

December 11, 1879.

THE PRESIDENT in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

Professor Joseph David Everett was admitted into the Society.

The President announced that he had appointed as Vice-Presidents :—

The Treasurer.

Mr. Busk.

Sir Joseph Hooker.

Mr. Simon.

Dr. Tyndall.

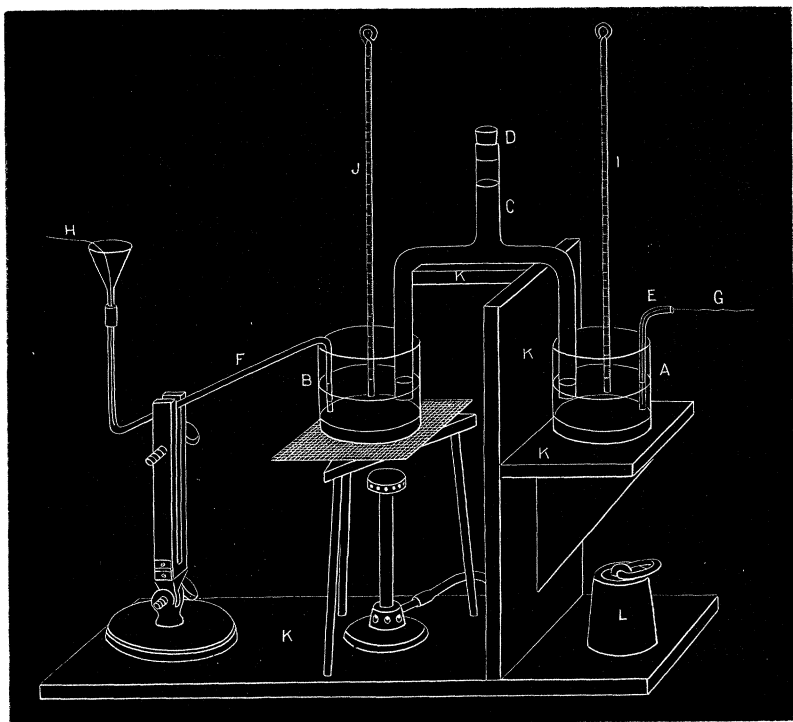
The following Papers were read :—

- I. “Thermo-Electric Behaviour of Aqueous Solutions with Mercurial Electrodes.” By G. GORE, LL.D., F.R.S. Received November 24, 1879.

In order to investigate this subject, I devised and constructed the following apparatus :—A and B are two thin glass basins, 81 millims. internal diameter (=5,153 sq. millims. of mercury surface), and 6·0 centims. deep; each containing a layer of mercury about 1·0 centim. deep, covered by a layer, about 3 centims. deep, of the aqueous solution to be examined. C is a thin bent glass tube, about 3 centims. diameter, filled with the liquid, and closed by means of a bung at D.* E and F are stout glass tubes, about 2 millims. bore, E having a platinum wire sealed into it at its lower end, and F being filled with mercury; the ends of these tubes are usually placed in the mercury previous to adding the liquid; and F is fixed so that the solution cannot enter it. G and H are terminal wires of platinum, touching the mercury, but not the liquid. I and J are thermometers, with their bulbs immersed in the pools of mercury. Each cup is closed by a bung (not shown in the sketch), to prevent loss of liquid by evaporation, also to support the thermometer and keep the tubes steady. The dish B is supported on wire gauze, placed upon an iron tripod with a Bunsen's burner beneath, and A is placed on a shelf level with

* It is not necessary to have the vertical limbs of this tube of as great a length as they are shown in the sketch.

it. K K K K is a wooden frame for supporting the apparatus, and L is a weight to keep it steady. This kind of apparatus was used in all the experiments, and acted very satisfactorily. I devised one of different construction for a similar purpose many years ago. (See "Phil. Mag." June, 1859.)



Liquid Thermo-Pair with Mercurial Electrodes.

The mercury employed was prepared by distilling the ordinary metal twice, then shaking it strongly in succession with dilute nitric acid, water, solution of cyanide of potassium, distilled water, and filtering it. Distilled water was used in making all the solutions.

