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6.

ON THE

THERMO-ELECTRIC ACTION

OF

METALS AND LIQUIDS.

BY

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It is well known that the degree of rapidity with which a metal immersed in an acid, alkaline, or saline liquid is corroded varies considerably with the temperature, and that the speed of corrosion usually increases with the heat; also a few experiments have been published (Gmelin's 'Handbook of Chemistry,' vol. i. p. 375) showing that changes of electrical state occur in metals under such circumstances; but a further examination of the relations of the temperature and chemical change to the electrical state has not, that I am aware, yet been made.

In an investigation on the development of electric currents by unequally heated metals in liquids (Phil. Mag. 1857, vol. xiii. p. 1), I found that hot

platinum was electro-negative to cold platinum in liquids of acid reaction, and positive to it in alkaline ones, provided in all cases chemical action was completely or sufficiently excluded. In the present experiments I have endeavoured to ascertain what electrical changes are produced in cases where chemical action more freely occurs, and I have therefore employed not platinum plates, but plates composed of a metal (copper) which is more easily corroded.

To effect the object I had in view, I used the apparatus shown in section in fig. 1, and in perspective, with its wooden support, in fig. 2.

Fig. 1.

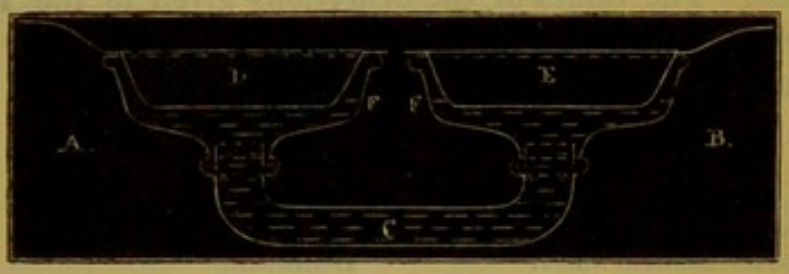
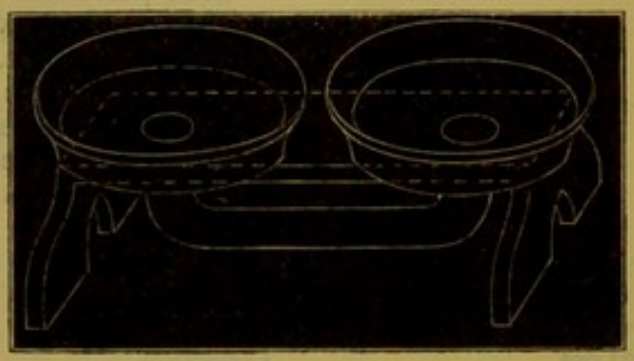


Fig. 2.



A and B, fig. 1, are two open thin glass dishes, 6½ inches diameter, and 1½ inch deep, with open necks. The dishes are joined together, water-tight, by a bent glass tube, C, about 1 inch in diameter; and the whole arrangement is securely fixed upon a wooden frame or stand, so that it may be at once placed in an exactly horizontal position, or inverted to pour out its contents. D and E are two dishes of sheet copper of moderate thickness, made from contiguous portions of a sheet of metal to ensure electrical homogeneity in the experiments. Wires of similar metals are attached to the dishes for the purpose of connexion with a galvanometer. A galvanometer, containing about 180 turns of moderately fine copper wire, is sufficiently sensitive for the experiments. The outside of the metal dishes must be made perfectly clean and bright immediately before each experiment.

In using the apparatus it is first set exactly horizontal, and a known and measured volume of the clear liquid to be examined, at the temperature of the atmosphere and sufficient to fill it to the line F F, is poured in; the metal dishes are then steadily placed in the glass vessels and connected with the galvanometer, taking care that no air-bubbles remain beneath them.

As soon as the galvanometer-needles have settled at zero, one of the dishes is quickly filled with boiling water, and the directions and amounts of the temporary and permanent deflections noted.

The following are Tables of results obtained with various liquids, the solutions being diluted in each case to a specified measure by addition of distilled water. Those of the experiments in which 20 ounces of liquid was used, were nearly all of them made with an apparatus in which the connecting-tube C was of somewhat less diameter; and the deflections obtained by that apparatus were less in extent than those obtained with the "new apparatus," because in the latter the conduction-resistance was somewhat less. The values of the deflections given in the Tables are in all cases those of the *temporary* ones; and the liquid used for diluting the solutions was in all cases *water*.

Pure Nitric Acid.

No.	Ounces of strong acid diluted to 20 ozs. with water.	Value of Deflection.	
1.	.... $\frac{1}{16}$	·0045	The hot plate was negative and much acted upon, especially with the stronger mixtures. With the stronger mixtures a little gas was evolved at 60° Fahr., and a large amount directly the heat was applied.
2.	.... $\frac{1}{8}$	·0012	
3.	.... $\frac{1}{4}$	·0039	
4.	.... $\frac{1}{2}$	·0497	
5.	.... 1	·1177	
6.	.... 2	·0356	
7.	.... 3	·0578	
8.	.... 4	·4954	

Pure Hydrochloric Acid.

No.	Ounces of strong acid diluted to 20 ozs.	Value of Deflection.	
1.	.... $\frac{1}{16}$	·0064	The hot plate was positive. The amount of stain upon the hot plate was very small, and was in the form of a dark line at the edge of the liquid.
2.	.... $\frac{1}{8}$	·0330	
3.	.... $\frac{1}{4}$	·1112	
4.	.... $\frac{1}{2}$	·2854	
5.	.... 1	·5731	
6.	.... 2	2·0446	

Chloric Acid.

