Philosophical Magazine Series 3 (1832-1850)

Taylor & Francis
Taylor & Francis Group

Philosophical Magazine Series 3

ISSN: 1941-5966 (Print) 1941-5974 (Online) Journal homepage: http://www.tandfonline.com/loi/tphm14

XIX. On some of the phænomena and laws of action of voltaic electricity, and on the construction of voltaic batteries, &c.

Christopher Binks & J.F. Daniell Esq. F.R.S.

To cite this article: Christopher Binks & J.F. Daniell Esq. F.R.S. (1838) XIX. On some of the phænomena and laws of action of voltaic electricity, and on the construction of voltaic batteries, &c. , Philosophical Magazine Series 3, 13:80, 135-145, DOI: 10.1080/14786443808649542

To link to this article: http://dx.doi.org/10.1080/14786443808649542

Published online: 01 Jun 2009.

Submit your article to this journal

Article views: 2

View related articles

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=3phm20

Download by: [University of California Santa Barbara] **Date:** 20 June 2016, At: 14:49

And by 1·63447 for the quantity of sulphate of barytes which it produces by precipitation.

2. To find the weight of the components and equivalents of any quantity of sulphate of potash, multiply it

by 0·449019 for the potassium it contains.
0·550981 for the sulphur and oxygen.
0·54067 for the potash.
0·45933 for the sulphuric acid.
And by 1·33633 for the quantity of sulphate of barytes which it produces by precipitation.

Example.—In the analysis of a sample of commercial alum, we have proceeded so far as to have nothing to separate but sulphate of potash from sulphate of soda, both of which alkalies have been detected by previous testing.

a. The mixture of sulphates weighs 7 grains.
b. It produces by precipitation 10·54687 grains of sulphate of barytes.
c. The weight of the mixture *a*, 7 grains, multiplied by 1·33633 gives 9·35431.
d. 9·35431 subtracted from 10·54687 gives 1·19256.
e. 1·19256 divided by 0·29814 gives 4.
f. The weight of the sulphate of soda in the mixture *a* is 4 grains.
g. The weight of the sulphate of potash is 3 grains.

The quantity of sodium equivalent to the sulphate of soda, is . . . . 4 × 0·326095
The equivalent of soda, is . . . . 4 × 0·43819
The quantity of potassium equivalent to the sulphate of potash, is . . . . 3 × 0·449019
The equivalent of potash, is . . . . 3 × 0·54067

The atomic weights employed in these calculations are those of Berzelius.

Glasgow, March 19, 1838.

XIX. *On some of the Phænomena and Laws of Action of Voltaic Electricity, and on the Construction of Voltaic Batteries, &c. By* Christopher Binks. *A second Communication, addressed to* J. F. Daniell, *Esq. F.R.S., &c., Professor of Chemistry in King's College, London. Part the Second.*

[Continued from Part i. p. 75.]

Section IV.

73. THE ultimate object of the following experiments is to determine on the most advantageous construction of the voltaic battery; that is, such a construction as shall com-

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

mand its greatest effects, of any kind, with the least expenditure of materials.

The process by which this end is attempted to be reached, is by first determining the laws of action affecting the operations of *single* arrangements; and afterwards, when this is completed, extending the examination into the phænomena of *compound* ones.

74. These examinations are, in the first instance, restricted to the phænomena of arrangements in which sulphuric acid, diluted, is employed as the exciting agent. It is then sought to determine, by extending the inquiry into the less familiar operations of other kinds of arrangement, such, for example, as include the sulphate of copper as an element, whether the same results can be obtained under these as under the former conditions, or in what respects they differ; the chief object through all being the application of the principles, thus sought to be established, to the construction of the battery.

To determine the comparative amount of voltaic action induced in any single arrangement by acid solutions of different degrees of strength.

75. The plates of the voltaic couple here used were of an equal size, each presenting an entire surface of four square inches to the action of the acid mixture; they were separated from one another by a distance of half an inch: this, as well as every other attendant condition, being, of course, maintained exactly alike in every trial. The acid mixture was composed, in the first instance, of one part by measure of common sulphuric acid, and 100 parts of water; and afterwards of larger proportions of acid, as shown in the subjoined table, in which the column of densities represents the actual strength of the mixture with the greater nicety. The amount of action in each case is estimated by the weight of zinc lost in a given equal time.

