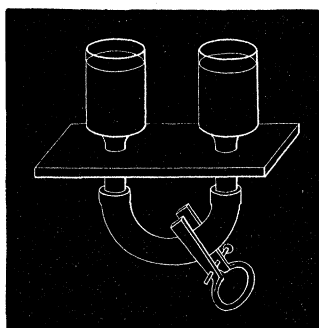


“Some Relations of Heat to Voltaic and Thermo-electric Action of Metals in Electrolytes.” By G. GORE, LL.D., F.R.S.
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In several papers on the “Thermo-electric Properties of Liquids,” &c., more particularly those in the “Philosophical Magazine,” January, 1857; the “Proc. Roy. Soc.,” No. 188 (1878), pp. 513–543; No. 199 (1879), and No. 208 (1880), I have shown the thermo-electric behaviour of numerous liquids with electrodes of platinum and mercury; and to a small extent with those of palladium, gold, silver, copper, and iron. In the present research, the subject has been examined in a different aspect, the object now being to ascertain the thermo-electric actions of a series of metals in particular liquids; and to examine the relations of the thermo-electric to the chemico-electric behaviour of metals in electrolytes, and to ordinary chemical corrosion, and the source of voltaic currents.

The following apparatus and method was employed for the thermo-electric experiments (see fig. 1). Two thin glass vessels of the form shown in the sketch, the cups of which were about 4 cm. wide and 5 cm. deep, with open legs 6 cm. long, and 13 mm. diameter, were

FIG. 1.



fixed in a piece of wood, and the limbs connected by an india-rubber tube. In using it to ascertain the thermo-electric behaviour of a particular metal with a liquid, the flexible tube was closed by a pinch tap, one limb and cup was nearly filled with the cold liquid, then the hot liquid (previously heated in a large closed flask) poured into the other; the pinch tap then taken off, the pieces of same metal wholly

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immersed in the liquid, and then connected with the galvanometer. Thermometers were supported in the liquid of the two cups, and the temperatures of the two portions of liquid and pieces of metal were in every case (except otherwise stated) 60° and 160° F. respectively. All the metals and compounds employed were the purest I could obtain, and liquids were avoided which would yield a metallic deposit upon the metals. A series of metals and one liquid were examined at a time. The most frequently recurring difficulty in the research was polarisation. In all the cases the thermal, electrolytic, and polarisation effects, produced in the liquids at the electrodes by the passage of the current, influence and modify the results by secondary action. When also the current is sufficiently strong, the positive metal is corroded.

By these means the thermo-electric couples found with one liquid and a series of metals were first classed into two groups, viz., those in which the metal was thermo-electro-positive, and those in which it was negative. To determine the series from the two groups, two similar apparatuses, as already described, were simultaneously used, one containing two pieces of one of the metals A, and the other, two of another metal B, from the same thermo-electric group, and so connected in single series, that the two currents opposed each other, and the one alone of greatest E.M.F. deflected the needle of the galvanometer. The following table exhibits the results, and the position of each metal in order of electro-motive power to the one next below, and to that next above it in the series, was thus in every case experimentally ascertained. The top metal in each column is the most positive in the particular liquid; and the metals above the dividing lines are those from which the current proceeds from the hot piece through the liquid to the cold one, and the ones below those lines the reverse.

The proportions of substances dissolved in each ounce of water to form the solutions were as follows: of potassic cyanide (containing 93·52 per cent. of the actual substance), fluoride, bromide, nitrate, iodide, chloride, sulphate and hydrate, sodic diphosphate, chloride, sulphate, potash alum and ammonia alum, 10 grains each, potassic carbonate 12 grains, anhydrous magnesian sulphate 4·8 grains, oxalic acid 2 grains, dextro-tartaric acid 1 grain, chloric acid 6 minims, hydrochloric, formic (sp. gr. 1·18), sulphuric, and nitric acids 1½ minims each. The liquids were selected of such a strength as was considered to be the most suitable, especially as regards rate of corrosion and strength of current. It was necessary in these experiments to continually remember that the results vary considerably with different specimens of the same metal, even when the metal is very pure and the pieces of it are cut from different parts of the same sheet.

Table I.—Thermo-electric Series of Metals in Liquids.

	1. KCy.	2. KF.	3. KBr.	4. KNO ₃ .	5. K ₂ CO ₃ .	6. Na ₂ HPO ₄ .	7. KI.	8. NaCl.
1.....	+ Sn	Al	Fe	Al	Al	Al	Sn	Pd
2.....	Al	Mg	Sn	Ni	Sn	Sn	Al	Cu
3.....	Pd	Sn	Ni	Fe	Pb	Cd	Fe	Sn
4.....	Ni	Fe	Co	Sn	Zn	Fe	Ni	Pb
5.....	Zn	Ag	Pb	Cd	Fe	Cu	Pd	Ni
6.....	Cd	Pt	Al	Cu	Cd	Pb	Pt	Fe
7.....	Fe	Au	Zn	Pb	Au	Ni	Au	Zn
8.....	Au	Pd	Mg	Pt	Cu	Pd	Zn	Cd
9.....	Pt	Pb	Pt	Au	Pt	Pt	Pb	Mg
10.....	Cu	Zn	Ag	Ag	Ag	Au	Cd	Al
11.....	Pb	Cd	Au	Pd	Pd	Ag	Cu	Pt
12.....	Ag	Ni	Pd	Zn	Ni	Mg	Ag	Ag
13.....	— Mg*	Cu	Cd	Mg†	Mg	Zn	Mg	Au

	9. HCl.	10. KCl.	11. K ₂ SO ₄ .	12. Acid, oxalic.	13. Acid, formic.	14. Acid, dextro- tartaric.	15. KHO.	16. H ₂ SO ₄ .
1.....	Ni	Ni	Ni	Al	Al	Ni	Cd	Al
2.....	Fe	Zn	Sn	Ni	Ni	Mg	Fe	Ni
3.....	Al	Al	Fe	Cu	Fe	Al	Cu	Fe
4.....	Mg	Cd	Al	Mg	Sn	Fe	Ag	Mg
5.....	Cu	Pb	Pb	Sn	Mg	Sn	Zn†	Cu
6.....	Sn	Fe	Ag	Cd	Cu	Pb	Pt	Pb
7.....	Pb	Sn	Cu	Pb	Pt	Cu	Sn	Pd
8.....	Ag	Cu	Mg	Fe	Pd	Zn	Pb	Sn
9.....	Zn	Ag	Zn	Zn	Ag	Cd'	Ni	Cd
10.....	Pt	Au	Cd	Ag	Cd'	Au'	Al†	Zn
11.....	Pd	Mg	Pd	Pd	Pb	Ag	Pd	Au
12.....	Cd	Pd	Pt	Au	Zn	Pd	Au	Ag
13.....	Au	Pt	Au	Pt	Au	Pt	Mg	Pt

Table I—(continued).

	17. Na ₂ SO ₄ .	18. HNO ₃ .	19. HClO ₃ .	20. MgSO ₄ .	21. Potash alum.	22. Ammonia alum.
1.....	Ni	Al	Al	Ni	Al*	Ni
2.....	Fe	Ni	Mg	Al	Mg†	Sn
3.....	Sn	Mg§	Pb	Cd	Ni†	Fe
4.....	Cd	Cu	Zn	Fe	Sn	Zn
5.....	Pb	Fe	Cd	Sn	Fe	Al
6... ..	Au	Pb	Sn	Cu	Pb*	Mg
7.....	Cu	Ag	Cu	Ag	Cd	Pb
8.	Al	Zn	Ag	Zn	Cu	Cd
9.....	Zn	Cd	Ni	Pd	Pd	Cu
10.....	Ag	Sn	Fe	Pt†	Zn	Ag
11.....	Mg	Pd	Pt	Au	Au	Au
12.....	Pd	Pt	Au	Mg	Pt	Pt
13.....	Pt	Au	Pd	Pb	Ag	Pd

* Indicates a gradual reversal with *one* metal only.

† Indicates that a temporary reversal occurred when the currents from the two contiguous metals (*i.e.*, the one marked and the one *above* it) were opposed.