No.	Ounces of strong acid diluted to 20 ozs.	Value of Deflection.	
1.	.... $\frac{1}{16}$	·0002	The hot plate was negative, and was but little acted upon. With the strongest mixture, the liquid in contact with the hot plate soon became green.
2.	.... $\frac{1}{8}$	·0016	
3.	.... $\frac{1}{4}$	·0040	
4.	.... $\frac{1}{2}$	·0287	
5.	.... 1	·1234	
6.	.... 2	·2005	

Hydrobromic Acid.

No.	Weak acid diluted to 10 ozs.	Value of Deflection.	
1.	.... $\frac{1}{2}$	·0149	Hot plate negative. Both plates much stained, the cold one the most so.
2.	.... 1	·0647	

Crystallized Boracic Acid.

The hot plate was positive. A series of six solutions was employed, containing from 50 grains to nearly 400 grains in 20 ounces by measure of water, the strongest being a saturated solution. The currents obtained were extremely feeble, and the plates were not tarnished.

Aqueous Hydrofluosilicic Acid.

Value of deflection ·1488. The hot plate was negative, and became a little tarnished.

Pure Sulphuric Acid.

No.	Ounces of strong acid diluted to 20 ozs.	Value of Deflection.	
1.	$\frac{1}{16}$	·0077	The hot plate was negative, and the plates were but little tarnished.
2.	$\frac{1}{8}$	·0161	
3.	$\frac{1}{4}$	·0418	
4.	$\frac{1}{2}$	·0878	
5.	1	·1044	
6.	2	·0327	
7.	4	·0037	
8.	8	·0319	

Pure Phosphoric Acid, solid.

No.	Grains of the glacial acid diluted to 20 ozs.	Value of Deflection.	
1.	100	·00005	The hot plate was positive, and the plates were not visibly tarnished.
2.	200	·00005	
3.	400	·00040	
4.	800	·00060	
5.	1600	·00370	

Chloride of Copper (Basic; solution filtered).

No.	Grains of the salt diluted to 12 ozs.	Value of Deflection.	
1.	100	·0025	Hot copper positive.
2.	500	·0198	" negative.
3.	1000	·0025	

Much action on both plates, especially the hot one, and basic chloride of copper formed.

Chlorate of Copper.

In a moderately strong solution of this salt, which had been digested with an excess of carbonate of copper and filtered, the hot plate was negative; value of deflection ·2997. Both plates were acted upon, but the hot one the most. The liquid had a feebly acid reaction.

Sulphate of Copper.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	249·5	·0016	Hot copper negative.
2.	499·0	·0081	Liquid acid.

Chloride of Cobalt.

No.	Ounces diluted to 12 ozs.	Value of Deflection.	
1.	½ oz. saturated solution	·1247	Hot copper positive. Liquid acid. No stains, except slightly at edge of hot liquid.
2.	3 ozs. " "	1·2726	

Protosulphate of Iron.

No.	Grains diluted to 12 ozs.	Value of Deflection.	
1.	200	·0198	Hot copper negative.
2.	800	·0794	No stains on either plate.

Chloride of Manganese.

No.	Grains diluted to 12 ozs.	Value of Deflection.	
1.	100	·0436	Hot copper positive. No stains.
2.	1000	1·0995	Liquid neutral, or very faintly acid.

Chromic Acid.

No.	Ounces of strong solution diluted to 12 ozs.	Value of Deflection.	
1.	½	·0987	Hot copper positive. Both plates much acted upon, apparently the cold one the most.
2.	2	18·8034	

Chloride of Chromium.

No.	Ounces of strong solution diluted to 10 ozs.	Value of Deflection.	
1.	½	·0293	Hot copper positive. The plates appeared unaffected. The solution was weakly acid to test-paper.
2.	1	·1319	

Nitrate of Lead.

No.	Grains.	Value of Deflection.	
1.	100 diluted to 12 ozs.	·0009	Hot plate negative. No stains.
2.	Saturated solution (undiluted)	·0259	Liquid extremely faintly acid.

Sulphate of Zinc.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	287	·0080	Hot copper negative. Liquid neutral.
2.	574	·0048	" positive.

Sulphate of Magnesium.

No.	Grains.	Value of Deflection.	
1.	50 diluted to 20 ozs.	·0001	Hot copper positive, and liquid neutral.
2.	100 " "	·0002	
3.	200 " "	·0006	
4.	246 " "	·0100	
5.	400 " "	·0036	
6.	492 " "	·0208	
7.	800 " "	·0130	
8.	1000 " "	·0228	
9.	2000 " "	·0607	
10.	Saturated solution (undiluted)	·0463	

Chloride of Calcium.

1400 grains diluted to 20 ounces. Value of deflection ·2935. Hot copper positive. Liquid neutral. Hardly any stain, most on hot plate.

Nitrate of Strontium.

No.	Grains diluted to 12 ozs.	Value of Deflection.	
1.	100	·0368	Hot plate positive. No stain. Liquid neutral.
2.	1000	·2321	

Chloride of Strontium.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	400	·2088	Hot copper positive. Liquid neutral. Hardly any chemical action, most on hot plate.
2.	800	·3277	
3.	1600	·6671	
4.	3200	·6654	

Nitrate of Barium.

No.	Grains.	Value of Deflection.	
1.	100 diluted to 20 ozs.	·0016	Hot copper positive. No stain. Liquid neutral.
2.	Saturated solution (undiluted)	·1170	

Chloride of Barium.