76. Table of the effects of acid mixtures of different degrees of strength. (No. 4.)

Parts by measure of Sulph. acid in 100 of water.	Specific gravity of the mixtures at Temp. 65° Fahr.	Quantity of Zinc in grains lost in a given time, or 10 minutes.	Effects compared with the first Result.
1	1·013	1·6	= 1
3	1·034	2·6	= 1·6
6	1·063	3·1	= 1·9
9	1·090	3·9	= 2·4
12	1·117	4·8	= 4·0
15	1·137	5·1	= 4·4
18	1·164	4·7	= 2·9
21	1·190	4·5	= 2·8
24	1·213	3·9	= 2·4

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

77. The comparative effects of these different acid solutions were then sought for under two distinct modifications of the experiments as just stated: first, when the elementary plates of the couple used were of a different size from those by which the results in the above table had been obtained; and secondly, when the two plates of the couple were placed at a different distance from one another than that stated above; but whilst every other attendant circumstance, in either case, was maintained precisely the same as at first.

78. For the former purpose a smaller couple was taken and immersed in the different acid mixtures successively, as before; when the weight of zinc lost, in the same time, was of course less in the aggregate than when the larger couple was employed; but the difference between the amount of loss occasioned by the different acid mixtures was precisely after the same rate as had been previously determined for the other couple, and as that rate is stated in the fourth column of the above table.

79. And when a couple was employed of the same size as the first (75.), but with its plates placed at a greater distance from one another than in either of the previous instances, in like manner to the last, the action in the aggregate was reduced by reason of the greater distance, but the comparative rate at which each acid mixture acted upon this couple was precisely the same as had already been found in the two previous instances.

80. It appears, therefore, that the comparative effects of these different acid solutions are the same whatever may be the size of the voltaic couple, or whatever may be the distance between its elementary plates; and the above table, therefore, represents the comparative rate in which dilute sulphuric acid of different degrees of strength acts upon any voltaic arrangement.

81. A review of this table shows, 1st, that the greatest amount of action induced in any arrangement by dilute sulphuric acid takes place when the mixture is in the proportion of about 15 parts by measure of ordinary acid, and 100 of water; or of the average specific gravity of 1·140: 2ndly, that the rate of increase of action is neither the same as the rate of increased proportions of the acid, nor of the specific gravity of the mixture, but occurs in some other simple rate, bearing however no very obvious relation to any apparent attendant circumstances.

82. The acid mixtures which will subsequently be employed in these experiments are the first four of the above table.

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

Section V.

To determine the comparative amount of action in any single voltaic arrangement when its plates are placed at different distances from one another.

83. The two plates of a voltaic couple may be either of an equal size, or unequal, and the difference in size which may exist between the two is unlimited.

The couple itself, considered as a couple, may either be large or small also, to an unlimited extent.

The distance between the two plates of any couple, whatever its size, or whatever the relative proportions of the plates, may also be varied without limitation.

The acid mixtures also, in which any voltaic couple is made to operate, may be of any required degree of strength.

84. The immediate object in hand is to determine the effects of distance; but these must be sought for under every possible condition of the arrangements as regards the size of the couple used, the relative proportions of its plates, and the strength of the exciting acid.

To determine the law of distance when the two elementary plates are of an equal size.

85. (*a*). A voltaic couple having on each plate an entire surface of 6 square inches, had its plates placed successively at the distance from one another of $\frac{1}{4}$ of an inch, 4 inches, and 24, and the quantity of hydrogen by measure, yielded in a given time at each of these positions, was respectively equal to

84. 58 and 39 { in 50ths of a cubic inch.

86. (*b*). Another couple, exactly one half the size of the last, yielded under precisely the same conditions the respective measures of

46. 31 and 21 { in 50ths of a cubic inch.

87. (*c*.) Another couple, one fourth the size of the first one, and placed under the same circumstances, yielded the numbers

26. 18 and 12 { in like measures of hydrogen in the same time.

88. These experiments determine that whatever may be the size of the couple itself, its elementary plates being *equal*, the influence of distance upon its action is the same.