In using the apparatus, the mercury was first poured into the basins; the tubes E and F placed, taking particular care that the mercurial column in F and its contact with the pool were complete. Two very shallow india-rubber bungs were next inserted in the lower ends of the bent tube C, the tube then put in position, and filled with the liquid. The solution was now put into the basins; the bung D inserted tightly, the shallow ones then removed, and the bungs inserted in A and B. The completeness of the circuit was next tested by attaching a galvanometer to the instrument, and, if necessary, a

minute swing of the needle was obtained by repeated connexion at proper intervals of time. B was now heated. About seven or eight minutes was usually occupied in raising its temperature the required number of degrees; the deflections at the various temperatures being noted. After an experiment had been made, the mercury and solution of both vessels were mixed and cooled, and the mercury filtered, before repeating the trial with the same liquid.

Care was taken to select solutions which had the least amount of chemical action upon the mercury; those of salts of the heavy and less positive metals were therefore not employed. No liquid was used which produced any visible film or dulness upon that metal when heated with it. It was found necessary to heat each solution to about 180° F., and keep it at that temperature some little time to expel dissolved air, and then cool it previous to making experiments, otherwise the results obtained in repetition experiments were not quite uniform. In a previous research on the thermo-electric properties of liquids ("Proc. Roy. Soc.," No. 188, 1878, pp. 513—543), in which platinum electrodes were employed, such previous heating was less necessary, probably because the thermo-electric currents were then stronger.* After heating and cooling the liquid, it was freely shaken with the mercury, and then filtered, previous to making experiments with it. With every liquid, one or more repetition experiments were made in order to obtain uniform results, and confirm their reliability; the amount of difference of deflection of the needles in such experiments did not exceed one degree. The galvanometer employed was an astatic one, having two coils, each of 50 ohms resistance, the two being connected and used as one of 100 ohms resistance.

I have ascertained by separate experiments of a different kind, that mercury when sufficiently agitated with solutions, neutral to test paper, of salts of the alkali metals, renders some of those liquids feebly alkaline; the effect, however, is so slight, requires such extensive and long-continued contact of the substances, that it appears consistent with the view that chemical action is not the cause of the currents in these thermo-electric experiments.

The following are the results obtained with different liquids in the above apparatus.

Behaviour of different Solutions.

Experiment No. 1. Ten ounces of water, and 2½ grs. of potassic cyanide of a high degree of purity. Cold mercury was positive 2°

* The greater strength of the currents with the platinum electrodes was partly due to the circumstance that each platinum electrode offered a surface of 71,680 sq. millims. of contact with the liquid, or fourteen times greater than that of the above-mentioned mercurial surface. The solutions employed were also much stronger.

steadily at 180° F.* Agitation either of the cold mercury (A), or of the hot mercury (B), did not alter the amount of the deflection.

No. 2. A solution† of 5 grs. of the cyanide. Cold mercury positive 14°. Agitation either of A or B had no effect.

No. 3. A solution of 50 grs. of the same salt. Cold mercury positive 45°. Stirring A decreased the deflection temporarily‡ to 34°, and stirring B decreased it to 9.

No. 4. A solution of 100 grs. of the same salt. Cold mercury positive 50°. Stirring A decreased the deflection to 41, and stirring B decreased it to 46.

No. 5. A solution of 10 minims of selenic acid (of sp. gr. 1·32 at 60° F.). Hot mercury positive 1½°. Stirring A increased the deflection to 5, and stirring B increased it to 4. There was a similarity of behaviour of this liquid to that of dilute sulphuric acid, each exhibited a zero point giving no current at about 120° F.; but the selenic acid gave a reverse current below that temperature, whilst sulphuric acid did not.

No. 6. A solution of 20 minims of the same acid. Cold mercury positive 3° at 120° F. Needles at 0 at 143° F., and hot mercury positive 3¾° at 180° F. Stirring A decreased the deflection to 1¼, and stirring B increased it to 5¾.

No. 7. A solution of 25 grs. of anhydrous selenate of sodium. Hot mercury positive 8°. Stirring A decreased the deflection to 5, and stirring B increased it to 14.

No. 8. A solution of 100 grs. of crystalline sulphate of ammonium. Hot mercury positive 12¼°. Stirring A increased the deflection to 29¼, and stirring B increased it to 19¼.