No.	Grains.	Value of Deflection.	
1.	50 diluted to 20 ozs.	·0016	Hot copper positive. Liquid neutral. A little copper was dissolved by the solution.
2.	100 " "	·0049	
3.	200 " "	·0145	
4.	244 " "	·0257	
5.	400 " "	·0214	
6.	488 " "	·0259	
7.	800 " "	·0234	
8.	1600 " "	·0802	
9.	Saturated solution (undiluted).	·3142	

Nitrate of Sodium.

No.	Grains diluted to 20 ozs.	Value of Deflection.		
1.	85	·0025	Hot copper negative.	Liquid neutral.
2.	255	·0328		
3.	510	·1015	" positive.	

Chloride of Sodium.

No.	Grains.	Value of Deflection.	
1.	12·5 diluted to 20 ozs.	·0001	Hot copper positive. Tarnish at edge of hot liquid, especially with the strongest solutions.
2.	25 " "	·0012	
3.	50 " "	·0081	
4.	75 " "	·0153	
5.	100 " "	·0293	
6.	150 " "	·0512	
7.	200 " "	·0819	
8.	250 " "	·1016	
9.	300 " "	·1160	
10.	400 " "	·1906	
11.	500 " "	·2241	
12.	600 " "	·2708	
13.	800 " "	·3473	
14.	1000 " "	·4884	
15.	2000 " "	·4237	
16.	Saturated solution (undiluted)	·3479	

Iodide of Sodium.

No.	Grains diluted to 12 ozs.	Value of Deflection.		
1.	100	·0100	Hot copper negative.	Liquid alkaline. No stains.
2.	1000	·0819	" positive.	

Carbonate of Sodium.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	286	·0468	Hot copper positive.
2.	572	·1673	Liquid alkaline.

Biborate of Sodium.

Six ounces of a saturated solution diluted to 12 ounces. Hot copper was positive; value of deflection ·0452.

Sulphate of Sodium.

No.	Grains diluted to 20 ozs.	Value of Deflection.		
1.	50	·0001	Hot copper negative.	Liquid neutral.
2.	100	·0009		
3.	200	·0016	" positive.	
4.	1000	·0170		

Phosphate of Sodium.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	358	·0382	Hot copper positive.
2.	716	·0648	Liquid alkaline.

Nitrate of Potassium.

No.	Grains.	Value of Deflection.	
1.	50 diluted to 20 ozs.	·0025	Hot plate positive. No stains at all on the plates. Solution quite neutral.
2.	100 " "	·0107	
3.	200 " "	·0259	
4.	400 " "	·0647	
5.	800 " "	·1328	
6.	1600 " "	·2997	
7.	Saturated solution (undiluted)	·2852	

Chloride of Potassium.

No.	Grains.	Value of Deflection.	
1.	25 diluted to 20 ozs.	·0010	Hot plate positive, and became tarnished at the edge of the liquid, especially with the stronger solutions. Traces of copper were found to have dissolved. The solutions were neutral to test-paper.
2.	50 " "	·0064	
3.	100 " "	·0145	
4.	200 " "	·0442	
5.	300 " "	·0667	
6.	400 " "	·0882	
7.	500 " "	·1239	
8.	600 " "	·1396	
9.	800 " "	·1874	
10.	1000 " "	·2443	
11.	2000 " "	·6371	
12.	Saturated solution (undiluted)	·8439	

Chlorate of Potassium.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	122·5	·0054	Hot plate positive, and became tarnished. Solution neutral.
2.	245·0	·0453	

Bromide of Potassium.

No.	Grains diluted to 20 ozs.	Value of Deflection.		
1.	100	·0497	Hot plate negative.	No stains. Liquid neutral.
2.	500	·1080	" positive.	
3.	1000	·3150		

Iodide of Potassium.

No.	Grains diluted to 12 ozs.	Value of Deflection.		
1.	100	·0259	Hot plate negative.	No stain. Liquid neutral.
2.	550	·0452		
3.	1000	·0159	" positive.	

Iodate of Potassium.

No.	Grains.	Value of Deflection.	
1.	100 diluted to 12 ozs.	·0064	Hot plate negative. Both plates much stained by formation of iodide of copper.
2.	Saturated solution (undiluted)	·0100	

Acid Carbonate of Potassium.

No.	Grains.	Value of Deflection.	
1.	50 diluted to 20 ozs.	·0049	Hot plate positive. The liquid on evaporation was green with dissolved copper. Liquid alkaline. Hot plate alone much tarnished.
2.	100 " "	·0170	
3.	200 " "	·0497	
4.	400 " "	·0818	
5.	600 " "	·1329	
6.	800 " "	·1978	
7.	1000 " "	·2441	
8.	2000 " "	·4210	
9.	Saturated solution (undiluted)	·5451	

Carbonate of Potassium.

No.	Grains.	Value of Deflection.	
1.	50 diluted to 20 ozs.	·0122	Hot plate positive.
2.	100 " "	·0382	
3.	200 " "	·1770	
4.	400 " "	·3719	
5.	800 " "	·7521	
6.	1600 " "	2·2400	
7.	2400 " "	3·7708	
8.	3200 " "	·4367	
9.	Saturated solution (undiluted)	·4031	

Acid Sulphate of Potassium.

Saturated solution (undiluted). Value of deflection ·1047. Hot plate negative.

Bichromate of Potassium.

No.	Grains diluted to 20 ozs.		Value of Deflection.	
1.	295	....	·0785	Hot metal positive.
2.	590	....	·1544	

Chrome Alum.