89. The total amount of action under condition *a*, at whatever position it is taken, greatly exceeds the total amount of action under *b* or *c*; but the ratio of the difference between

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

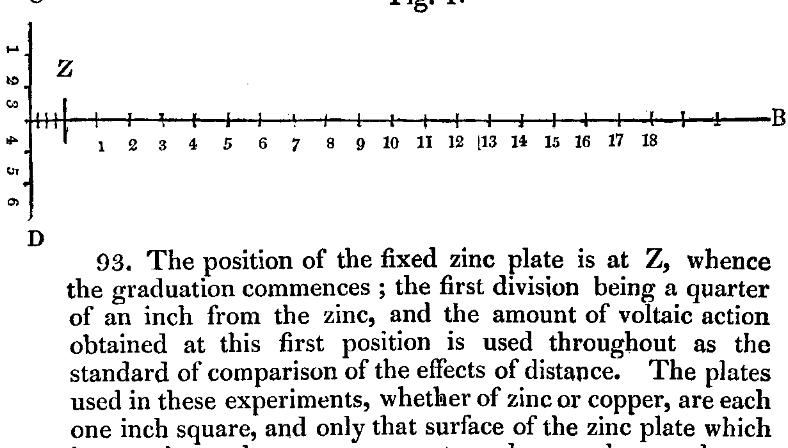
the amount of action obtained at any of the three different positions in *a* is the same as the ratio found for these positions respectively in *b* and *c*.

90. 12 : 26 (in *c*) : : 21 : 45·5 (in *b*) being as near an approach to 46, the real number, as could be looked for in actual experiment; and the same ratios are maintained with no material alteration throughout.

91. These preliminary trials show, therefore, that I may select any-sized couple which may appear most convenient for the following more extended experiments upon the effects of distance; and that the results obtained by the couple now to be used will be true equally for this one condition and for every other as regards the dimensions of the couple employed.

92. To facilitate references to positions and numbers in the following experiments, let the mass of liquid in which they are conducted be represented by the following diagram, in which the horizontal line is supposed to pass through the centre of the mass contained in the graduated trough already described (36. p. 64), and the vertical line, also passing through the centre, to represent its depth.

Fig. 1.



93. The position of the fixed zinc plate is at Z, whence the graduation commences; the first division being a quarter of an inch from the zinc, and the amount of voltaic action obtained at this first position is used throughout as the standard of comparison of the effects of distance. The plates used in these experiments, whether of zinc or copper, are each one inch square, and only that surface of the zinc plate which is opposite to the copper presents a clear amalgamated surface; the contrary surface, as well as the connecting wire, being well covered with wax to preclude the contact of the acid, and to restrict its action to the clear amalgamated surface alone. But both surfaces of the copper are clear, and consequently brought into operation.

94. The experiments are first gone through with an acid mixture composed of 1 part by measure of sulphuric acid, and 100 of water, its specific gravity being 1·013; and are after-

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

wards repeated with other acid mixtures of the strength stated in the subjoined table. The copper plate being moveable at pleasure, is fixed, first, at the nearest position to the zinc, and afterwards in succession at each succeeding position marked upon the horizontal line. All other particulars affecting such experiments have already been sufficiently adverted to throughout section 3rd, and the observances there stated as necessary being fully discussed in that section, will in no instance be restated or again referred to in the course of the details that now follow. The amount of voltaic action obtained at each position, is estimated by the length of time in seconds required for the production of $\frac{1}{10}$th of a cubic inch of the hydrogen which is evolved from the copper plate.

95. Table showing the effects of distance, (No. 5.), in which the comparative amount of voltaic action is estimated by the length of time in seconds required for the production of one measure of gas.

Distance, in inches, of the two plates from one another.	Proportions by measure of the acid and water, and specific gravity of the mixtures. Temperature 55° Fahrenheit.			
	1 part acid, 100 water. Sp. gr. 1·013.	3 parts acid, 100 water. Sp. gr. 1·034.	6 parts acid, 100 water. Sp. gr. 1·063.	9 parts acid, 100 water. Sp. gr. 1·090.
	Time.	Time.	Time.	Time.
$\frac{1}{4}$	180″	85″	60″	45″
1	245	135	110	95
2	370	170	120	120
4	375	155*	125	125
6	345*	170	120*	125
8	400	170	130	125
10	460	170	130	140
12	485	185	130	145
14	515	200	145	145
16	530	205	145	145
18	545	215	165	130*
20	590	220	165	145
22	640	230	165	145
24	655	235	165	145
26	660	265	190	145
28	680	295	190	145
30	690	290	190	170
32	790	300	190	200
34	805	310	220	210
36	825	360	220	170
38	885	365	200	170
40	900	370	230	170
42	910	370	240	170
44	920	370	240	170

96. The results which are registered in this table were

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

those which were obtained the latest of all from the experiments gone through to determine the law of distance. No reliance was placed upon the first attempts made to determine this question, nor upon any, till by innumerable repetitions of experiments, and a perfect familiarity with the precautions necessary to be observed in their course, I had become assured that the whole were accurately performed, and that by the regulations adopted every possible or probable source of error likely to arise from the method here employed was precluded. The above results may therefore be considered to show correctly the peculiar phænomena attendant upon voltaic action, in the kind of arrangement here brought into action.

