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Table V. shows that the degree of accuracy did not materially differ under the three varying conditions. The magnet therefore does not appreciably interfere with the measurements. The mean error of all three positions of the magnet is 0.22 per cent., which is very low.

In conclusion, I may mention that a smaller model of the galvanometer, intended for practical use, is now being made, which will contain all the recent improvements, viz. the fine-wire coil besides the solid ring, the tangent-scale, the secant-marks, the air-damping, and the compensating-magnet. The latter will be so arranged that the "constant" will be considerably increased as compared with that due to the earth's magnetism alone; thus the needle should be much less influenced by outer disturbances than before.

Woolwich, June 1883.

XIV. *The Influence of Current, Temperature, and Strength of Electrolyte on the Area of Electrification.* By ALFRED TRIBE, *F.Inst.C., Lecturer on Chemistry in Dulwich College.*

IN the study of the subject of this paper I have employed the "electro-chemical method" described by me in the *Philosophical Magazine*, 1881, xi. p. 446. It will be remembered that by this method images of the electrifications produced on metallic plates are rendered evident to the eye, and also that I have almost invariably employed as *analyzers* plates of silver, and as the electrolyte a solution of copper sulphate. The areas of the electrifications were found by measuring the copper and peroxide of silver respectively deposited or formed on the analyzing plate, the copper giving the area of the — electrification, and the silver peroxide that of the + electrification. The sum of the two electrifications subtracted from the total area of the plate, it will be seen, gives the area of non-electrification, *i. e.* the intermedial space, or that part of the plate which separates the + and —, and where the electromotive force is incapable of initiating electro-chemical action. These measurements are of course only relative.

The following conditions were common to the several experiments to be described:—an electrolytic cell 120 millim. broad, 128 deep and 305 long, filled to within 8 millim. with copper-sulphate solution; copper electrodes of the same area as the ends of the cell; a plate (analyzer) of fine silver, 67 × 7 millim., weighing 0.75 gram, placed lengthwise midway between the electrodes, and between the surface of the liquid and the bottom of the cell. The time of each experiment was six minutes. The diagram shows the general

arrangement—B being the battery; G, tangent-galvanometer; R, rheostat; and S, switch.

I. *Influence of Current.*—In this series of experiments a 5-per-cent. solution of copper sulphate was employed. The results obtained and the current employed are set out in the following table. The numbers refer to lengths in millimetres of the several electrifications and intermedial spaces.

Current in ampères.	— electrifi- cation.	Intermedial space.	+ electrification.	+ referred to — as unity.
0.1	4	...	nil.	.....
0.2	13	...	signs at end edges.	.....
0.4	18	30	19	1.05
0.6	18	18	31	1.72
0.8	16	16	35	2.19
1.0	17	12	38	2.23
1.2	18	11	38	2.11
1.4	19	10	38	2.00
1.6	21	8	38	1.81
1.8	22	7	38	1.72
2.0	23	6	38	1.65

The usual sign of + electrification was invisible on the analyzer in the first experiment, but the — was sufficiently marked to permit of measurement.

The relation which I have already shown to exist between the magnitude of the intermedial space on an analyzer and the force required to separate an electrolyte into its constituent ions (Phil. Mag. Oct. 1881) naturally led me to look for some well-defined relation between the intermedial space on the analyzers and the current. The electromotive force between the electrodes, and therefore, as it may be supposed, of the molecules of the electrolyte, varied of course with the

strength of the current; and the electromotive force set up on the analyzers might consequently also be supposed to vary in the same way. Now as the force required to overcome the affinity of the ions was constant, and as the electromotive force decreases from the ends of an analyzer in the position of the ones employed, it might be expected that the intermedial space would decrease in proportion as the electromotive force increased between the electrodes. That such a relation exists would appear to be fairly well established by the results of this series of experiments. In the annexed table the intermedial spaces are given in millimetres side by side with the numbers calculated on the supposition that the spaces vary inversely as the electromotive force of the electrolytic molecules.

Current.	Found.	Calculated.
0.4	30	30
0.6	18	20
0.8	16	15
1.0	12	12
1.2	11	10
1.4	10	8.5
1.6	8	7.5
1.8	7	6.7
2.0	6	6

There are two other points brought out by these experiments to which I would direct attention. The one is the want of uniformity in the increase of the opposite electrifications with the increase of current; and the other is the remarkable constancy of the + electrification from one to two ampères.

II. *Influence of Strength of Electrolyte.*—In this series of experiments the current was constant, one ampère being employed. The strengths of copper sulphate used for the several experiments are given in the annexed table of results.

Percentage of CuSO ₄ .	— electrifi- cation.	Intermedial space.	+ electrifi- cation.	+ referred to — as unity.
1	27	7	33	1.14
2	25	8	34	1.36
4	18	12	37	2.05
6	15	14	38	2.53
8	14	16	37	2.64
10	12.5	18.5	36	2.88
12	12	22	33	2.75
14	10	28	29	2.9
16	9.5	29.5	28	2.94