No.	Grains diluted to 20 ozs.		Value of Deflection.	
1.	249·8	....	·0019	Hot metal negative. Liquid of acid reaction.
2.	499·6	....	·0064	

Aqueous Ammonia.

Copper in a mixture of 4 ounces of water and 400 grains of aqueous ammonia at 180° Fahr. was electro-positive to copper in the same mixture at 66° Fahr.

Nitrate of Ammonium.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	80	·0002	Hot plate negative. Acid reaction.
2.	240	·0228	
3.	480	·0590	

Chloride of Ammonium.

No.	Grains.	Value of Deflection.	
1.	25 diluted to 20 ozs.	·0020	Hot copper positive. Solutions extremely faintly acid. Both plates tarnished by the stronger solution; but the hot one the most so, and a little copper was dissolved.
2.	50 " "	·0029	
3.	100 " "	·0147	
4.	200 " "	·0647	
5.	400 " "	·1583	
6.	800 " "	·5551	
7.	1000 " "	·6744	
8.	1600 " "	·6258	
9.	2000 " "	·7479	
10.	Saturated solution (undiluted)	·1210	

Aqueous Hydrocyanic Acid.

Scheele's strength. The hot plate was feebly positive. Value of deflection ·0006.

Cyanide of Potassium.

No.	Grains diluted to 12 ozs.	Value of Deflection.	
1.	100	·2854	Hot copper positive. Much gas evolved from the hot plate only in the strongest solution.
2.	1000	1·8164	

Ferrocyanide of Potassium.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	500	·0136	Hot plate positive. Liquid feebly alkaline. Both plates became pink like new copper.
2.	1000	·0045	

Oxalic Acid.

No.	Grains.	Value of Deflection.	
1.	25 diluted to 20 ozs.	·0001	The hot plate was negative, and the plates were not tarnished at all.
2.	50 " "	·0002	
3.	100 " "	·0006	
4.	200 " "	·0016	
5.	400 " "	·0064	
6.	Saturated solution (undiluted)	·0070	

Glacial Acetic Acid.

The hot plate was negative. Seven solutions, containing from $\frac{1}{16}$ ounce to 4 ounces by measure of the acid in 20 ounces by measure, gave only extremely feeble currents. The plates remained bright.

Acetate of Sodium.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	50	·0016	Hot plate positive, Solution alkaline to test-paper.
2.	100	·0070	
3.	200	·0198	
4.	400	·0594	
5.	800	·1328	
6.	1600	·2202	
7.	2000	·2850	
8.	2727	·2997	

Acetate of Zinc.

No.	Grains diluted to 20 ozs.	Value of Deflection.	
1.	50	·0001	Hot plate positive.
2.	100	·0006	
3.	200	·0016	
4.	400	·0025	
5.	500	·0020	
6.	800	·0020	
7.	1000	·0012	
8.	1600	·0004	
9.	2000	·0001	

Crystallized Tartaric Acid.

The hot plate was negative. Eight different solutions, varying in strength from 50 to 3200 grains in 20 ounces by measure of the solution, were tried; but very feeble currents were obtained, and the plates were not tarnished.

Crystallized Citric Acid.

The hot plate was negative. With a series of seven solutions, varying in strength from 50 to 3200 grains in 20 ounces of liquid, more feeble results, even, than those with tartaric acid were obtained, and the plates were not tarnished. Probably, with this substance and with others where the resulting currents were very feeble, more distinct effects would be obtained by employing a galvanometer of much greater electrical resistance.

Several experiments similar to those already described were made with the apparatus shown in fig. 3. The apparatus consists of a glass beaker containing the liquid, and two platinum electrodes—A being a disk of platinum rivetted to a platinum wire enclosed by a glass tube, B, and C a platinum crucible (for receiving the boiling water) with a platinum wire rivetted to it.

Experiment 1.—With a solution of 100 grains of citric acid in 2 ounces of distilled water, the hot platinum cup was negative, the value of the temporary deflection being ·0007.

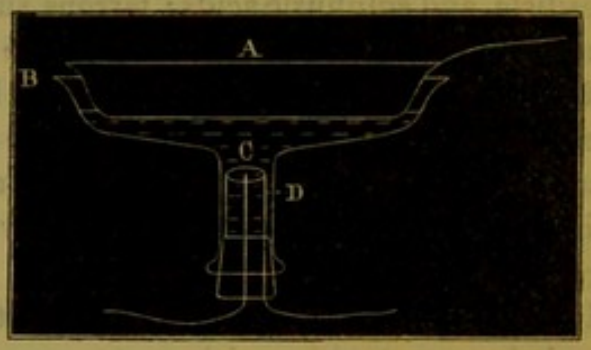
Experiment 2.—With 100 grains of tartaric acid in 2 ounces of water, the hot cup was negative, value of deflection ·0001.

Experiment 3.—With 100 grains of racemic acid in 2 ounces of water the hot cup was negative, value of deflection ·00005.

The negative condition excited in the hot platinum cup in the solutions of citric and tartaric acid agrees with the results obtained with copper in those liquids.

Fig. 3.

Fig. 4.



I have already shown (Phil. Mag. 1857, vol. xiii. p. 1) that the currents obtained with platinum electrodes are not due to the influence of atmospheric air upon the liquid and metal at their line of mutual contact; for, in the experiments there recorded, atmospheric air was entirely excluded, and the liquids were previously well boiled.