‡ Magnesium was first negative, then positive, then negative 38 degrees.

§ Magnesium was first positive, then negative, then positive 30 degrees.

Remarks.—Of the foregoing cases, only those in which the metals are not at all corroded, are entirely thermo-electric, the remainder are concrete ones involving the additional influences of ordinary chemical corrosion and of voltaic action, and this fact must be remembered.

The currents were feeble in solutions of hydrochloric, formic, and dextro-tartaric acids, notwithstanding that the corrosion of the more electro-positive metals appeared to be as strong as usual, and the currents were so weak with cadmium in formic, and cadmium and gold in tartaric acid, that the positions of those metals as given in columns 13 and 14 are uncertain. The direction of the currents obtained with aluminium, also with magnesium, in a solution of one grain of lævo-tartaric acid per ounce of water, was the same as in a solution of the same strength of ordinary or dextro-tartaric acid. By opposing to each other also the thermo-electric currents from those two solutions either with aluminium or magnesium, that from the one of the lævo-acid was in each case found to have slightly the greatest electric potential.

In some separate experiments, the strength of thermo-electric current from platinum at 60° and 160° F., in a solution of potassic cyanide, varied directly as the strength of the liquid, the deflection

of the galvanometer needle, with a solution containing .3 grain of the salt per ounce of water being 1.0, with .6 grain 2.0, 6.0 grains 8.25, and 12.0 grains 11.0. The hot platinum was positive. With mercury at those temperatures, in solutions of .5 grain, 5.0 grains, and 10.0 grains of that salt per ounce of water, the hot metal was negative, and the deflections were 14.0, 45.0, and 50.0 respectively.*

The first point to be observed with regard to the table is, that out of 286 instances contained in it, including an average variety of liquids of alkaline, neutral, and acid reaction, in 87 or 30.42 per cent. only, or a proportion of 1 to 2.27, was the hot piece of metal negative to the cold one.

The thermo-electric order of metals in liquids was with every solution widely different from the ordinary thermo-electric order of metals alone, with no one liquid did more than three out of the thirteen metals agree in position in both the orders. It is remarkable that magnesium, a metal so very corrodible, so highly chemico-electro-positive, and so considerably thermo-electro-positive, in the series of metals only, is so often the most thermo-electro-negative in these series; in each case however where magnesium was at or near the bottom of the thermo-electric series, it was covered with a thin film of insoluble matter (see also pp. 261, 270, and 278).

The following list of the number of times each metal was positive and negative in Table I is inserted for future reference:—

Table II.

	Positive.	Negative.
Fe.....	21	1
Sn.....	20	2
Al.....	19	3
Ni.....	19	3
Pb.....	18	4
Cu.....	17	5
Zn....	15	7
Cd.....	14	8
Ag.....	13	9
Mg.....	12	10
Pd.....	11	11
Pt.....	11	11
Au.....	9	13
	199	87
Proportion.....	2.287 to 1.0.	

* See "Proc. Roy. Soc.," No. 199, 1879, Experiments 1—4. Mercury was tried in a different apparatus.

With regard to the influence of composition of the liquid, the salts of simple chemical character, such as potassic cyanide, fluoride, bromide, and nitrate, gave the largest proportion of thermo-electro-positive couples; the more complex ones, such as the double sulphates, gave the largest number of negative ones. I have not examined whether this is related to differences of specific heat of the salts. Even the highly thermo-positive metal nickel was rendered thermo-negative in solutions of potassic hydrate and chloric acid, and similarly with the thermo-positive metals platinum and palladium, each in eleven different liquids, and with aluminium in solution of potassic hydrate, sodic sulphate, and ammonia alum. The usually thermo-negative metal iron was more frequently positive than any other metal, it was strongly so in solutions of potassic bromide, hydrochloric acid, caustic potash, and sodic sulphate, and so also was the thermo-negative metal cadmium in solution of caustic potash.

The liquids in which the hot metal was thermo-electro-positive in the largest proportion of cases were those containing highly electro-positive bases, such as the alkali metals; thus, the highly chemico-electro- and thermo-electro-positive body potassium, forms the highly thermo-electro-negative compounds potassic cyanide, fluoride, bromide, nitrate, carbonate, and iodide. From a much smaller number of facts, I had previously drawn the conclusion that, provided ordinary chemical action is absent, liquids of alkaline reaction are usually thermo-electro-negative, and acid ones, thermo-electro-positive. This is largely confirmed in the present table in the cases of the least corrodible metals, gold and platinum.

In every experiment of this kind, the two pieces of metal were simultaneously immersed in the hot and cold portions of liquid respectively, and no cases of reversal of direction of current therefore occurred; many would have happened had the metals been slowly heated in the liquids. In a subsequent series of similar experiments, in which the one limb of the vessel was gradually heated after immersion of the electrodes, a number of such instances were observed (see p. 281). Bleekrode also ("*Poggendorff's Annalen*," 1870, vol. cxxxviii, p. 571; "*Annales de Chimie*," April, 1870; also "*Philosophical Magazine*," 1870, vol. xl, p. 311) has recorded a few of such cases.

In order to obtain a thermo-electric series of all the strongest thermo-positive and negative couples in Table I, the electric potentials of most of the top and bottom couples were measured. The remaining members were omitted because their currents were very variable in potential, probably in consequence of polarisation, and of alterations of rapidity of diffusion of the layers of liquid in contact with the electrodes. The electric potential usually declines quickly (but occasionally only a little), hence the numbers obtained depend upon the degree of rapidity with which the determinations are made. The

time usually occupied varied from one to two minutes. All the measurements, except those of Tables XI and XIV (pp. 273 and 277), were made by *balancing* the current to be measured, by one of equal potential from two thermo-electric piles, each consisting of about 300 pairs of iron and German silver wires, the accuracy of which was occasionally tested by means of a Clark's standard cell.* (For a description of the pile, see "Proc. Birm. Phil. Soc.," vol. iv, pt. 1.)

With the two pieces of metal at 60° and 160° F. respectively, the following numbers and series were found, in which the top couple of the upper section is the most positive, and the bottom one of the lowest division is the most negative.

Table III.—Electric Potentials of Thermo-electric Couples.

Metal.	Liquid.	Volts.
Al	Na ₂ HPO ₄	·6621
„	Formic acid	·4392
„	HNO ₃	·4317
Ni	Tartaric acid	·3447
Al	HClO ₃	·3051
„	KF	·2914
„	H ₂ SO ₄	·2778
Ni	K ₂ SO ₄	·2428
„	Am alum	·1972
Sn	KCy	·1827
Ni	MgSO ₄	·1757
Fe	KBr	·1702
Ni	KCl	·1439
„	HCl	·0978
„	Na ₂ SO ₄	·0975
Cd	KHO	·0877
Total		4 ·1475
Average		·2592
Pb	MgSO ₄	·0119
Au	HCl	·0140
„	Formic acid	·0236
Mg	KI	·0282
Pt	Na ₂ SO ₄	·0324
Pd	Am alum	·0441
Au	K ₂ SO ₄	·0504
„	HNO ₃	·0660

* Nearly all the measurements of potential in this research were made with the aid of a Thomson's reflecting galvanometer, having a resistance of 3040·7 ohms.

Table III—(continued).

Metal.	Liquid.	Volts.
Mg	KCy	·0691
Pt	Tartaric acid	·0761
Ag	K alum	·0844
Pd	HClO ₃	·0985
Mg	KHO	·1169
Pt	H ₂ SO ₄	·1403
Mg	K ₂ CO ₃	·1498
Total		1·0057
Average		·0670

Remarks.—The current from the strongest pair in this series had about one hundred times greater potential than that from a single pair of bismuth and antimony with an equal difference of temperature.

Not only were the thermo-electro-positive combinations of metals and electrolytes about double the number of the negative ones (see Table I) : but the range of potential of the strongest of the former was about 4·12 times that of the latter, as shown by this table. The facts that there is a much larger number of thermo-electro-positive metals than of thermo-negative ones ; also of thermo-electro-positive combinations of metals with liquids than of negative ones, and that the positive elements of each of these classes are usually the strongest, indicate that electro-positive action in metals generally is more frequently increased than decreased by rise of temperature.