As already mentioned, the same strength of current flowed for equal times in the several experiments. It may therefore, I think, be assumed that the same quantity of electrification was set up on the analyzers, and, further, that the differences in the magnitude of the electrifications were determined by an influence or influences other than that of the quantity of electricity which flowed into the electrolyte. The resistance of a solution of copper sulphate increases, as is well known, with its dilution; and as the current was constant throughout, the electromotive force of the molecules of the several solutions necessarily increased in the same proportion as their resistances. The variations in the electromotive force must therefore again be regarded as the chief cause of the differences in the magnitude of the electrifications, and consequently also of the intermedial spaces. It is certain that the electrolytic radicals of sulphate of copper were separated on the analyzers in each of the experiments; but it by no means follows that the molecular decompositions were identical in each case; for it is known that the molecular constitution of salts in solution varies within certain limits with variations in the proportion of water. The relation already shown to obtain between the intermedial space and the electromotive force of similarly constituted molecules would lead to the conclusion that the intermedial spaces in this series of experiments would be inversely proportional to the resistances of the solutions, supposing that their molecular constitutions were similar. I have not the resistances for the exact strengths of the solutions; but, taking approximations to these, I find the relation referred to holds good in solutions varying from 6 to 12 per cent. of copper sulphate—*i. e.* where the viscosity on the one hand, and the tendency to decomposition of the metallic salt on the other, perhaps differ so little as to be practically inappreciable. The data &c. are set out in the annexed table:—

Strength of copper-sulphate solution.	Approximate resistance.	Intermedial space.	Resistance $\times$ by intermedial space.
6 per cent.	1.6	14	22.4
8 "	1.3	16	20.8
10 "	1.16	18.5	21.5
12 "	1.04	22	22.8

III. *Influence of Temperature.*—In this series of experiments the current was also constant, an ampère being again employed. The strength of electrolyte was likewise constant, *Phil. Mag.* S. 5. Vol. 16. No. 98. August 1883. I

a 5 per cent. solution of copper sulphate being employed. The temperatures are given in the annexed table of results:—

Temperature.	— electrification.	Intermedial space.	+ electrification.	+ referred to — as unity.
4° C.	19	12	36	1.90
8°	17	12	38	2.23
16°	16.5	14.5	36	2.18
24°	16.5	16.5	34	2.06
32°	17	18	32	1.88
40°	19	20	28	1.47
56°	21	27	19	0.90
72°	22	31	14	0.63
88°	25	36	6	0.24

As a rule, the boundaries of the electro-deposits are nearly or quite straight; the peroxide-of-silver boundaries, however, in the experiments above 32° C. were concave. Thinking that this concavity arose from the time being insufficient, I repeated some of the experiments, prolonging the time to 20 minutes; but the results were practically the same. The intermedial spaces in the higher-temperature experiments also exhibited signs of slight oxidation, which I am inclined to attribute to the disturbing influence of convection-currents.

It will be observed that the intermedial space increased as the temperature increased. This, again, agrees with the principle connecting the area of the spaces with electromotive force; for as the temperature increased, of course the resistance of the solution decreased; the electromotive force of the molecules necessarily also decreased; and the magnitude of the intermedial spaces increased, in accordance with the principle referred to. I have not the resistances of the solutions at the temperatures of my experiments, and cannot, therefore, institute a numerical comparison.

The very small + electrifications at the high temperatures is very noticeable; and I have thought that this may be not unconnected with differences in the action of heat itself on the opposite electricities.

It will be noticed that one feature common to the experiments described is the inequality in the magnitude of the electrifications of opposite sign on the several analyzing plates. This fact naturally attracted my attention some years ago (Proc. Roy. Soc. no. 181, 1877); and the work of this paper was undertaken mainly in the hope of throwing light on the subject. I cannot say it has brought about the desired result. It has, however, cleared away one or two speculations, suggested the direction of further inquiry, and shown, among

other things, that the condition of the electrolytic field affects not only the area of the electrifications, as this was to be foreseen, but also the ratio of the — to the + electrification. The numbers in the fifth columns in the above tables show the great diversity in this respect; and in my recent paper (*Phil. Mag.* June 1883) I referred to more examples, under conditions, too, where it appeared very difficult to imagine the nature of the difference in the condition of the surrounding molecules. As to the meaning of this disparity in the ratio of the electrifications, I am unable to form a conception satisfactory to myself.

The work has moreover established the definite relation already pointed out between intermedial space and electromotive force. And on an examination into the effects of what I have named "Dissymmetry in the Electrolytic Discharge," in the light of this relation, I believe I observe a difference of electromotive force of the molecules where the dissymmetry manifests itself, *i. e.* on the + and — sides of non-uniform fields. The evidence consists in differences in the area of the spaces on analyzers in corresponding parts of the field relative to the electrodes, or sides of the trough. I find that the area of the intermedial space on an analyzer on the + side is invariably smaller than that on the — side, from which it would follow that the electromotive force of the molecules on the + side is invariably the greater. This conclusion is supported by another observation of a somewhat different character. On the analyzers *c* and *d*, shown in fig. 1, p. 393 of my paper in the June number of the *Philosophical Magazine*, it is evident that a greater amount of electrochemical action was set up on *c*; and *c*, it will be observed, is on the + side of the trough, where it has been inferred that the electromotive force of the molecules is the greater. I think it not improbable that this difference in electromotive force is related to Faraday's observation ('*Experimental Researches*,' Series xii., xiii.) that "Negative electricity discharges into air at a somewhat lower tension than positive electricity." The molecules surrounding the electrode discharging + electricity would, of course, be differently affected electrically than when the electrode was discharging — electricity; and if this be true of molecules of air, why may it not be equally true of the molecules of a solution of copper sulphate or other electrolyte. A difference in the electromotive force of molecules in corresponding positions would appear, then, to be a feature of dissymmetry in certain electrolytic fields; but the more noteworthy effect of this dissymmetry is seen in the differences in the area of like electrifications on the correspondingly placed analyzers.

June 25, 1883.