To test the influence of *size* of the *cold* electrode, I took a platinum dish, A (see fig. 4), 5 inches wide and 1½ inch deep, in a glass vessel of the annexed form, B, closed at its lower end by a cork, and containing in its neck two platinum electrodes, one consisting of a wire, C, and the other of a sheet 2 inches long and 2 inches wide in the form of a cylinder, D.

With a cold mixture composed of 3½ ounces of water and ¼ of an ounce by measure of strong sulphuric acid, and the *sheet* of platinum as the lower electrode, on pouring boiling water into the dish a deflection of the value of ·0064 was obtained, the cold electrode being positive; but with the *wire* as the lower electrode no perceptible deflection occurred. These results were obtained repeatedly. The electric currents are therefore largely dependent upon the size of the cold electrode.

General Results.

The chief fact brought out conspicuously by these experiments with copper dishes is, that in many cases an increase of chemical action produced by heat, instead of making the hot metal electro-positive, makes it considerably negative.

The results show that hot copper was positive to cold copper in the following liquids:—hydrochloric, hydrocyanic, boracic, and tribasic or orthophosphoric acids; chloride of copper (weak solution); chloride of cobalt; chloride of manganese; chromic acid; chloride of chromium; sulphate of zinc (weak solution); sulphate of magnesia; chloride of calcium; nitrate and chloride of strontium; chloride of barium; nitrate of sodium (strong solution); chloride, iodide, carbonate, and biborate of sodium; sulphate

of sodium (strong solution); tribasic phosphate of sodium; nitrate, chloride, and chlorate of potassium; bromide of potassium (strong solution); iodide of potassium (strong solution); carbonate, acid carbonate, and bichromate of potassium; aqueous ammonia; chloride of ammonium; cyanide and ferrocyanide of potassium; acetate of zinc; and acetate of sodium. And negative in the following ones:—nitric, chloric, hydrobromic, hydrofluosilicic, and sulphuric acids; ferrous sulphate; chloride of copper (strong solution); sulphate of copper; sulphate of zinc (strong solution); nitrate and iodide of sodium (weak solutions); bromide and iodide of potassium (weak solutions); iodate of potassium; chrome alum; nitrate of ammonium; oxalic, acetic, tartaric, and citric acids. The number of liquids in which hot copper was positive was thirty-six, and of those in which it was negative was twenty.

In several instances where the hot metal was negative with a weak solution, it became positive with a strong one—for instance, with sulphate of zinc, nitrate, iodide, and sulphate of sodium, bromide and iodide of potassium; but with chloride of copper the reverse occurred. These results may be connected with the fact that in weak neutral solutions the chemical action is generally the most feeble, and therefore interferes the least with the direct influence of the heat in producing electric currents.

The influence of free hydrochloric, hydrocyanic, boracic, orthophosphoric, and chromic acids was to make the hot copper positive; whilst that of nitric, chloric, hydrobromic, hydrofluosilicic, sulphuric, and some of the organic acids was to make it negative.

In consequence, probably, of the small amount of interference by chemical action in solutions of oxalic, acetic, tartaric, and citric acids, the direct influence of the heat made the copper negative—similar to its influence on platinum in all acid liquids which do not attack that metal.

The nature of the acid in a salt appears to exert much more influence than that of the base on the direction of the current; for instance, in nearly all chlorides, including those of a considerable variety of bases, hot copper was positive, probably because copper is more readily attacked by acids than by bases.

In all decidedly alkaline liquids the hot copper was positive; this is similar to the behaviour of platinum in such solutions, and is probably due to the same cause, viz. the direct influence of the heat, as well as to chemical action.

The results also show that the quantity of the current obtained with any given liquid generally increases with the number of molecules of the substance contained in the solution; in some cases, however, as with sulphuric acid, carbonate of potassium, chloride of ammonium, and acetate of zinc, there was a limit to this increase; and beyond that limit the quantity of the current decreased up to the point of saturation of the liquid.

In the great majority of cases the value of the deflection increased much more rapidly than the strength of the solution, particularly with solutions

of sulphate of magnesia, and also of hydrochloric acid and of chloride of sodium, probably because two causes operated, viz. increased strength of solution and diminished conduction-resistance; in a very few cases, however, the opposite result took place, as with solutions of chloride and nitrate of strontium.

Inversions of the direction of the deflection by difference of strength of the liquid occurred with solutions of chloride of copper, sulphate of zinc, nitrate, iodide, and sulphate of sodium, bromide and iodide of potassium.

Irregularities of the amount of deflection were very apt to take place with liquids which gave strong deflections, or which acted much upon the copper plates (for instance, nitric acid), especially if bubbles of air remained under the plates, or the dishes were wetted on their side above the liquid by the solution.

In certain acid liquids, viz. nitric, chloric, hydrobromic, hydrofluosilicic, and sulphuric acids, the hot copper was strongly negative (notwithstanding the chemical action upon it was distinct, and in some cases even strong); this is similar to the electrical behaviour of platinum in such liquids, and may be attributed either to the more direct influence of the heat alone (such as occurs with platinum plates), or to a different influence of the chemical action produced by the heat. Both these causes probably operate in such cases.

It is probable that in all cases where the hot copper was positive in liquids of strongly acid reaction, the positive condition was due to chemical action alone.

With some liquids, especially with solutions of hydrocyanic, boracic, acetic, tartaric, and citric acids, the deflections were very feeble, and the chemical action on the plates not perceptible; whilst with others, such as nitric and chloric acids, solutions of the chlorides of strontium, sodium, potassium, and ammonium, and of carbonate, acid carbonate, and cyanide of potassium, the deflections were considerable, and the chemical action distinct, and in some cases strong. In none of the liquids (except hydrobromic and chromic acids) did the hot plate appear to be *less* stained or corroded than the cold one; probably in all cases it was the most corroded, although in some cases the corrosion was not perceptible.