In the present table, the acids in contact with the chemico-electro-negative metals platinum, gold, and palladium, are thermo-electro-positive ; and in contact with the positive ones, aluminium and nickel, they appear negative. In this table also, as in Table I, aluminium, a strongly chemico-electro-positive metal, is conspicuously the most thermo-electro-positive one. The highly chemico-electro-negative metals also, silver, palladium, gold, and platinum, are present only in the thermo-negative division. In apparent opposition to this, but still largely in accordance with Table I, it is remarkable that magnesium, a metal highly chemico-electro-positive, and also considerably thermo-positive in the series of metals only, is the most thermo-negative in this series (see also pp. 255, 261, 270, and 278).

In order to ascertain the influence of strength of liquid upon the sequence of the various thermo-electric series, another set of experiments, similar to those of Table I, was made, with all the solutions of five times the strength, except those of sodic diphosphate, which was four times, and those of potassic and ammoniac alum, and potassic sulphate, each of which was only three times. The results are shown in

the following table. The temperatures of the hot and cold pieces of metal were 60° and 160° F. respectively.

Table IV.—Thermo-electric Series of Metals in Strong Solutions.

	KCy.	KF.	KBr.	KNO ₃ .	K ₂ CO ₃ .	Na ₂ HPO ₄ .	KI.	NaCl.
1.....	Sn	Ag	Ni	Ni	Sn	Sn	Sn	Ni
2.....	Al	Sn	Fe	Al	Al	Al	Fe	Fe†
3.....	Ni	Al	Sn	Fe	Zn*	Pb	Al*	Cu*
4.....	Au	Fe	Cu	Cu	Cd†	Ni	Ni	Sn
5.....	Pd	Pt	Pb	Sn	Pb*	Pd	Pt	Cd
6.....	Pt*	Au	Ag	Pb	Fe	Pt	Pd	Pb
7.....	Zn*	Pd	Zn*	Au	Cu	Au	Pb	Pd
8.....	Fe	Ni*	Pt	Ag*	Au	Ag	Au	Ag
9.....	Cu	Pb	Pd	Cd*†	Ag	Cu	Zn	Zn*
10.....	Pb	Zn†	Au	Pt	Pt	Fe†	Cu	Mg
11.....	Ag	Cd	Cd*	Pd	Pd	Cd	Ag	Al
12.....	Cd	Cu†	Mg*	Mg*	Ni	Zn†	Mg	Au
13.....	Mg*	Mg	Al*	Zn	Mg	Mg	Cd	Pt

	HCl.	KCl.	K ₂ SO ₄ .	Oxalic acid.	Formic acid.	Dextro-tartaric acid.	KHO.	H ₂ SO ₄ .
1.....	Ni	Ni	Mg	Al	Al	Mg	Ag	Al
2.....	Cu*	Fe†	Al*	Fe	Mg	Ni	Cu	Ni†
3.....	Fe	Cu	Ni	Ni	Ni	Al	Cd	Pb
4.....	Pb*	Sn	Ag	Mg	Fe	Fe†	Fe†	Mg
5.....	Al*	Zn	Fe	Sn	Pb	Sn	Pt	Fe*
6.....	Mg	Cd	Sn	Ag	Cd	Cd	Au	Sn
7.....	Sn	Al	Pb	Cu	Sn	Cu	Pd	Cd
8.....	Cd*	Mg	Cu	Au	Pd	Pb	Pb	Cu
9.....	Zn	Au	Au	Pb	Ag	Zn	Zn	Pd
10.....	Pt	Ag	Pd	Pd	Au	Au*	Sn†	Zn
11.....	Au	Pd	Cd	Cd	Cu	Ag*	Mg	Au
12.....	Ag	Pt	Zn	Zn	Zn	Pt	Ni*	Ag
13.....	Pd	Pb	Pt	Pt	Pt	Pd	Al*†	Pt

Table IV—(continued).

	Na ₂ SO ₄ .	HNO ₃ .	HClO ₃ .	MgSO ₄ .	K alum.	Am alum.
1.....	Ni	Al	Al	Al*	Al*	Al
2.....	Fe	Mg	Mg	Ni	Ni	Ni
3.....	Au	Fe	Cd*	Fe	Mg	Fe
4.....	Mg	Ni†	Ni	Pt	Fe	Sn
5.....	Sn	Cu	Fe	Sn	Sn	Mg†
6.....	Cd	Au	Pb	Cd	Pd	Cd
7.....	Cu*	Ag	Zn†	Pd	Pb	Ag
8.....	Zn	Pb	Pd	Au	Pt	Pt
9.....	Pb	Cd	Sn	Pb	Ag	Pd
10.....	Al	Pd	Cu*	Cu	Cd	Zn
11.....	Ag	Sn	Ag†	Ag†	Cu*	Cu
12.....	Pd	Zn	Au	Mg	Zn	Au
13.....	Pt	Pt	Pt	Zn	Au	Pb*

* Indicates a gradual reversal with *one* metal only.

† Indicates that a temporary reversal occurred when the currents from the two contiguous metals (*i.e.*, the one marked and the one *above* it) were opposed. A few reversals also took place with non-contiguous metals.

Remarks.—This table contains 23·42 per cent., or a proportion of 1 to 3·27, of instances of metals thermo-electro-negative in liquids. A comparison of it with Table I shows that a large increase of strength of liquid increased the number of instances of metals thermo-positive in liquids from 199 to 219, or from 69·58 to 76·58 per cent., thereby further showing the influence of the liquid upon the apparent thermo-electric character of the metal, and indicating that increased concentration of the solution was usually accompanied, either by an increase of thermo-electro-negative, or decrease of thermo-electro-positive property of the liquid; or that the metals, under the new condition, were more electro-positive. No thermo-electric reversals occurred during the experiments for making Tables I and IV, because the metals were not *gradually* heated.

Increased strength of liquid also greatly altered the order of the series in every case, and produced a very large number of reversals of position or of relative electro-motive force of the metals; out of the total 286 instances, 36 only were not reversed. With some particular strength of liquid, therefore, intermediate between those employed in forming the two tables, the currents from each two metals, which were reversed in position, must balance each other. Many reversals of

thermo-electric sign also of single metals occurred, and in all these, viz., 64, with some intermediate strength of liquid, and the two pieces of metal at 60° and 160° F. respectively, no thermo-electric current would be produced. Magnesium suffered a very great depression of electro-motive force from near the top to quite the bottom of the series in solution of potassic fluoride by increased strength of the liquid; and many other great changes of position of metals in other solutions were similarly produced.

The depression of magnesium to about the bottom of the thermo-electric series in nine different liquids in Table I, and about the same number in Table IV, may have been due to the already-mentioned (p. 255) circumstance that in all the solutions, except those of acids and salts of acid reaction, magnesium becomes coated with an adherent film of white basic salt. In not one of the solutions of acids or acid salts was magnesium thus coated, or its position depressed. On the other hand, the coating of basic salt had no such effect in the solution of weak potassic fluoride; if also the coating caused the magnesium to be thermo-electro-negative in so many liquids, the hot magnesium would probably have been positive at the first instant of immersion, before the coating had time to sufficiently form, but it was not. (See Table I, Notes.)

Both in weak and strong solutions, silver, copper, palladium, and cadmium usually gave thermo-currents of the least electro-motive force, and aluminium and nickel were conspicuously thermo-positive and platinum and magnesium frequently the most thermo-negative.

Many of these results agree with the circumstance that with unequally heated metals in liquids, great changes of strength, and even reversals of current, frequently occur without any apparent cause, but probably in consequence of alteration of chemical composition and

Table V.