97. The first consideration which naturally follows a review of the above table, is that of the singular difference in the effects of distance upon voltaic action; as those effects are determined by this method of experimenting, and those already deduced by the indications of the magnetic needle. Referring to the nearest authority at hand, I find that the law of distance as determined by the needle is as follows:

98. "The deflection produced by a pair of plates in an acid solution of uniform strength varies inversely as the square root of the distance between them, a law previously established by Cumming. Thus, if a plate of zinc be placed successively at 1, 4 and 9 inches from a plate of copper, the deflecting powers will be in the ratio of 3, 2, and 1; that is, only twice as great at 1 inch as at 4, and only three times as great at 1 inch as at 9*."

99. As the magnetic galvanometer, of whatever construction, is employed as a measurer only of comparative quantities of electricity, and not of the absolute quantity evolved by any arrangement, it is in this relation merely that the indications of that instrument are now brought into comparison with those afforded by the method here used for the same purpose. When the quantities of electricity evolved at the several distances are estimated by the indications of the needle (that is, by their power to deflect the needle, in opposition to the power of the earth's magnetism, or to any other power substituted for it, as in the torsion galvanometer) then those quantities differ from one another by the rate just stated; but when estimated directly by the quantities of matter expended in producing them (on which principle the plan now used is founded), then they differ from one another at these several distances by a rate totally different from that de-

* Dr. Ritchie.

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

termined by the indications of the needle; thus placing the results of these two methods of estimating such effects completely at variance.

100. On referring to the above table it will be seen that no such law, nor any making the most remote approach to it, can be deduced from the results obtained by the present method of testing such phænomena.

101. The difference between the degrees of voltaic action obtained at the first position, and at the last, in the first column of this table, amounts only to the difference between 5 and 1, nearly; the voltaic action yielded at the first or nearest position being about five times greater than that yielded at the most remote. The distance from one another of the two plates at the first position is $\frac{1}{4}$ of an inch, and at the last is 44 inches, and these distances comparatively are as 1 and 44×4 or 176; the distance of the two plates from one another being 176 times greater at the last than at the first position.

102. Now had the law of distance found by the method here employed been the same as that determined by the magnetic galvanometer, we should have had the amount of action at the first position greater than that at the last, by the square root of the difference in their distances, or by the square root of 176; but in actual experiment it is only 5 times greater instead of about 13 times, in round numbers.

103. This discrepancy in the results obtained by these two methods, in neither of which there is reason to doubt the correctness of the observations, leads to the suspicion that either the one or the other of them is an incorrect measure of comparative quantities of voltaic electricity, or that both are unfit to be applied to that purpose; or at least are imperfect in their indications; a conjecture which has given rise to the inquiry contained in the second part of this paper as already mentioned (13.). A comparison between these two methods will then be instituted, when it will be shown that there is reason to conclude that the needle does not take cognizance of the *whole* effects resulting from voltaic action, but only of a part of its attendant phænomena; and when also an attempt will be made, experimentally, to distinguish between the two kinds of action induced by such voltaic arrangements, of which each method is suspected to be respectively the measurer. But not further to anticipate that inquiry at this moment, I proceed to examine some other results afforded by this table.

104. The difference between the amount of action obtained at the first and last positions has been seen to be as 5 to 1

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

with the acid mixture of the first strength; but it will be observed that this difference is progressively less as the mixture increases in strength. With the second mixture the difference is about $4\frac{1}{4}$ to 1; with the third it is 4 to 1; and with the fourth it is $3\frac{3}{4}$ to one nearly—showing that the stronger the acid, or the greater its density, or the greater the activity of the generating agents, the less marked are the effects, in decreased action, caused by the difference in the relative distance of the two plates.

105. Again, it is observable that the decrease in action occasioned by increased distance does not proceed at a rate corresponding to that increase in distance, as the copper plate is removed successively to each position from end to end. The greatest effects of this removal through an equal distance occur in the first two or three positions in every column; after which the effects of removal are much less marked throughout.