The amount of deflection was not always proportionate to the amount of chemical action; for instance, with solutions of chloride of copper and iodate of potassium there was considerable corrosion, but only feeble currents, probably because the plates became covered with a badly conducting film, whilst with hydrochloric acid, chloride of cobalt, chloride of manganese, and nitrate of potassium the reverse occurred.

I consider the currents in all these experiments of difference of temperature to be due either, 1st, to the direct influence of heat, the effect of which is to make the hot copper negative in acid liquids and positive in alkaline ones (see Phil. Mag. 1857, vol. xiii. p. 1); 2nd, to chemical action, which sometimes overpowers the direct influence of heat and reverses the effect;

or, 3rd, to both these influences combined. The more ultimate cause, however, of the phenomena in these cases must be sought for in the *molecular movements* produced by heat in the metals and liquids.

The currents obtained with copper plates were no doubt influenced in their amounts (if not also in their direction) by the oxidizing action of the air upon the liquid and metal at their line of mutual contact; for we know that metals in contact with liquids oxidize much more quickly if oxygen has access to their wet surfaces. And the currents were also influenced by the action of unequal temperature upon this air-contact line; for we know that wet metals oxidize still more rapidly if heat is applied.

Influence of line of contact of liquid and metal with the air.

That the length of line of contact of the liquid and copper with the air is capable of producing electric currents was shown by the following experiments:—

Two strips of sheet copper of the annexed form, fig. 5, $\frac{3}{4}$ inch wide, and

Fig. 5.

Fig. 6.

12 inches long in the longest limb, were cut from contiguous parts of a sheet of copper, and, after being perfectly cleaned, were coiled into the shape represented by the annexed sketch, fig. 6. They were then placed in a flat-bottomed porcelain dish and connected with the galvanometer, one of the spirals being supported at about $\frac{1}{4}$ inch higher than the other by means of a triangle of glass rod. The liquid to be examined was then poured into the dish until it just (and completely) covered the lower spiral, and the direction and amount of the permanent deflection noted. The positions of the spirals were then reversed and the electrical effects again noted.

Experiment 1.—With a liquid composed of 100 grains of cyanide of potassium dissolved in 12 ounces of water, whichever of the spirals was only partly submerged and therefore had the longest air-line, was strongly electro-negative to the wholly submerged one.

Experiment 2.—With a mixture of one measure of strong nitric acid and ten measures of water, deflections of somewhat less amount, but in precisely similar directions to those of experiment 1, took place.

Experiment 3.—With dilute hydrobromic acid the directions of the deflections were also similar, but still less in amount.

Experiment 4.—With a half-saturated solution of borax very feeble de-

flections, agreeing in direction with those of the other experiments, were obtained.

These results show the necessity (which I have already mentioned) of excluding air-bubbles from beneath the copper dishes, and of not wetting the sides of the dishes by the liquid above the level of their immersion.

To ascertain the influence of *difference of temperature* of the air-contact line I soldered two strips of perfectly similar sheet copper, each 12 inches long and ½ inch wide, in the form of circular hoops 4 inches in diameter upon the bottoms of two tin cups, and ground the edges of the strips perfectly level, and soldered copper wires to them for connecting with the galvanometer. Two glass triangles were now put into the apparatus, fig. 1, one in each dish, to support the cups, and a mixture of one measure of nitric acid and 12 measures of distilled water poured in until it just touched the edges all round of the perfectly horizontal copper rims resting on the triangles. After the needles of the galvanometer had settled at zero, about ten ounces of boiling water was poured into one of the cups; a temporary deflection of the value ·0560, and a permanent one of value ·0759, were produced, the hot metal being negative. The direction of the current in this experiment agrees with that obtained with the same mixture and the copper dishes; and the result indicates that a large proportion of the quantity of the current obtained with copper dishes in dilute nitric acid was due to the action of the air-contact line.

The influence of the air-line is largely *chemical*. "A piece of copper wire *wholly submerged* in the acid [dilute sulphuric] so as to entirely exclude any portion of it coming into contact with the air, has remained for many months without imparting the slightest tinge to the liquid." "But on suffering the liquid to evaporate so as to bring the upper end of the metal near to its surface, the instant the slightest portion becomes exposed chemical action immediately begins."

"Two equal portions of wire were similarly placed in acid, only that one was fully exposed to the atmosphere in an open tube, while the other was placed in a phial, the acid occupying half its height, and was kept closely corked for several weeks—after which the fully exposed metal had lost in weight two-fifths more than the one which had been excluded from contact with fresh portions of air, showing that contact with the atmosphere in bulk is necessary to the fullest action"*.

Experiments with Liquids of unequal strength.

To throw some light upon the questions,—1st, Is the quantity of the current simply a result of the difference of number of molecules of liquid which touch the hot plate compared with those which touch the cold plate? and, 2nd, What amount of difference of strength of a liquid is equal to the amount of difference of temperature employed?—I brought the two

* "On the Theory of the Voltaic Pile," Bridgman, Phil. Mag. Nov. 1869.

copper dishes into contact with liquids of unequal strength instead of unequal temperature.

The tube C (fig. 1) was filled with the stronger mixture and closed at its end in the dish A by an india-rubber bung, and the dish B filled to the line F with the same mixture; the dish A was then filled with the weaker mixture up to the same level and the bung slowly withdrawn. The two copper dishes, previously connected with the galvanometer, were next simultaneously immersed in the mixtures and the effect noted. The following are the results obtained by this method :—

Nitric Acid.