Liquid.				Metals.	Volts.
20 minims of H_2SO_4	to each ounce of water,	unboiled.....		Pt —	·0792
"	"	boiled.....		" —	·0579
10 grains of K_2SO_4	"	unboiled.....		Ni +	·0996
"	"	boiled.....		" +	·1249
"	"	" repeated..		" +	·1000
$6\frac{1}{4}$ minims of HCl	"	unboiled.....		Cu +	·1034
"	"	boiled.....		" +	·1210

strength of the liquid by irregularities of diffusion at the surfaces of the metals; this is largely proved by the great effect which is usually produced by stirring the liquid. Bouty refers such variations partly to the presence of dissolved air and partly to movements of flow of

the liquid. (See "Comptes Rendus, Académie des Sciences, Paris," vol. xc, 1880, pp. 917—920.)

Some experiments were made to ascertain the effect of pre-boiling the liquid upon the degree of thermo-electric potential. With the two pieces of metal at 60° and 160° F. respectively, the results are as given in Table V (p. 261).

With the object of ascertaining the influence of degree of concentration of the liquid upon the thermo-electric potential, the degrees of potential of nearly all the currents from the top and bottom members of the series in Table IV were measured by the method of balance (see p. 257); those only being omitted which were very

Table VI.—Potentials of Thermo-couples in Strong Solutions.

Metal.	Liquid.	Strong solution. Volts.	Weak solution. Volts.
Al	MgSO ₄	·6034	
„	K alum	·5700	
„	Am alum ..	·5084	
Sn	Na ₂ HPO ₄ ..	·4469	
Al	HNO ₃	·3253	·4317 = ·1064 decrease.
Sn	KI	·2846	
Ag	KF	·2084	
Ni	KCl	·1861	·1439 = ·0422 increase.
Al	HClO ₃	·1652	·3051 = ·1399 decrease.
„	H ₂ SO ₄	·1634	·2778 = ·1144 „
„	KNO ₃	·1615	
„	KBr	·1438	
Ni	Na ₂ SO ₄	·1361	·0975 = ·0386 increase.
Ag	KHO	·1349	
Sn	KCy	·0971	·1827 = ·0856 decrease.
Mg ..	Tartaric acid	·0822	
Ni	HCl	·0790	·0978 = ·0188 „
Mg	K ₂ SO ₄	·0712	
„	Formic acid.	·0576	
Ni	NaCl	·0299	
Fe	Oxalic acid .	·0294	Total 4·4844. Average ·2135.
Cd	KI	·0154	
Pb	Am alum...	·0182	
Pd	Tartaric acid	·0384	
Au	K alum	·0448	
Pt	H ₂ SO ₄	·0503	·1403 = ·0900 decrease.
Pd ..	HCl	·0707	
Pt	K ₂ SO ₄	·0906	
Mg	KF	·0944	
Al	KHO	·1105	
Pt	Oxalic acid .	·1404	
Mg	Na ₂ HPO ₄ ..	·1425	
Pt	HNO ₃	·1673	
Mg	K ₂ CO ₃	·2478	·1498 = ·0980 increase.
Pt	HClO ₃	·3644	Total 1·5955. Average ·1139.

variable. The pieces of metal were in each case at 60° and 160° F. respectively. The foregoing Table VI contains the results:—The degrees of potential of those cases in which the same metals were used with the weaker liquids are inserted for convenience of comparison.

Remarks.—Several of the remarks made on Table III (p. 258), apply to this one. Whilst also there were six cases in which the

Table VII.—Potentials of Thermo-electric Couples.

Liquid.	Metal.	Volts.
6¼ minims of H ₂ SO ₄ to each ounce of water	Pt — Ag — Cu +	·1773 ·0880 ·0525
31¼ " " " " 	Pt — Ag — Cu +	·3347 ·0484 ·0108
1 volume of H ₂ SO ₄ and 9 volumes of water	Pt — Ag — Cu continually reversing	·1089 ·0415
1 " " 4 " " 	Pt — Ag — Cu —	·2234 ·0488 ·0138
·72 minim of strong selenic acid to each ounce of water..	Pt —	·1541
1·45 " " " " " ..	" —	·1273
2·9 " " " " " ..	" —	·0747
5·75 " " " " " ..	" —	·0293
11·5 " " " " " ..	" +	·0330
2·5 grains of chromic acid " " ..	Pt —	·0433
5·0 " " " 	" —	·1416
10 " " " 	" —	·0137
12½ grains of glacial phosphoric acid to each ounce of water	Pt —	·1815
25 " " " " " ..	" —	·2027
50 " " " " " ..	" —	·1687
1¼ minim of HNO ₃ to each ounce of water.....	Pt —	·2636
6¼ " " " " 	" —	·2617
31¼ " " " " 	" +	·2850
156¼ " " " " 	" +	and — variable
312½ " " " " 	" —	·2354
2·5 grains of iodic acid " " 	Pt —	·0484
5 " " " " 	" —	·0633
20 " " " " 	" —	·0451
60 " " and 62¼ minims of H ₂ SO ₄ to each } ounce of water	Pt —	·2895
120 grains of iodic acid and 125 minims of H ₂ SO ₄ to each } ounce of water	" —	·2120

thermo-electric potential was decreased by increased strength of liquid, there were only three in which it was increased,* and both the total and average amount of decrease was greater than that of increase.

The determinations in Table VII of the thermo-electric potentials of metals in liquids, the pieces of metal being at 60° and 160° F. respectively, illustrate more fully the influence of strength of liquid.

Remarks.—In fifteen cases the thermo-electric potential was decreased, and in eight increased by additional strength of liquid, and the total amount of decrease was greater than that of increase. As greater strength of solution was usually attended by decreased thermo-electric potential, it would be interesting to ascertain whether this was related in any degree to the diminished specific heat of the liquid, or to changes of diffusive power of its constituents.

The following additional determinations of thermo-electric potential by the method of balance were also made with electrodes at 60° and 160° F. respectively.

Table VIII.—Thermo-electric Potentials.

Liquid.	Metal.	Volts.
A half saturated solution of pure cupric sulphate.....	Pt —	·0177
Ditto ditto ditto	Ag —	·0547
Ditto ditto ditto	Cu —	·0617*
10 grains of ammoniac nitrate to each ounce of water	Pt +	·0882
10 " " phosphate " "	" +	·0057
10 " sodic diphosphate " "	Sn +	·2437
13 $\frac{3}{4}$ " " selenate " "	Pt —	·0688
10 " " hyposulphite " "	" +	·0545
10 " chloride of cobalt " "	" —	·0288
100 " potassic fluoride " "	Ag +	·1045
100 " " hydrate " "	" +	·1464
100 " " cyanide " "	Pt +	·0970
10 " " ferrocyanide " "	" +	·0527

* This = ·00034 volt for 1° C. Bouty obtained ·0007 of one Daniell's element. ("Compt. Rend.," vol. xc, p. 917.)

No difference of potential was observable on opposing the current from two thermo-electric couples of tin in solution of potassic cyanide, one being composed of large electrodes and the other of small ones. By opposing those from the same metal and liquid, the one couple having a large hot electrode and a small cold one, and the other the reverse, no definite result occurred.

Very few researches have been made on the thermo-electric properties of liquids. H. Wild ("Poggendorff's Annalen," vol. ciii, pp. 353—411, 1858) has shown that when two vertical columns of

* This is a usual circumstance.

different electrolytes at 60° F., of different specific gravities, and not mutually decomposable, are placed end to end upon each other as distinct strata in mutual contact, the lighter one being the uppermost, and the junction of the two is heated, a thermo-electric current is produced. He has also shown that this current varies in strength with the kind of solution and the degree of its concentration.—That the electromotive force of the resulting current is nearly proportional to the difference of temperature up to that of 50° of the portions of liquid at the contact surface.—That with two portions of solution of different degrees of strength of the same salt, the current passes from the weaker to the stronger one.—And that when equal volumes of the two solutions contain chemically equivalent weights of salts of two different metals, the order of the liquids in electric tension series is the same as that of their metals. Further, that the order of the series with solutions of all neutral salts of the type $R.SO_4$, agrees with that of the ordinary chemico-electric series of their metallic bases in the case of salts of K, Na, Mg, Mn, Fe, Ni, CO, Zn, Cu, and Ag, thus :—

Table IX.