106. At those positions distinguished by an asterisk, there occurs a slight increase of action compared with the amount immediately preceding it, instead of a decrease as might have been expected. A similar anomaly, though not to the same extent, presents itself at several successive positions throughout every column, where the voltaic action appears to alternate, or to be suspended between increase and decrease in its amount, compared with the amounts obtained at the adjacent positions. Taking the first column by way of example, it will be seen that scarcely in any two instances does the removal of the plate through an equal distance produce an equal effect in the resulting action. The difference in effect caused by removing the plate from 8 inches to 10 amounts to 60″, whilst that yielded by the change from 10 to12 amounts only to 25″. The following table, derived from the first column above, will serve to show the nature and extent of this alternation more clearly. The first line contains the successive distances to which the plate is removed; the second, the difference between the amount of decrease obtained at each position and the one preceding it.

Table (No. 6.)

107. (Distance of the two plates from one another, by successive equal steps of two inches each).

10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44.

(Amount of decrease resulting from increased distance, obtained at each position, compared with the decrease at that immediately preceding).

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

60″, 25″, 35″, 15″, 15″, 45″, 50″, 15″, 5″, 20′, 10″, 100″, 15″, 20″, 60′, 15′, 10″, 10″.

108. This peculiar result is equally, or even more, obvious in the remaining columns of the former table, No. 5; and it is observable that the particular positions at which the alternation occurs are different in each. In the latter columns, in which (by reason of the greater activity of the action, the time over which each experiment extends is progressively shorter), the difference in many instances is so little, if any, as to be scarcely discernible; and they consequently present at several positions a series of numbers equal in amount and following each other in succession.

109. It was first attempted to arrive at the law of distance, by the results afforded at fewer and more remote positions of the plates, than those given in the above tables; for instance, the positions were taken at ¼ of an inch, 1 inch, 4, 12 and 24 inches; and the amounts of action obtained at these presented a very regular decrease corresponding to the increase in distance. But some occasions arose, in which it became necessary to test the action of the plates at other positions intermediate to those already tried, when the results obtained were occasionally so greatly at variance with any anticipated by the former trials, that it became necessary to carry the copper plates through shorter successive positions from end to end, to determine whether or not those which had thus been accidentally detected were merely the result of accident, or of some error in the method of observation, or were in fact part of the general phænomena attendant upon the voltaic action, as it takes place in the kind of arrangements here brought into operation. Hence the long columns of observations contained in the former table No. 5, in the place of which it might have been presumed beforehand, that a very few experiments comparatively would have been equally competent to decide the point in question, viz. the effects of distance.

110. I should have continued, as at first, to attribute these unlooked for results to some accidental circumstance, had not their invariable recurrence under like conditions of experiment, shown that they had some connexion, whatever that might be, with the general phænomena attending these operations, and were due neither to inaccuracy nor to accident.

111. It might be suspected, among other attempts to account for it, that the plan here resorted to (see 64) of changing the zinc plate after every two or three immersions, might have some share in producing this apparent alternation in effect. But the same results follow precisely if one plate only

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016

be used throughout. Or, again, that it might arise in part from the practice of determining the measure of hydrogen, sometimes by a division near the top of the long tubular meter here used, and sometimes at the bottom of it; under which different circumstances, the volume of an equal measure of gas would be a little different by reason of the varying strain upon its elasticity. But the trifling variation that might have arisen from this cause, was also avoided by invariably refilling the meter after each single experiment, so that the $\frac{1}{10}$th of a cubic inch of gas was always under a uniform pressure. But in short, after the utmost attention to the subject, I could discover no peculiarity attending this particular method of experimenting to which this effect could be attributed, with the most remote appearance of probability.

112. Such alternation then must be considered as a part of the general phænomena attending operations of this kind, however unexpected or inexplicable it may be in the present state of our acquaintance with the subject generally.

113. I was unwilling in the first instance to register the results as they stand above, expecting that every succeeding repetition of experiment would show a greater regularity in the operation of the arrangements; or such a regularity as, by preconceived notions, derived chiefly from the law above quoted (98), I had been led to anticipate. It is obvious however, that the operations brought into exercise by voltaic arrangements of this description at least, are of a mixed and complicated kind, influenced in some parts by causes as yet undetected, and are certainly such as cannot be fully included in any law similar to that just alluded to. The removing of the plates further from one another does not affect their action, merely by decreasing its amount, much less does that decrease occur in the ratio stated in that law.

114. Perceiving at this stage of the inquiry no satisfactory or probable way of accounting for this peculiar result, I proceed on to the further experiments, in which it will be seen that other indications of the same phænomenon can be detected in every direction, whether or not the results finally obtained may be considered in every respect as contributing satisfactorily to its explanation.

[To be continued.]

Downloaded by [University of California Santa Barbara] at 14:49 20 June 2016