Experiment 1.—In A, 1 volume of acid diluted to 80 volumes. In B, 1 volume diluted to 40. Copper in A was positive temporarily, value ·0270; and permanently, value ·0198.

Experiment 2.—In A, 1 volume of acid diluted to 40 volumes. In B, 1 volume of acid diluted to 20 volumes. The copper plate in A was first positive temporarily, value of deflection ·0064; and then that in B permanently, value ·2850.

Experiment 3.—In A, 1 volume of acid diluted to 40 volumes. In B, 1 volume diluted to 10 volumes. Copper plate in B was positive temporarily, value ·4863; and permanently, value ·0819.

Hydrochloric Acid.

Experiment 1.—In A, 1 volume of acid diluted to 40 volumes. In B, 1 volume diluted to 20 volumes. The copper in B was positive temporarily, value ·9608; and permanently, value ·1087.

Experiment 2.—In A, 1 volume of acid diluted to 40 volumes. In B, 1 volume diluted to 26·66 volumes. The copper in B was positive temporarily, value ·3479; and permanently, value ·0702.

Chloric Acid.

In A, 1 volume of acid diluted to 80 volumes. In B, 1 volume diluted to 40 volumes. The copper in B was positive temporarily, value ·0036; and permanently, value ·0009.

Sulphuric Acid.

In A, 1 volume of acid diluted to 80 volumes. In B, 1 volume diluted to 40 volumes. The copper in B was positive temporarily, value ·0467; and permanently, value ·0330.

On examining these results, it will be perceived, 1st, that only in one half the number of the experiments did increased strength of liquid produce electrical currents similar in direction to those produced by increased temperature; and therefore the heat does not act simply by causing a greater number of molecules of each individual substance to touch the hot plate; and, 2nd, that only in one of the experiments was the copper in the weaker liquid both temporarily and permanently positive to that in the

stronger; whilst in five of the experiments the copper in the stronger liquid was temporarily and permanently positive to that in the weaker. Increase of strength of the liquid therefore made the copper *positive* in five cases out of six.

In the fourth experiment with hydrochloric acid with difference of temperature, and in the second one with difference of strength, the mixture in each case consisting of 1 volume of acid diluted to 40 volumes with water, an increase of temperature from 16° to about 98° C. produced a deflection of the value ·2854, whilst an increase of strength to 1 volume in 26·66 gave a deflection in the same direction of the value ·3479. An increase of temperature of about 82° C. was not quite equal in electrical effect to an increase of 50 per cent. in the number of molecules of the acid which touched the plates.

In the third experiment with chloric acid with difference of temperature, and in the single one made with difference of strength, the mixture in each instance consisting of 1 volume of the acid diluted to 80 volumes with water, an increase of temperature of about 82° C. produced an electrical effect of ·0040; whilst an increase of 100 per cent. in the number of molecules of the acid which touched the plates produced an opposite electrical effect of ·0036.

In the third experiment with sulphuric acid with difference of temperature, and in the single one made with difference of strength, each being with a mixture of 1 measure of acid in 80 of water, an increase of temperature of about 82° C. caused an electrical effect of ·0418, and an increase of 100 per cent. in the number of molecules of acid which touched the plates caused an opposite electrical effect of ·0467.

A liquid thermo-electric battery.

Acting upon the general results thus obtained in this subject, I constructed a liquid thermo-electric battery consisting of twelve glass tubes,

Fig. 8.

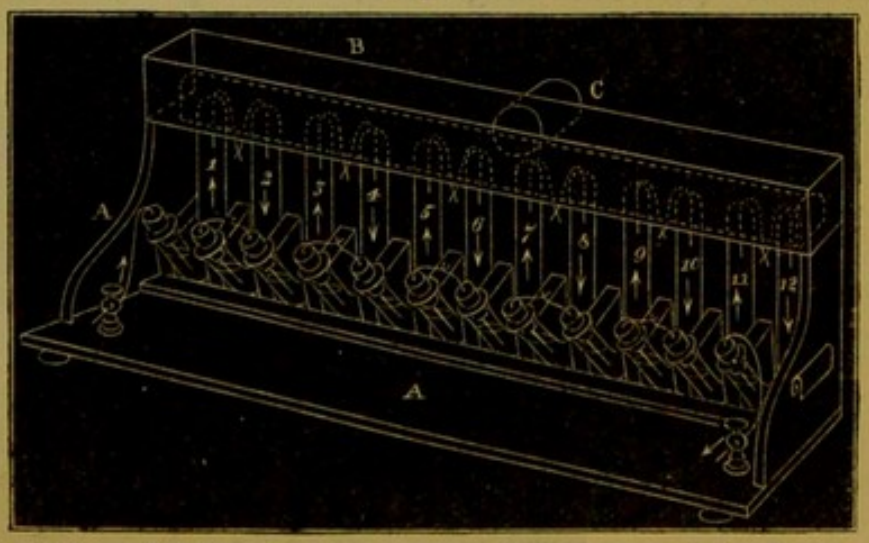


Fig. 7.

$\frac{3}{4}$ of an inch in diameter and 10 inches long, closed at one end (and containing a platinum wire hermetically sealed in that end), and bent to the

form shown in fig. 7, each tube being filled with a conducting liquid, and its outer end closed by a cork, in which was fixed a second platinum wire to dip into the liquid.