No. 9. A solution of 50 grs. of crystalline ammoniac alum. Cold mercury positive 2°. Stirring A increased the deflection to 5½, and stirring B decreased it slightly.

No. 10. A solution of 100 grs. of the same salt. Cold mercury positive 4°. Stirring A had no effect; stirring B reversed the deflection 2°.

No. 11. A solution of 40 minims of formic acid of sp. gr. 1·18. Hot mercury positive 3½°. Stirring A had no effect; stirring B increased the deflection to 7.

No. 12. A solution of 80 minims of the same acid. Hot mercury positive 5°. Stirring A increased the deflection to 6, and stirring B increased it to 7.

No. 13. A solution of 100 grs. of potassic nitrate. Hot mercury

* All the deflections, except those otherwise stated, were taken at the temperature of 180° F.

† Unless otherwise described, 10 ozs. of water was used in every case to form the solution.

‡ All the alterations of deflection caused by stirring were only temporary.

positive 10° . Stirring A increased the deflection to 30, and stirring B increased it to 20.

No. 14. A solution of 100 grs. of crystalline potassic sulphate. Hot mercury positive 12° . Stirring A increased the deflection to 30, and stirring B increased it to 22.

No. 15. Seventy-nine volumes of water, and one of pure sulphuric acid. Cold mercury positive $1\frac{1}{4}^{\circ}$. Stirring A increased the deflection to 10, and stirring B increased it to 4.

No. 16. Thirty-nine volumes of water, and one of the same acid. Hot mercury positive $6\frac{3}{4}^{\circ}$. Stirring A increased the deflection to 11, and stirring B increased it to 13.

No. 17. Nineteen volumes of water, and one of the same acid. Cold mercury positive, $14\frac{1}{2}^{\circ}$ at 120° , and $6\frac{1}{4}^{\circ}$ at 180° F. Stirring A increased the deflection to 30, and stirring B increased it to 19.

No. 18. A solution of 50 grs. of pure and partly dehydrated* sodic carbonate. Hot mercury positive 19° . Stirring A increased the deflection to 41, and stirring B increased it to 25.

No. 19. A solution of 50 grs. of pure and partly dehydrated potassic carbonate. Hot mercury positive 12° . Stirring A increased the deflection to 18, and stirring B did not affect it.

No. 20. A solution of 100 grs. of crystalline sodic sulphate. Hot mercury positive $2\frac{1}{2}^{\circ}$. Stirring A increased the deflection to $8\frac{1}{2}$, and stirring B increased it to 5.

No. 21. A solution of 100 grs. of ammoniac nitrate. Hot mercury positive $4\frac{1}{4}^{\circ}$. Stirring A increased the deflection to 16, and stirring B increased it to 20.

No. 22. A solution of 100 grs. of crystalline boracic acid. Hot mercury positive 2° . Stirring either A or B did not alter the amount of deflection.

No. 23. A solution of 100 grs. of sodic nitrate. Hot mercury positive 6° . Stirring A increased the deflection to 30, and stirring B increased it to 18.

No. 24. A solution of 100 grs. of crystalline phosphate of sodium. Hot mercury positive 8° . Stirring A increased the deflection to 28, and stirring B increased it to 21.

No. 25. A solution of 50 grs. of baric nitrate. Hot mercury positive $7\frac{1}{2}^{\circ}$. Stirring A increased the deflection to 22, and stirring B increased it to 16.

No. 26. A solution of 50 grs. of crystalline nitrate of strontium. Hot mercury positive 10° . Stirring A increased the deflection to 14, and stirring B increased it to 17.

No. 27. A solution of 100 grs. of crystalline phosphate of ammonia. Hot mercury positive 28° . Stirring A increased the deflection to 38, and stirring B increased it to 32.

* See page 482.

No. 28. A solution of 50 grs. of crystals of borax. Hot mercury positive $10\frac{1}{2}^{\circ}$. Stirring A increased the deflection to 22, and stirring B increased it to 15.

No. 29. A solution of 50 grs. of crystalline sodic hyposulphite. Cold mercury positive 4° . Stirring A decreased the deflection to 3, and stirring B had no effect.

