zinc sulphate, saturated at 15°·3 C. . . .	..	..	..	..	..	..	−·430	−·284	..	..	−·164	..	−·095	..	..	..	..
	Zinc sulphate solution; specific gravity, 1·125 at 16°·9 C. . . .	..	..	..	..	..	..	−·238	..	..	..	..	..	..	..	..	..	..
	1 distilled water, mixed with 1 saturated solution zinc sulphate .	..	..	..	..	..	..	..	..	..	..	..	..	−·093	..	..	..	..
	1 distilled water, mixed with 3 saturated solution zinc sulphate .	..	..	..	..	..	..	−·444	..	..	..	..	..	−·102	..	..	..	..

* Depending on the carbon.

MEAN contact differences of potential in volts; solids with liquids, and liquids with liquids—*continued.*

		Carbon.	Copper.	Iron.	Lead.	Platinum.	Tin.	Zinc.	Amalgamated zinc.	Brass.	Mercury.	Distilled water.	Alum solution, saturated at 15° C.	Copper sulphate solution, saturated at 15° C.	Zinc sulphate solution, saturated at 15°·3 C.	Zinc sulphate solution; specific gravity, 1·125 at 16°·9 C.	1 distilled water, 3 saturated solution zinc sulphate.	Strong nitric acid.
Dilute sulphuric acid.	Distilled water, with a slight trace of sulphuric acid . . .	..	..	..	..	..	..	−·241	..	..	..	..	..	..	..	..	..	·078
	Distilled water, with about one-fifth per cent. of sulphuric acid	..	..	..	..	..	..	−·289	..	..	..	..	..	..	..	..	..	..
	Distilled water, with about one-third per cent. of sulphuric acid	..	..	..	..	..	..	−·312	..	..	..	..	..	..	..	..	..	..
	By weight— 20 distilled water, 1 strong sulphuric acid . . .	..	..	..	..	..	..	−·344	..	..	..	..	..	..	..	..	..	..
	By volume— 10 distilled water, 1 strong sulphuric acid . . .	About −·035	..	..	..	..	..	..	−·358	..	..	..	..	..	..	..	..	..
	By weight— 5 distilled water, 1 strong sulphuric acid . . .	..	..	..	..	..	..	..	−·429	..	..	..	..	..	..	..	..	..
	1 distilled water, 5 strong sulphuric acid . . .	·01 to ·3	..	..	−·120	..	−·256	..	..	·016	..	..	..	..	..	..	..	..
Concentrated.	Sulphuric acid . . .	·55 to ·85*	1·113	..	·720 to 1·252	1·600 to 1·300	..	..	·848	..	..	1·298	1·456	1·269	1·699	..	..	..
	Nitric acid	..	..	..	..	·672	..	..	..	..	..	..	..	..	..	..	..	..
	Mercurous sulphate paste	..	..	..	..	..	..	..	..	..	·475	..	..	..	..	..	..	..

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* Depending on the carbon.

The average temperature at the time these experiments were made was about 16° C. All the liquids and salts employed were chemically pure; the solids, however, were only commercially pure. The numbers in a vertical column below the name of a substance are the differences of potential, in volts, between that substance and the substance in the same horizontal row as the number, the two substances being in contact. Thus lead is positive to distilled water, and the contact difference of potentials is 0·171 volt.