Thermo-electric Series.		Chemico-electric Series.
K_2SO_4	K
$MgSO_4$	Mg
$ZnSO_4$	Zn
$FeSO_4$	Fe
$NiSO_4$	Ni
$CuSO_4$	Cu

Solutions of the salts KCl, KBr, KI, also follow a similar order, but those agreeing with the formula $R_2O_3SO_3$ do not obey this rule, nor do acids in general.

E. Becquerel also ("Annales de Chimie et de Physique," 4th series, 1866, vol. vii, pp. 392—397) similarly heated the mutual contact portions of two electrolytes about 10° to 80°, and found the following effects: A saturated solution of sulphate of copper was positive to a mixture of 1 part of sulphuric acid and 19 parts of water; water acidulated with hydrochloric acid was positive to a solution of sodic chloride, rendered alkaline by caustic potash; strong nitric acid was positive to a solution of 1 part of caustic potash in 10 parts of water; solution of cadmium sulphate was positive to a dilute one of ammoniac chloride, and no current was produced by heating the junction of a solution of persulphide of potassium and a diluted one of the same salt.

One of the chief objects of this research being to obtain new knowledge respecting the relation of thermo-electric action of liquids and metals to chemico-electric action, the chemico-electric

positions in series of all the foregoing combinations of metals and liquids were determined at the temperatures of 60° and 160° F. respectively, in order to compare the two series, and ascertain how far the differences in chemico-electric position at different temperatures agreed with the thermo-electric relations of the particular combinations of metal and liquid at those temperatures. All the solutions were of the same degree of strength as those used in forming the thermo-electric series of Table I. The experimental results are shown in the following table:—

Table X.—Chemico-electric Series at 60° and 160° F.

	1 KCy.		2 KF.		3 KBr.		4 KNO ₃ .		5 K ₂ CO ₃ .	
	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.
1	Mg	Al	Al	Al	Mg	Mg	Mg	Mg	Mg	Al
2	Al	Zn	Mg	Mg	Zn	Zn	Zn	Zn	Al	Mg
3	Cu	Cu	Zn	Zn	Cd	Cd	Cd	Cd	Sn	Sn
4	Zn	Cd	Cd	Sn	Al	Al	Pb	Fe	Pb	Zn
5	Cd	Sn	Sn	Cd	Pb*	Pb	Fe	Pb	Zn	Pb
6	Sn	Mg	Fe	Fe	Fe	Fe	Sn	Al	Cd	Cd
7	Ag	Ag	Pb	Pb	Sn*	Sn	Al	Sn	Fe	Fe
8	Ni	Ni	Cu	Ni	Ni	Ni	Ni	Ni	Ni	Cu
9	Pb	Pd	Cu	Cu	Cu	Cu*	Ag	Cu	Cu	Ni
10	Au	Au	Pd	Pd	Ag	Ag	Cu	Pd	Pd	Pd
11	Pd	Pb	Pt	Pt	Pd	Pd	Pd	Ag	Au	Au
12	Fe	Fe	Ag	Ag	Au	Au	Au	Au	Pt	Pt
13	Pt	Pt	Au	Au	Pt	Pt	Pt	Pt	Ag	Ag

	6 Na ₂ PO ₄ .		7 KI.		8 NaCl.		9 HCl.		10 KCl.	
	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.
1	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg
2	Zn	Al	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn
3	Pb	Cd	Cd	Cd	Al	Al	Cd	Cd	Al	Al
4	Cd	Zn	Pb	Fe	Cd	Cd	Al	Al	Cd	Cd
5	Sn	Sn	Al	Pb	Pb	Fe	Fe	Fe	Pb	Pb
6	Al	Pb	Sn	Al	Fe	Pb*	Sn	Sn	Fe	Fe
7	Fe	Fe	Fe	Sn	Sn	Sn	Pb	Pb	Sn*	Sn
8	Cu	Cu	Cu	Cu	Ni	Cu	Ni	Ni	Cu	Cu
9	Ni	Ni	Ag	Ag	Cu†	Ni	Cu	Cu	Ni	Ni
10	Pd	Pd	Ni	Ni	Ag	Ag	Ag	Ag	Ag	Ag
11	Pt	Pt	Au	Au	Au	Au	Au	Au	Au	Pd
12	Au	Au	Pd	Pd	Pd	Pd	Pt	Pt	Pd	Au
13	Ag	Ag	Pt	Pt	Pt	Pt	Pd	Pd	Pt	Pt

Table X—(continued).

	11 K ₂ SO ₄ .		12 Oxalic acid.		13 Formic acid.		14 Dextro-tartaric acid.		15 KHO.	
	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.
1	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Al	Al
2	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn*	Zn
3	Cd	Cd	Cd	Al	Cd	Cd	Cd	Cd	Sn	Mg
4	Fe	Fe	Sn	Cd	Fe	Fe	Fe	Al	Mg	Sn
5	Pb	Al*	Al	Sn	Pb	Al	Sn*	Fe	Pb	Cd
6	Sn	Pb	Fe	Fe	Sn	Sn	Pb	Sn	Fe	Pb
7	Al	Sn	Pb	Pb	Al	Pb	Al	Pb	Cd	Fe
8	Cu	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Cu	Cu
9	Ni	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Ni	Ni
10	Au	Ag	Ag	Ag	Au	Ag	Ag	Ag	Au	Au
11	Pd	Pd	Pd	Au	Ag	Au	Au	Au	Pd	Pt
12	Ag	Au	Au	Pd	Pt	Pd	Pd	Pd	Pt	Pd
13	Pt	Pt	Pt	Pt	Pd	Pt	Pt	Pt	Ag	Ag

	16 H ₂ SO ₄ .		17 Na ₂ SO ₄ .		18 HNO ₃ .		19 HClO ₃ .		20 MgSO ₄ .	
	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.	Cold.	Hot.
1	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg
2	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn	Zn
3	Cd	Al	Cd	Cd	Cd	Al	Cd	Al	Al	Al
4	Fe	Cd	Pb	Fe	Fe	Cd	Fe	Cd	Cd	Cd
5	Sn*	Fe	Fe	Pb*	Pb	Fe*	Al	Pb	Pb	Fe
6	Pb	Sn	Al*	Al	Al	Pb*	Sn	Sn	Fe	Pb
7	Al	Pb	Sn	Sn	Sn	Ni	Pb	Fe	Sn	Sn
8	Ni	Ni	Ni	Ni	Ni	Sn	Ni	Ni	Ni	Ni
9	Cu	Cu	Cu	Ag	Cu	Cu	Cu	Cu	Cu	Cu
10	Au	Ag	Ag	Cu	Ag	Au	Ag	Ag	Au	Ag
11	Pd	Pt	Pd	Pd	Pt	Pt	Au	Au	Ag	Au
12	Ag	Au	Pt	Pt	Au	Pd	Pd	Pd	Pd	Pd
13	Pt	Pd	Au	Au	Pd	Ag	Pt	Pt	Pt	Pt

Table X—(continued).

	21 Potash alum.		22 Ammonia alum.	
	Cold.	Hot.	Cold.	Hot.
1	Mg	Mg	Mg	Mg
2	Zn	Zn	Zn	Zn
3	Cd	Al	Cd	Cd
4	Fe	Cd	Fe	Fe
5	Pb	Fe	Al	Al
6	Al	Sn*	Pb	Sn
7	Sn	Pb	Sn	Pb
8	Ni	Ni	Ni	Ni
9	Cu	Cu	Cu	Cu
10	Pt	Ag	Pd	Pd
11	Au	Pt	Ag	Ag
12	Ag	Au	Au	Au
13	Pd	Pd	Pt	Pt

* Indicates a temporary reversal with the two contiguous metals, *i.e.*, the one marked and the one *above* it.

† Indicates that a current occurred on contact only between the marked one and the next above it.

Remarks.—The currents obtained from two contiguous base metals were usually much stronger than those from contiguous noble ones. The influence of rise of temperature in altering the relative positions of the various metals in the series may be rendered more evident by drawing cross lines between those which are altered. It might have been supposed that as chemical action is usually increased by heat, the hot piece of metal would in nearly every instance have been either more electro-positive or less electro-negative than the cold one, and that the orders of the chemico-electric series of metals with each liquid at 160° would have been nearly always the same as at 60° F. The results exhibited by Table X, however, show that out of 22 liquids, in two only, *viz.*, dilute hydrochloric acid and solution of potassic bromide, was the order of the hot series of metals exactly the same as that of the cold one. In all these cases of voltaic as well as of thermo-electric action, change of temperature was attended by change of electric state.