No. 30. A solution of 10 grs. of crystals of sodic sulphite. Hot mercury positive $2\frac{1}{2}^{\circ}$. Stirring A increased the deflection to 5, and stirring B had no effect.

No. 31. A solution of 50 grs. of the same salt. Hot mercury positive 13° . Stirring A increased the deflection to 15, and stirring B had no effect.

No. 32. A solution of 50 grs. of potassic sulphite. Cold mercury positive 9° . Stirring A increased the deflection to 13, and stirring B made hot mercury positive 12° .

No. 33. A solution of 50 grs. of crystalline phosphate of sodium and ammonium. Hot mercury positive 5° . Stirring A increased the deflection to 9, and stirring B increased it to 7.

No. 34. A solution of 100 grs. of the same salt. Hot mercury positive 2° . Stirring A increased the deflection to 4, and stirring B had no effect.

No. 35. A solution of 50 grs. of formiate of sodium. Hot mercury positive 4° . Stirring A increased the deflection to 20, and stirring B increased it to 10.

No. 36. A solution of 100 grs. of the same salt. Hot mercury positive 6° . Stirring A increased the deflection to 10, and stirring B increased it to 11.

By arranging the foregoing results in a series with the solution at the top, in which the hot mercury was the most positive at 180° F., and that at the bottom in which it was most negative, the following order was obtained. The horizontal line separates those liquids in which the hot metal was positive from those in which it was negative.

	Amount of deflection.
1. Phosphate of ammonium.....	28.0 +
2. Carbonate of sodium	19.0
3. Sulphite of sodium (50 grs.)	13.0
4. Sulphate of ammonium	12.75
5. Carbonate of potassium }	12.0
6. Sulphate of potassium }	12.0
7. Borax.....	10.5
8. Nitrate of potassium }	10.0
9. Nitrate of strontium }	10.0
10. Selenate of sodium }	8.0
11. Phosphate of sodium }	8.0

	Amount of deflection.
12. Nitrate of barium.....	7·5
13. Nitrate of sodium.....	6·0
14. Formiate of sodium (100 grs.) }	6·0
15. Microcosmic salt (50 grs.) }	5·0
16. Formic acid (80 minims) }	5·0
17. Nitrate of ammonium.....	4·25
18. Formiate of sodium (50 grs.).....	4·0
19. Selenic acid (20 minims)	3·75+
20. Formic acid (40 minims)	3·5
21. Sulphate of sodium.....	2·5
22. Sulphite of sodium (10 grs.) }	2·5
23. Microcosmic salt (100 grs.) }	2·0
24. Boracic acid.....	2·0
25. Selenic acid (10 minims.)	1·5
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26. Sulphuric acid (1 in 80).....	1·25—
27. Ammonia alum (50 grs.).....	2·0
28. Cyanide of potassium ($2\frac{1}{2}$ grs.) }	2·0
29. Hyposulphite of sodium }	4·0
30. Ammonia alum (100 grs.) }	4·0
31. Sulphuric acid (1 in 20).....	6·25
32. Sulphuric acid (1 in 40).....	6·75
33. Sulphite of potassium.....	9·0
34. Cyanide of potassium (5 grs.).....	14·0
35. Cyanide of potassium (50 grs.).....	45·0
36. Cyanide of potassium (100 grs.)	50·0

To ascertain whether this order agreed with that of a series arranged according to the different degrees of electromotive force of the various couples, I simultaneously employed two apparatuses similar to that already described (but with basins of 75 millims. internal diameter), charging one of them with one solution, and the other with another which was next to it in the above series, connecting them with the two wires respectively of the differential galvanometer, so that their currents circulated in opposite directions through the coil of that instrument, and ascertaining which gave the strongest current at 160° F. By this means the following series was obtained, in which the couple giving the strongest positive current is at the top, and that giving the most powerful negative current at the bottom, as in the previous list. The horizontal line separates those liquids in which the hot metal was positive from those in which it was negative. The relative positions of the solutions in the two series, although they agree in the main, are not identical; for instance, nitrate of potassium occupies the eighth place in the first series, and the second place in

the second series; phosphate of ammonium, sulphate of ammonium, &c., are also changed in position. Such changes were probably affected by the circumstance, that whilst in the first series the electrodes were 81 millims. diameter ($=5,153$ sq. millims. of surface), and the current from a single apparatus circulated through a continuous double length of wire in the coil of the galvanometer, in the second series the electrodes were only 75 millims. diameter ($=4,418$ sq. millims.), and the current from a single apparatus circulated through a single half length of the coil. The temperatures at which the deflections were noted were also different in the two series. The surface of one electrode in the smaller apparatus was about $\frac{1}{16}$ and in the larger one $\frac{1}{4}$ of that of one of the platinum electrodes in the apparatus already referred to (see foot note, p. 474).