Fig. 8 represents the apparatus; A A is a wooden stand supporting a tin box, B. The box is water-tight, and has in its lower surface a long semicircular cavity (shown by dotted lines) to receive the upper ends of the twelve tubes. To the back of the box is fixed a short cylinder of tin, C, closed at its outer end. When the apparatus is in action, the box is filled with hot water, and the water kept boiling by means of a lamp placed beneath the tube C. The twelve tubes were kept in position by divisions of wood fixed to the back of the stand, as shown in the figure.

The tubes 1, 3, 5, 7, 9, and 11 were filled with a previously boiled and cooled mixture of $\frac{1}{4}$ of an ounce of sulphuric acid, and 19 ounces of distilled water; and the others, viz. 2, 4, 6, 8, 10, and 12, with a similarly prepared solution of 110 grains of hydrate of potassium dissolved in 19 ounces of distilled water.

The platinum wires were connected, in the order shown in the sketch, by means of small binding-screws not represented in the figure.

On connecting the terminals with a galvanometer containing about 180 turns of moderately coarse copper wire, and applying heat to the upper electrodes and ends of tubes by means of the boiling water, no deflection of the needles took place; but on substituting a Thomson's reflecting galvanometer, which offered a resistance of 3040·7 B.A. units (=77872·327 miles of copper wire $\frac{1}{16}$ of an inch thick), a deflection of 40 degrees was readily obtained, the hot platinum wire in the dilute acid being negative, and that in the alkali positive, as shown by the direction of the arrows in the sketch.

From these results it is evident the quantity of the electric current produced was exceedingly small, and its intensity considerable. By employing electrodes of larger surface, such as spirals of platinum wire and more concentrated liquids, the quantity of the current would be very largely increased. (See Phil. Mag. 1857, vol. xiii. p. 1.)

Fig. 9.

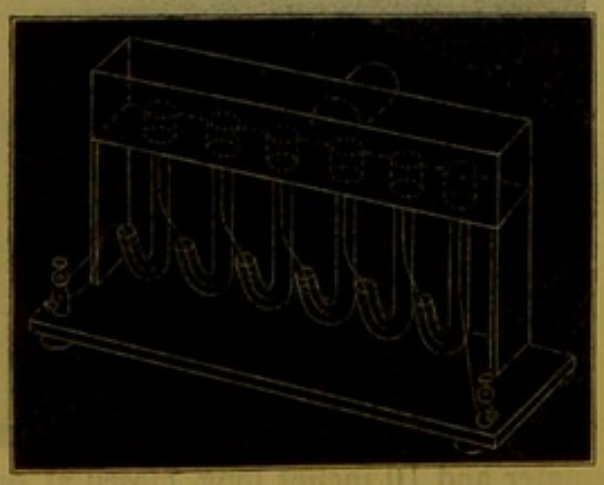


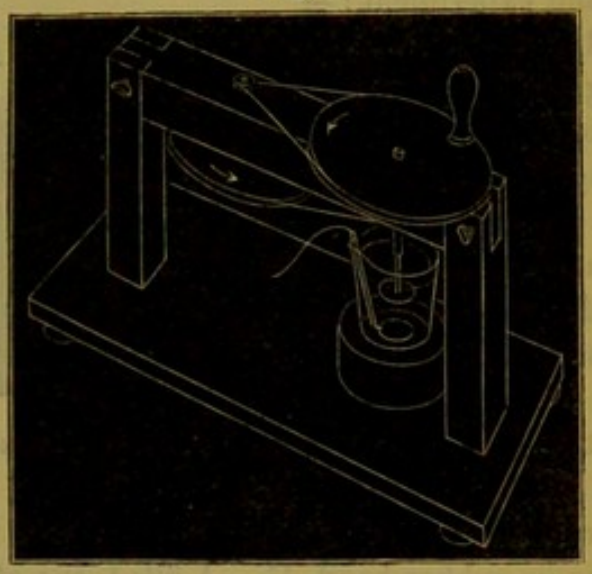
Fig. 9 represents a simpler arrangement of this apparatus, in which only

one kind of liquid, either acid or alkaline, is employed. The electrodes in this arrangement must be disposed in the order represented by the figure.

Influence of Friction.

To ascertain if the *friction* of one of the electrodes against the liquid had similar effects to those produced by the direct application of heat, I employed the apparatus shown in fig. 10. The sketch does not require explanation.

Fig. 10.



Experiment 1.—By immersing two stout copper wires vertically in an acidulated solution of cupric sulphate and rotating one of them at a speed of about 5000 revolutions per minute, the rotating wire became electro-positive.

Experiment 2.—With a saturated solution of borax, the rotating wire was positive.

Experiment 3.—With a solution of cyanide of potassium, the rotating wire was negative.

Experiment 4.—With stout platinum wires in an acidulated solution of cupric sulphate, the rotating wire became negative.

Experiment 5.—With platinum wires in a solution composed of 200 grains of carbonate of potassium in 40 ounces of distilled water, the rotating wire was faintly positive, and similarly in a very dilute solution.

Experiment 6.—With two platinum disks one above the other in a strong solution of carbonate of potassium, revolving the upper disk at a speed of about 5000 revolutions per minute made it electro-positive.

Experiment 7.—With an acidulated solution of cupric sulphate, the revolving disk became feebly negative.

On comparing these results with those obtained by unequal temperature, we find that the directions of the currents in the two classes of cases were reverse with copper in solutions of acidulated cupric sulphate and cyanide of potassium, and similar in a solution of borax; and with platinum in solutions of acidulated cupric sulphate or carbonate of potassium the in-

SOME TIGHT
GUTTERS