By tabulating separately, and comparing the numbers of instances in which the respective metals occur on the several lines of Tables I and X, it will be at once seen that in the thermo-electric series the metals generally, whilst occupying the same parts of the table as those

of the chemico-electric ones, are much more distributed, those of each particular metal occupying about double the number of lines. This probably indicates that in these thermo-electric actions voltaic influence modified the effects; also that heating one of the pieces of metal only of a voltaic pair usually increased the amount of their electric difference, making most metals more positive and some more negative, whilst heating the second one also, usually neutralised to some extent the effect of heating the first one only.

Tabulating the members thus also shows that gold and platinum are the least distributed of the metals of the thermo-electric series, they are also the least corrodible. Platinum, gold, palladium, and silver occupy in all cases the lower half only of the table in the voltaic series, and in nearly all cases also in the thermo series. Aluminium, tin, and iron preponderate in the upper section of both tables. These facts also indicate that voltaic influence operates in most of these thermo-electric actions. An examination of Table II further supports this conclusion.

As the electrical effect of heating a voltaic couple may be viewed as being in a greater degree composed of the united consequences of heating each of the two metals separately (see pp. 270, 271, and 281), I have compared the chemico-electric series in the weak solutions at 60° F., Table X, p. 267, side by side with the thermo-electric ones of the same metals in the same liquids of Table I, in a similar manner as the two chemico series are themselves compared. By such a comparison it was found that magnesium, zinc, and cadmium suffered usually very great depressions of position and electromotive force in the series by the influence of heat (see pp. 276, 278). In such a table of comparison, magnesium was depressed 21 times through a total of 144 places; zinc was lowered 20 times through a sum of 123, and raised through 1 only; and cadmium sank 17 times through 87, and rose 3 times through a total of 8. All these numbers follow the same order as the specific gravities, atomic weights, and specific heats of those metals. All the other metals behaved in a very different manner from this. The same effects may be rendered evident in another way by tabulating the number of instances in which each of those metals respectively occurs in the several lines of Table I and of the cold columns of Table X. Tables I and II also show that, notwithstanding the highly volta-positive character of this group of metals, magnesium was thermo-negative 10, cadmium 8, and zinc 7 times, and that they were nearly as often thermo-negative as silver. This effect is least conspicuous with the weak solutions of potassic chloride, carbonate, and hydrate, and was not manifestly affected by increased strength of liquid. The similar behaviour in this respect of the whole of the magnesium group of metals, suggests the conclusion that the frequent and great depressions in position of magnesium in the thermo-electric

series (Tables I and IV, pp. 253 and 259) were not always due to a film of insoluble matter (pp. 261, 270, and 278). I have not examined whether this phenomenon is related to the great thermal capacity and expansibility by heat of those metals. The liquid in which the metals generally were least altered in position by heating one of them was the weak solution of potassic chloride, it suffered also very few voltaic reversals by rise of temperature (see Table X, p. 266).

By making similar comparisons of the thermo series of Table I with the "hot" chemico series of Table X, it was observed, that whilst heating only one metal of a voltaic pair to 160° F. depressed the relative positions of the magnesium group of metals a total of 354 places, and raised them only 9 (see p. 269); heating subsequently the second one in addition, raised them from the latter position a total of 345 places, and depressed them only 5, and therefore restored them nearly 98 per cent. towards their former positions. This appears to be in harmony with the fact that the orders of the voltaic series at 60° and 160° F. are not widely different (see Table X, p. 260. By similar tabular comparisons and reckonings, the electrical effect of heating the first electrode was found to be usually a little greater than that of heating the second one.

The extremely negative position of magnesium in many thermo-electric series, both with weak and strong solutions, does not appear to be explicable either by its strongly volta-positive character, its own thermo-positive character amongst metals, or by the thermo-electric properties of the liquids, but requires the assumption of some other cause operating. The thermo-electric positions of several other metals, such as aluminium, nickel, and palladium, &c., in particular liquids, are also, though in a less degree, inexplicable by these causes alone.

Many of the metals in Table X (p. 260) were reversed in their order of position in the series by rise of temperature; the total number not reversed was 174, and of reversed 112, or 1.55 to $1.0 = 64.51$ per cent. The reversals varied in number in different liquids; most occurred with nitric and sulphuric acids and potassic cyanide (8 in each). Every metal suffered reversals; the number was greatest with aluminium (30) and lead (23), and least with zinc and nickel (4). The metals which most frequently crossed each other were aluminium with lead and with iron, each seven times. Reversals were less frequently caused in chemico-electric series by a rise of temperature of 100° F. than in a thermo-electric series by a difference of strength of liquid, the proportion in the former case being 174 out of 286, and in the latter 250 out of 286 (see p. 258).

Regarding the effect of heating two different metals simultaneously in the chemico-electric experiments (shown in Table X, p. 260), as being chiefly composed of the two effects of heating the same metals separately (as shown in the thermo-electric series of Table I), I have

compared the relative positions in Table X of the metals which have crossed each other by simultaneous heating to 160° F. with those of the same metals in Table I, as determined by heating them separately to that temperature in the same liquids. I thus found that out of the total 83 instances of crossing 72 are explicable in this manner, and the remaining 9 are but feeble exceptions, both as regards their relative positions in the chemico- and in the thermo-electric series, and also as regards their relative degrees of electromotive force, 7 out of the 9 couples being composed of noble metals, which give relatively feeble currents. No instance occurred in which the reversal was produced by alteration of potential of one metal only; 32 happened in which it was due to one metal increasing and the other decreasing in that power; 37 in which it was due to both metals increasing simultaneously, but at different rates; and 5 in which it was a result of simultaneous but unequal diminution of potential in the two metals. The differences of order of the chemico-electric series at 60° and 160° F. in Table X, and the coincident reversals, are therefore results of the combined effect of heat upon the two individual metals, as shown in Table I. In the cases of reversal, the number of instances in which a metal becomes positive by rise of temperature was more than twice as great as those in which it became negative; this agrees with the proportion of thermo-positive and negative members in Table I (see pp. 253 and 254), and with the statement that heat usually increases electro-positive activity.

It is evident that as in certain cases a given metal is chemico-electro-positive at 60° to another metal, whilst at 160° F. it is negative, it must at some intermediate temperature be neutral to it and produce no current; the electric potentials of the two metals must at that point be equal and opposite. A number of experiments were therefore made in order to ascertain the temperatures of these neutral points at which reversal took place. The solutions employed were all of them of the same composition as those used in determining the chemico-electric series (p. 269). The following are the results:—In *Potassic cyanide*: Mg and Al, 80° F.; Mg and Zn, 146°; Pb and Pd, 84°. *Potassic fluoride*: Sn and Cd, 146°. *Potassic nitrate*: Pb and Fe, 65°; Al and Sn, 90°; Ag and Pd, 182°. *Potassic carbonate*: Mg and Al, 106°. *Sodic diphosphate*: Al and Cd, 150°; Al and Zn, 124°; Al and Pb, 100°; Al and Sn, 120°. *Potassic iodide*: Fe and Pb, 120°; Fe and Al, 160°. *Sodic chloride*: Fe and Pb, 60°; Cu and Ni, 72°. *Potassic chloride*: Au and Pd, 65°. *Potassic sulphate*: Pb and Al, 170°; Ni and Cu, 64°; Ag and Pd, 100°. *Oxalic acid*: Al and Cd, 152°; Al and Sn, 122°; Au and Pd, 62°. *Formic acid*: Al and Sn, 176°; Al and Pb, 185°; Pd and Pt, 110°. *Dextro-tartaric acid*: Al and Fe, 177°; Al and Sn, 182°; Al and Pb, 154°. *Potassic hydrate*: Cd and Pb, 138°; Cd and Fe, 68°. *Sulphuric acid*: Al and

Cd, 154°; Al and Fe, 110°; Al and Sn, 100°; Al and Pb, 68°; Pt and Au, 185°. *Sodic sulphate*: Fe and Pb, 62°; Ag and Cu, 176°. *Nitric acid*: Al and Cd, 140°; Al and Fe, 116°; Al and Pb, 86°; Au and Pt, 130°; Ag and Pt, 64°. *Chloric acid*: Al and Cd, 144°; Al and Fe, 120°; Pb and Fe, 184°. *Magnesian sulphate*: Fe and Pb, 65°; Ag and Au, 182°. *Potassic alum*: Al and Cd, 140°; Al and Fe, 132°; Al and Pb, 130°; Sn and Pb, 182°; Ag and Pt, 70°. *Ammonic alum*: Sn and Pb, 102°. The cases of chemico-electric reversal in which both metals diminished in potential were: Au and Pd in potassic sulphate, also in oxalic acid; Fe and Sn in chloric acid; Au and Ag in magnesian sulphate; and Pb and Al in potassic alum. As visible chemical corrosion of metal is not necessary to thermo-electric action of metals in liquids, reversals occurred with non-corroded, as well as with corroded metals.