	Difference of amount of deflection.
1. Sulphate of ammonium	1.0 +
2. Nitrate of potassium	3.0
3. Phosphate of ammonium	3.0
4. Sulphite of sodium (50 grs.)	0.75
5. Carbonate of sodium	1.0
6. Carbonate of potassium	1.5
7. Sulphate of potassium	0.25
8. Nitrate of strontium	0.25
9. Phosphate of sodium	0.25
10. Borax	1.5
11. Selenate of sodium	1.5
12. Nitrate of barium	0.25
13. Nitrate of sodium	1.0
14. Formiate of sodium (100 grs.)	1.0
15. Microcosmic salt (50 grs.)	0.75
16. Formiate of sodium (50 grs.)	0.75
17. Formic acid (80 minims)	2.0
18. Nitrate of ammonium	1.5
19. Sulphate of sodium	0.25
20. Sulphite of sodium (10 grs.)	0.25
21. Microcosmic salt (100 grs.)	2.0
22. Boracic acid	
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23. Ammonia alum (50 grs.)	very slight—
24. Cyanide of potassium ($2\frac{1}{2}$ grs.) ...	0.75
25. Ammonia alum (100 grs.)	1.0
26. Hyposulphite of sodium	1.0
27. Cyanide of potassium (5 grs.)	13.0
28. Cyanide of potassium (50 grs.)	2.25
29. Cyanide of potassium (100 grs.)	

Remarks.—Many of the remarks which I have made in a previous paper on the thermo-electric properties of liquids (Proc. Roy. Soc., vol. xxvii, pp. 535–538) respecting the cause of the currents, apply to the results obtained in the present research; and I consider that the causes of the currents and of their direction are similar in the two cases.

On examining the results it will be observed that the effects are not manifestly related to the chemical nature of the solutions; thus, the liquids in which hot mercury is positive include those of acid, as well as those of alkaline reaction; and similarly with the solutions in which cold mercury is positive. To what extent chemical action occurred in the experiments and operated as a cause of electric currents, would be a difficult point to completely prove, because the amount required to produce such feeble currents would be so extremely small; the result of a general examination of the phenomena, however, does not support the hypothesis that the currents were of chemical origin.

The evident cause of the currents was heat, and the direction of them was probably due to molecular changes in the liquid attendant upon alteration of temperature. In nearly all cases the magnitude of the current increased with the amount of difference of temperature; the apparent, but not real, exceptions were those in which a reversal, or an advance towards it, occurred.

The strength of the solution manifestly affected the quantity, and in some cases the direction of the current, as may be perceived with the solutions of potassic cyanide (Nos. 1, 2, 3, and 4), selenic acid (Nos. 5 and 6), ammonia alum (Nos. 9 and 10), formic acid (Nos. 11 and 12), sulphuric acid (Nos. 15, 16, and 17), and phosphate of sodium and ammonium (Nos. 33 and 34). If the cause of the current, in the case of sulphuric acid, was chemical action, the direction of the current would probably not have been reversed by mere alteration of temperature, or by variation of strength of the mixture. If, also, the cause of the currents in general was of a chemical nature, the currents would probably have been much stronger, especially with the stronger solutions, and would have increased in all cases, with the strength of the solution, until the latter was much more concentrated than those which were employed.

Stirring either portion of the liquid influenced the deflection in 59 cases out of 72, increased it in 49, and decreased it in 10 of those cases. Stirring the cold portion altered the current in 31 cases out of 36, and stirring the hot portion changed it in 28 cases out of 36. Stirring the cold portion also had a greater average magnitude of effect upon the current than stirring the hot portion. Stirring a liquid of acid reaction increased the current in 13 cases out of 20, decreased or reversed it in 3 cases, and had no effect in 4 cases. Stirring an alkaline one increased the deflection in 12 cases out of 24, decreased it

in 5, and had no effect in 7. The effects of stirring upon the amount of deflection were greater in alkaline liquids than in those of acid reaction.