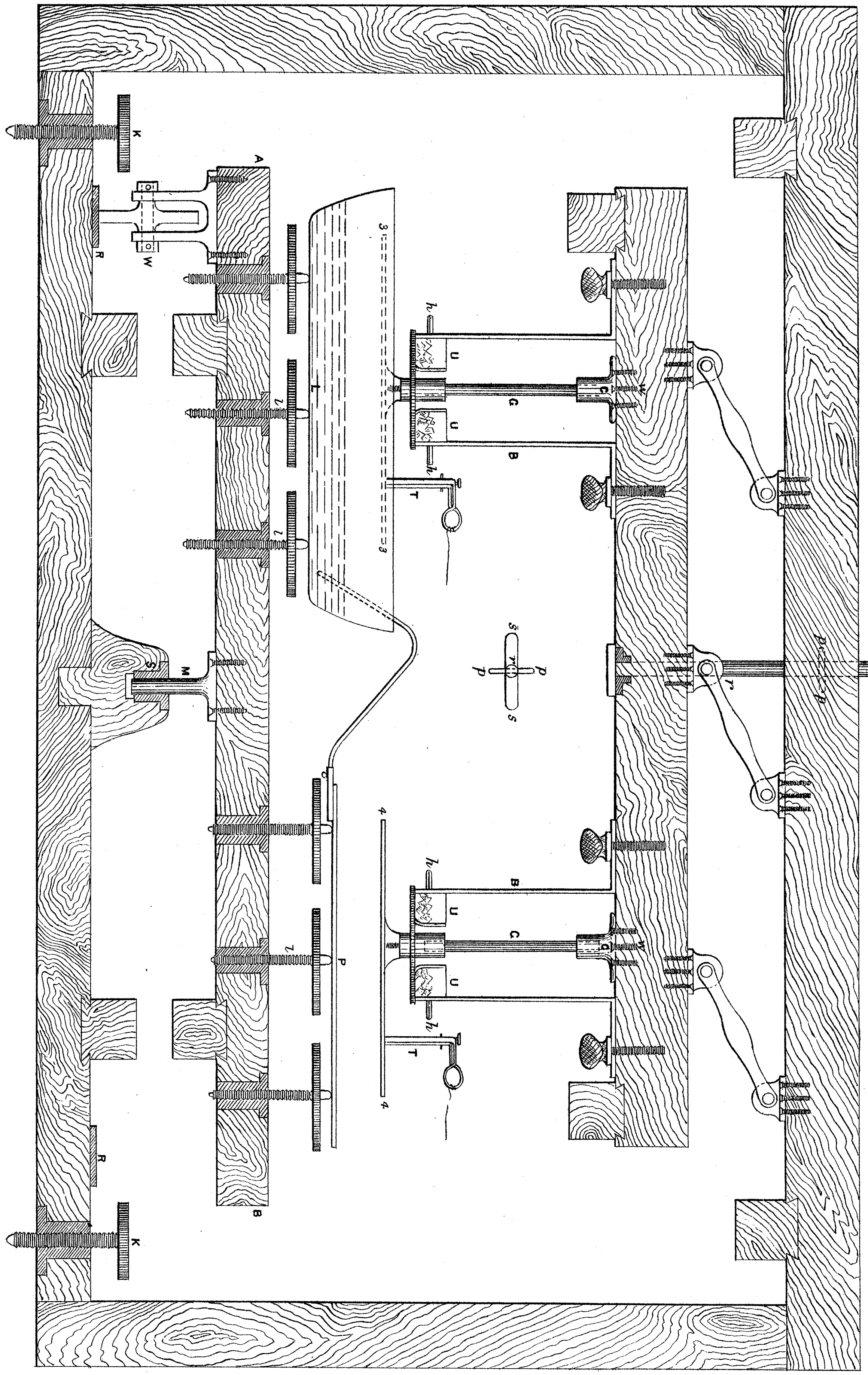
MEAN contact differences of potential in volts; solids with solids.

	Carbon.	Copper.	Iron.	Lead.	Platinum.	Tin.	Zinc.	Amalgamated zinc.	Brass.	
Carbon	0	·370	·485*	·858	·113	·795*	1·096	1·208*	·414*	The average temperature at the times these experiments were made was about 18° C.
Copper	— ·370	0	·146	·542	— ·238	·456	·750	·894	·087	
Iron	— ·485*	—·146	0	·401*	— ·369	·313*	·600*	·744*	—·064	
Lead	— ·858	—·542	—·401*	0	— ·771	—·099	·210	·357*	—·472	
Platinum . . .	— ·113*	·238	·369	·771	0	·690	·981	1·125*	·287	
Tin	— ·795*	—·456	—·313*	·099	— ·690	0	·281	·463	—·372	
Zinc	—1·096	—·750	—·600*	—·210	— ·981	—·281	0	·144	—·679	
Amalgamated zinc	—1·208*	—·894	—·744	—·357*	—1·125*	—·463	—·144	0	—·822*	
Brass	— ·414	—·087	·064	·472	— ·287	·372	·679	·822*	0	

The numbers without an asterisk were obtained directly by experiment, those with an asterisk by calculation; using the well-known assumption that in a compound circuit of metals all at the same temperature there is no electromotive force.