Very slight circumstances altered the position of a chemico-electric reversal point in the scale of temperature, and even caused it to pass beyond the limits of the scale and of observation. A different sample of metal or of salt, and other circumstances, often produced this effect; the results are therefore very variable.

Out of the total 83 cases of reversal obtained by sudden immersion of the pairs of metals, first at 60° and then at 160° F. (see Table X), only 54 were reobtained on heating the metals gradually in the liquids, and 11 of those so obtained occurred at temperatures higher than those employed when the metals were suddenly heated. Gradually heating the metals appeared therefore to cause in some cases the reversals either to disappear or to occur at a higher temperature (probably in consequence partly of polarisation). This effect was more common in a solution of potassic cyanide than in dilute sulphuric or nitric acids.

It may be observed also with regard to some of these cases that the temperatures at which the reversals took place were usually lower the weaker the electromotive force; this was the case with aluminium in relation to cadmium, iron, tin, and lead in dilute sulphuric acid; also with that metal in relation to cadmium, iron, and lead in nitric acid; and less distinctly in solution of potassic alum and other liquids.

The influence of heat upon the chemico-electric series of Table X was further examined by measuring the degrees of electric potential, both at 60° and 160° F., of the extreme top and bottom metals in the respective liquids of that table. The results are given in Table XI.

Remarks.—In 12 cases the voltaic potential was increased, and in 6 decreased; the total amount of increase was 5 times that of decrease, and the average proportion of increase for the 18 instances was .10 volt for 100° F. rise of temperature. By comparing these cases with the thermo-electric positions of the same metals caused by the same difference of temperature in Table I, the two were found

Table XI.—Influence of Temperature on Potential of Voltaic Couples.

Solutions.	At 60° F.		At 160° F.		Increase.	Decrease.
	Volts.		Volts.			
1. KCy	Mg	± Pt .. 1·48	Al	± Pt .. 1·54
2. KF	Al	„ Au.. 1·11	„	„ Au.. 1·80	·69	..
3. KBr	Mg	„ Pt .. 1·67	Mg	„ Pt .. 1·75	·08	..
4. KNO ₃	„	„ „ .. 1·35	„	„ „ .. 1·59	·24	..
5. K ₂ CO ₃	„	„ Ag.. 1·67	Al	„ Ag.. 1·70
6. Na ₂ HPO ₄ ..	„	„ „ .. 1·51	Mg	„ „ .. 1·53	·02	..
7. KI	„	„ Pt .. 1·58	„	„ Pt .. 1·44	..	·14
8. NaCl	„	„ „ .. 1·50	„	„ „ .. 1·53	·03	..
9. HCl	„	„ Pd.. 1·61	„	„ Pd .. 1·70	·09	..
10. KCl	„	„ Pt .. 1·44	„	„ Pt .. 1·53	·09	..
11. K ₂ SO ₄	„	„ „ .. 1·50	„	„ „ .. 1·48	..	·02
12. Oxalic acid .	„	„ „ .. 1·73	„	„ „ .. 1·88	·15	..
13. Formic „ „	„	„ „ .. 1·84	„	„ „ .. 2·08	·24	..
14. Tartaric „ „	„	„ „ .. 1·68	„	„ „ .. 1·84	·16	..
15. KHO	Al	„ Ag.. 1·37	Al	„ Ag.. 1·28	..	·07
16. H ₂ SO ₄	Mg	„ Pt .. 1·92	Mg	„ Pd .. 1·95
17. Na ₂ SO ₄	„	„ Au.. 1·64	„	„ Au.. 1·61	..	·03
18. HNO ₃	„	„ Pd.. 1·81	„	„ Ag.. 1·88
19. HClO ₃	„	„ Pt .. 1·73	„	„ Pt .. 2·13	·39	..
20. MgSO ₄	„	„ „ .. 1·75	„	„ „ .. 1·64	..	·11
21. K alum	„	„ Pd.. 1·81	„	„ Pd .. 1·73	..	·08
22. Am alum....	„	„ Pt .. 1·70	„	„ Pt .. 1·84	·14	..

to harmonise in 13 of the cases, but not in the remaining 5. These results also agree with the fact that heat usually increases electric potential of metals in liquids. The influence of increase of temperature on chemico-electromotive force was usually the reverse of that of increased strength of liquid upon thermo-electric potential (see pp. 264, 268).

The following additional determinations of the chemico-electric potential of two different metals, and with different liquids, all at about 60° F., by the balance method, were made:—

Table XII.—Chemico-electric Potentials.

Liquid.		Metals.	Volts.
25 grains of KF	in one ounce of water	Pt + Ag —	·0157
50 „ „	„ „	„ + „ —	·0447
100 „ „	KHO „ „	„ + „ —	·0354
50 „ „	K ₂ CO ₃ „ „	„ + „ —	·0195
50 „ „	Na ₂ HPO ₄ „ „	„ + „ —	·0024
40 „ „	K ₂ SO ₄ „ „	Ag + Pt —	·0266
10 „ „	KCl „ „	Sn + Cu —	·2400

As rise of temperature diminishes in certain cases the chemico-electric potential of a metal in an electrolyte (see Table XI, p. 273), this fact may suggest the idea that when a metal is thermo-electro-negative in a particular liquid its degree of rapidity of corrosion is lessened by rise of temperature. This question was subsequently investigated (see p. 285).

By first comparing the orders of the chemico-electric series (Table X) of metals in hot solutions of potassic bromide and chloride, side by side with each other, and then those in hot solution of potassic cyanide and dilute sulphuric acid, similarly, the influences of small and of great difference of chemical composition of the liquid were conspicuously seen. In the former case only four of the metals were altered in position, whilst in the latter ten were displaced. The differences also between the orders of the series obtained with dilute hydrochloric acid and solution of potassic chloride, each at 60° F., were much greater than between those obtained with that acid or that salt at 60° and 160° F. A much greater effect was produced in these cases by a difference of liquid than by one of 100° F. of temperature.

With the object of ascertaining the effect of increased strength of liquid upon the order of the chemico-electric series of metals in electrolytes at 60° F., a similar set of experiments to those employed in constructing Table X were made. The strengths of solutions were the same as those used in making the thermo-electric determinations of Table IV (p. 259).

Table XIII.—Chemico-electric Series of Metals in Strong Solutions (at 60° F.).