Influence of previously heating the Solution.

Having observed, even with solutions formed with water which had been preboiled to expel dissolved air, that unless such liquids had been further heated to 180° F. (and cooled), after the salt, &c., had dissolved, the currents obtained in successive experiments with such a solution were not quite uniform in amount, but always decreased, I examined this circumstance.

Twenty ounces of distilled water was boiled and cooled; the salt to be employed was then dissolved completely in it, and the solution shaken with pure mercury. The mixture was then divided into two equal portions, one of those portions raised to a temperature of 180° F. in a covered glass vessel, and the evaporated water condensed and returned to the mixture, so that the solution remained unaltered in composition; the liquid was then cooled. These preheated and non-preheated portions were employed respectively to charge the two apparatuses already described. The two thermo-pairs were then simultaneously excited, their currents allowed to circulate in opposite directions through the coils of the galvanometer, and the deflection noted when the hot portions of the two liquids had simultaneously acquired a temperature of 160° F. The following is a brief statement of the results.

Twenty ounces of distilled water, and 200 grs. of crystals of sodic phosphate. The non-preheated portion of solution yielded the strongest current; deflection 1°.

Twenty ounces of water and 2 drms. of sulphuric acid. The non-preheated portion gave the strongest current; deflection .25°.

Twenty ounces of water and 100 grs. of partly dehydrated sodic carbonate. The non-preheated portion gave the strongest current; deflection .33° at 140° F., and .25° at 160° F.

Twenty ounces of water and 200 grs. of baric nitrate. The non-preheated portion yielded the strongest current; deflection 1°.

The same mixture as the last; one portion of the solution was preheated with mercury, instead of being preheated alone. The non-preheated portion gave the strongest current; deflection 1° at 180° F.

In each of these five experiments the non-preheated portion of liquid yielded the current of greatest electromotive force. This accords with the original observation that repetition experiments always yielded weaker currents (see p. 480).

In order to ascertain whether preheating the one portion of salt before dissolving it had the same effect upon the current as heating it after having been dissolved, the following experiments were made:—

Preboiled and cooled 20 ozs. of distilled water, and divided into two exactly equal portions. Took two portions of 50 grs. each of partly dehydrated sodic carbonate; heated one portion to 180° F. for fifteen minutes until it ceased to evolve moisture (it lost 12.4 grs.), and cooled it. Dissolved the two separate portions of salt in the separate quantities of water, and tested the solutions against each other in the two apparatuses. No difference of strength of current occurred at any temperature up to that of 180° F.

In another experiment of this kind, 200 grs. of ammonia alum were divided and treated as above. The solution of the non-preheated portion gave the strongest current; deflection $.75^{\circ}$ at 180° F.