The numbers in a vertical column below the name of a substance are the differences of potential, in volts, between that substance and the substance in the same horizontal row as the number, the two substances being in contact. Thus lead is positive to copper, the electro-motive force of contact being 0·542 volt.

The metals were those of commerce, and therefore not chemically pure.



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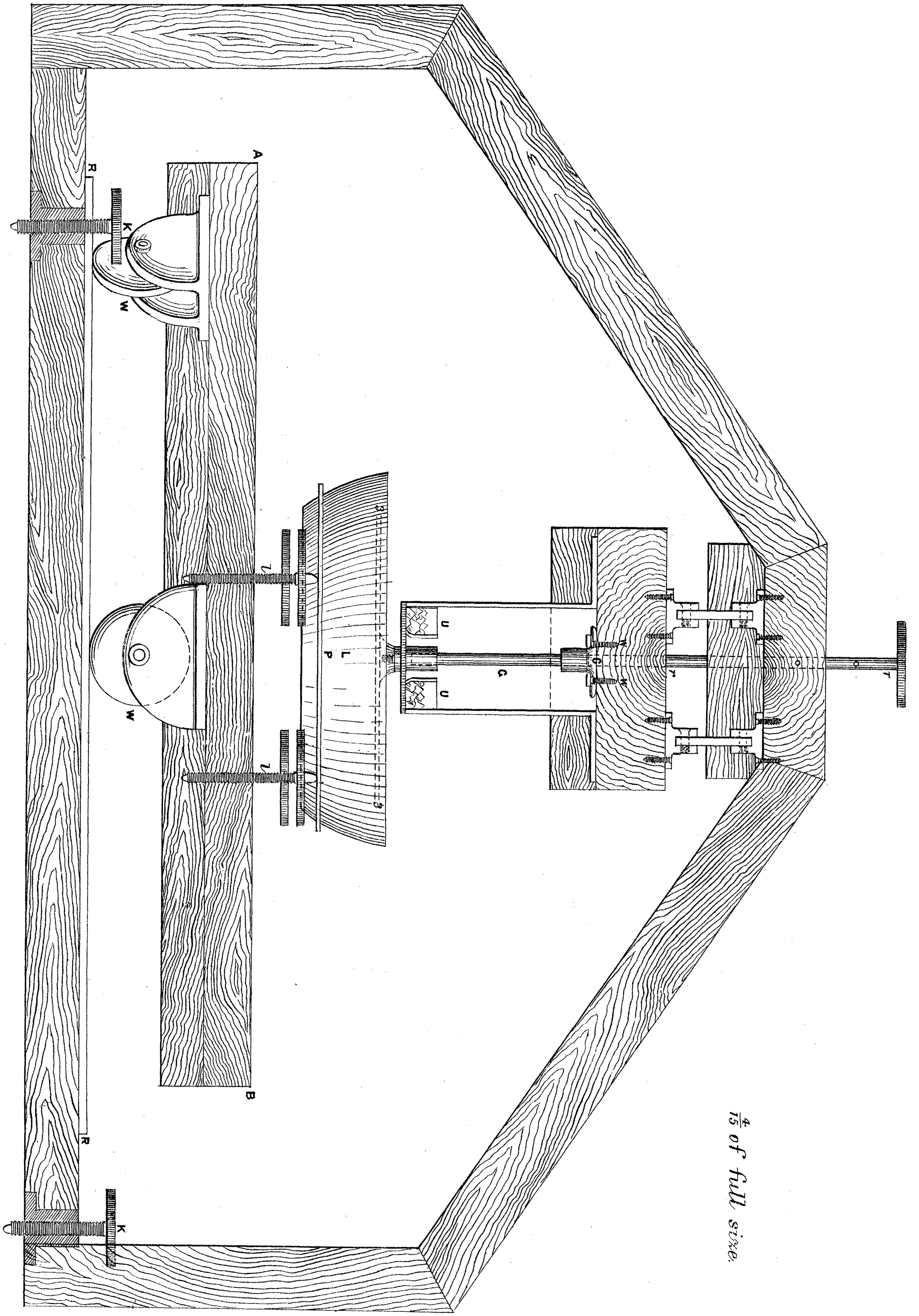

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