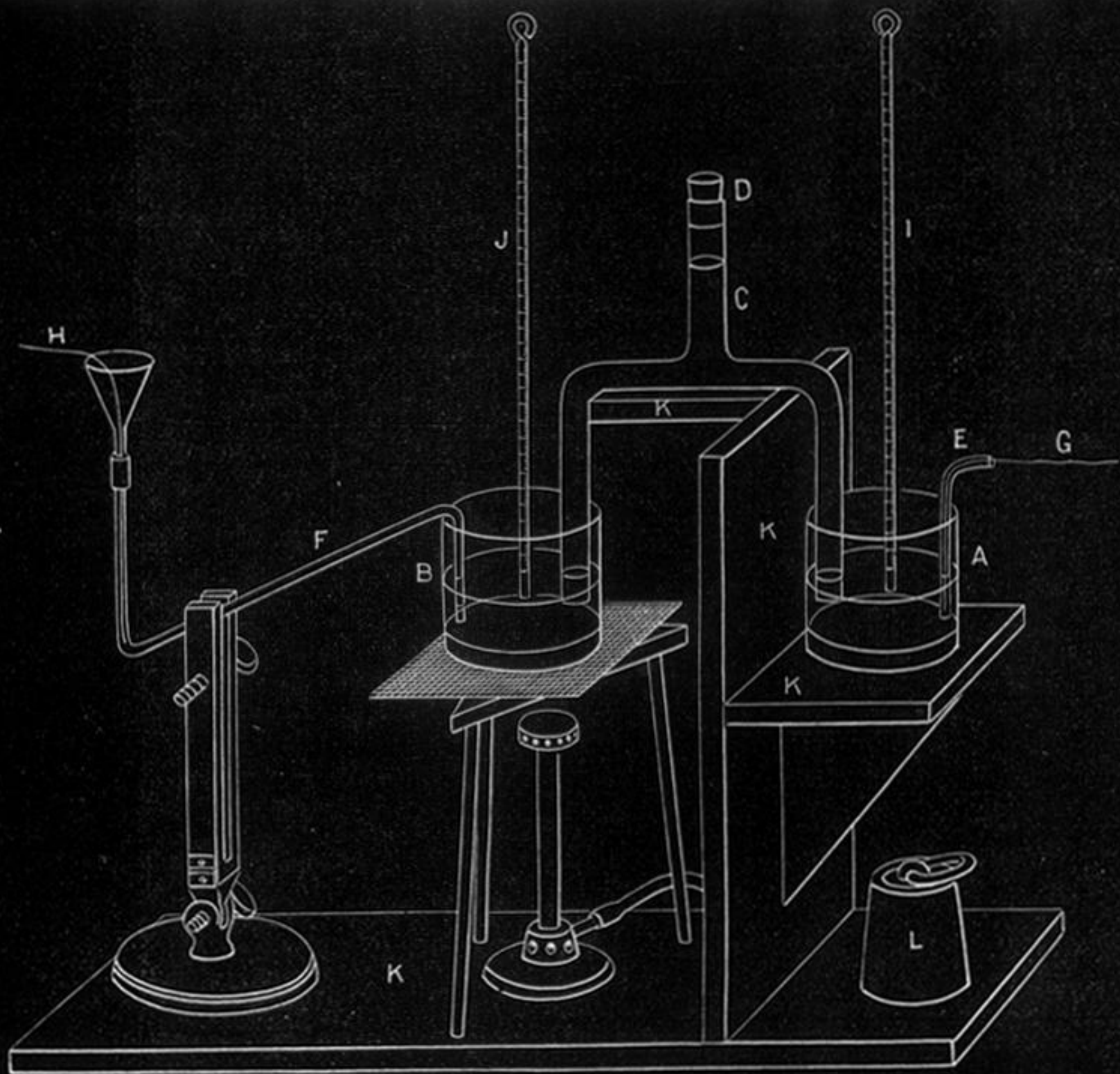
Remarks.—The conclusion I draw from these last two experiments and results, combined with those of the previous ones, is that pre-heating the salt either before or after solution usually weakens the current, both in thermo-electropositive and in thermo-electronegative liquids.

In the several classes of cases described in this paper, it is evident that the currents are not due to chemical action, but to heat acting upon and altering particular molecular structures, and that the difference of electromotive power in different liquids is not due to differences of chemical action, but probably to differences of molecular arrangement of the solutions. Also that in the class of experiments where the liquids compared had the same chemical composition, but had been differently treated, the differences of molecular arrangement were less, and the currents obtained were consequently more feeble. A difference of strength of current caused by repetition of experiments, or by continuance of heat, also renders manifest the change of molecular arrangement; and the above method may be employed for detecting molecular differences in conducting liquids having the same chemical composition.

In the class of cases in which the differences of molecular arrangement were the least, and the currents the most feeble, the direction of the currents was the most uniform. This is in accordance with the common truth in science that the smallest phenomena are the most constant.

II. "Quantitative Spectroscopic Experiments." By Professor G. D. LIVEING, M.A., F.R.S., and Professor JAMES DEWAR, M.A., F.R.S. Received November 27, 1879.

The well-known expansion of the lines of sodium and other metals, when increased quantities of the metals are introduced into the flame or arc, seems to afford a means of attaining a quantitative spectrum analysis in certain cases, if the relations between the width of



Liquid Thermo-Pair with Mercury Electrodes.