	KCy.	KF.	KBr.	KNO ₃ .	K ₂ CO ₃ .	Na ₂ HPO ₄ .	KI.	NaCl.
1.....	Zn	Al	Mg	Mg	Mg	Mg	Mg	Mg
2.....	Mg	Zn*	Zn	Zn	Al	Zn	Zn	Zn
3.....	Al	Mg	Cd	Cd	Pb*	Cd	Cd	Al
4.....	Cu	Cd	Al	Pb	Zn	Al	Pb	Cd
5.....	Cd	Sn	Pb	Fe	Cd	Pb	Al*	Pb
6.....	Sn	Pb	Sn	Al*	Sn	Fe	Fe	Sn
7.....	Ag	Fe	Fe	Sn	Fe	Sn	Ag*	Fe
8.....	Ni	Cu	Cu	Ni	Cu	Cu	Cu	Cu
9.....	Au	Pd	Ag	Ag	Ni	Ni	Sn	Ag
10.....	Pb	Au	Ni	Cu	Pd	Pd	Pd	Ni
11.....	Fe	Pt	Pd	Pd	Au	Pt	Au	Au
12.....	Pd*	Ni	Au	Au	Pt	Au	Ni	Pd
13.....	Pt	Ag	Pt	Pt	Ag	Ag	Pt	Pt

Table XIII.—(continued).

	HCl.	KCl.	K ₂ SO ₄ .	Oxalic acid.	Formic acid.	Dextro-tartaric acid.	KHO.	H ₂ SO ₄ .
1.....	Mg	Mg	Mg	Mg	Mg	Mg	Al	Mg
2.....	Zn	Zn	Zn	Zn	Zn	Zn	Zn*	Zn
3.....	Al	Cd	Cd	Cd	Cd	Cd	Sn*	Cd
4.....	Cd*	Al	Al	Sn	Fe	Fe	Mg	Fe
5.....	Sn	Fe	Fe	Al	Sn	Sn	Cd	Sn
6.....	Fe	Pb	Pb	Fe	Pb	Pb	Fe	Pb
7.....	Pb	Sn	Sn	Pb	Al	Al	Pb	Al
8.....	Ni	Cu	Ni	Ni	Ni	Ni	Cu	Ni
9.....	Cu	Ni	Cu	Cu	Cu	Cu	Ni	Cu
10.....	Ag	Ag	Ag	Ag	Au	Ag	Ag	Au
11.....	Au	Au	Pd	Au	Ag	Au	Pt	Pd
12.....	Pd	Pd	Au	Pd	Pd	Pd	Au	Ag
13.....	Pt	Pt	Pt	Pt	Pt	Pt	Pd	Pt

	Na ₂ SO ₄ .	HNO ₃ .	HClO ₃ .	MgSO ₄ .	K alum.	Am alum.
1.....	Mg	Mg	Mg	Mg	Mg	Mg
2.....	Zn	Zn	Zn	Zn	Zn	Zn
3.....	Cd	Cd	Cd	Cd	Cd	Cd
4.....	Fe	Pb	Al	Fe	Fe	Fe
5.....	Pb*	Fe	Pb	Al	Pb	Pb
6.....	Sn	Sn*	Sn	Pb	Sn	Sn
7.....	Al	Al	Fe	Sn	Al	Al
8.....	Ni	Ni	Ni	Ni	Ni	Ni
9.....	Cu	Cu	Cu	Cu	Cu	Cu
10.....	Ag	Ag	Ag	Pd	Ag	Ag
11.....	Pd	Pt	Au	Au	Pt	Pd
12.....	Au	Au	Pd	Ag	Au	Au
13.....	Pt	Pd	Pt*	Pt	Pd	Pt

* Indicates a temporary reversal with the two contiguous metals, *i.e.*, the one marked and the one *above* it.

Remarks.—The usual strength of the current obtained in this series of experiments was but little greater than those obtained with the weaker liquids at the same temperature. Silver was nearly always the most volta-electro-negative metal in alkaline liquids, except in potassic cyanide, whether they were strong or weak (see Tables X and XIII). Copper was remarkably volta-positive, both in hot and cold weak solution of potassic cyanide (see Table X), and in a strong cold one.

Difference of strength of solution, like difference of temperature, altered the order of the series with nearly every liquid. In the same total number of instances (286), the number of reversals of position in the orders, in liquids of four or five times the strength, was 74, whilst that produced by a difference of temperature of 100° F. was 83; therefore the usual amounts of chemico-electric molecular change produced in the metals and liquids by these two causes were not widely different. In twenty-nine cases the reversals produced by increased strength of liquid, occurred with the same metals and liquids as those produced by rise of temperature. Whilst also with the 286 members of the thermo-electric series in Table IV (see p. 260), a variation of strength of liquid greatly altered the sequence, and produced no less than 236 reversals, it caused only a moderate degree of change of order, and only 74 reversals in the chemico-electric series. This conspicuous difference between effects of increased strength of liquid upon the thermo- and chemico-electric series, is perhaps explicable by the circumstance that a thermo-electric couple, consisting of an unequally heated metal and electrolyte, behaves like a feeble voltaic combination of two metals and two liquids, and is a more complex arrangement than a voltaic element of two metals and one liquid, such as was used in forming the above Table XIII.

The influence of strength of solution upon the electric potential of the extreme top and bottom members of the "cold" columns of the chemico-electric series of Table X, was also examined by the method of balance; the liquids employed being the same as those used in ascertaining the influence of the same condition upon the order of the thermo-electric series of Table IV (p. 259). All the solutions were used at 60° F. The results, placed side by side with those obtained with the weaker liquids, are shown in Table XIV.

Remarks.—In twelve cases the electric potential was increased, and in five decreased by increased strength of the solutions. The total amount of increase was 3·55 times that of decrease, and the average proportion of increase for the seventeen instances was ·095 volt per 100° F. rise of temperature. The results when compared with those in Table XI, p. 273, show that the increased strength of the liquid had about the same average degree of effect as a rise of temperature of 100° F. in increasing the chemico-electric potential. The influence of increased strength of liquid upon chemico-electric potential was different from that upon thermo-electric potential, in the former it was usually attended by an increase, and in the latter by a decrease, see Tables VI, VII.

The electric potential of a voltaic couple appears to be in certain cases decreased by rise of temperature (see Table XI, p. 273). This circumstance is a consequence of the fact that by accession of heat many metals become electro-negative, and others electro-positive in

Table XIV.—Influence of Strength of Liquid on Voltaic Potential.

Solutions.	Weak.		Strong.		Increase.	Decrease.
	Metals.	Volts.	Metals.	Volts.		
1. KCy	Mg ± Pt	1·48	Zn ± Pt	1·32
2. KF	Al ± Au	1·11	Al ± Ag	1·09
3. KBr	Mg ± Pt	1·67	Mg ± Pt	1·53	..	·14
4. KNO ₃	" ± "	1·35	" ± "	1·59	·24	..
5. K ₂ CO ₃	" ± Ag	1·67	" ± Ag	1·73	·06	..
6. Na ₂ HPO ₄ ..	" ± "	1·51	" ± "	1·46	..	·05
7. KI	" ± Pt	1·58	" ± Pt	1·50	..	·08
8. NaCl	" ± "	1·50	" ± "	1·75	·25	..
9. HCl	" ± Pd	1·61	" ± "	1·95
10. KCl	" ± Pt	1·44	" ± "	1·75	·31	..
11. K ₂ SO ₄	" ± "	1·50	" ± "	1·68	·18	..
12. Oxalic acid.	" ± "	1·73	" ± "	1·61	..	·12
13. Formic " "	" ± "	1·84	" ± "	1·87	·03	..
14. Tartaric " "	" ± "	1·68	" ± "	1·80	·12	..
15. KHO	Al ± Ag	1·37	Al ± Pd	1·48
16. H ₂ SO ₄	Mg ± Pt	1·92	Mg ± Pt	1·98	·06	..
17. Na ₂ SO ₄	" ± Au	1·64	" ± "	1·76
18. HNO ₃	" ± Pd	1·81	" ± Pd	1·57	..	·24
19. HClO ₃	" ± Pt	1·73	" ± Pt	2·17	·44	..
20. MgSO ₄	" ± "	1·75	" ± "	1·82	·07	..
21. K alum	" ± Pd	1·81	" ± Pd	1·87	·06	..
22. Am "	" ± Pt	1·70	" ± Pt	2·12	·42	..

liquids (see Tables I and IV); when therefore a combination in which the volta-positive metal is thermo-negative, and the negative one is thermo-positive, is heated, the electric potential tends to diminish, notwithstanding that the internal resistance usually decreased. The following are selected cases of this kind, the data of which are derived from comparison of Tables III and VI with Table X, pp. 257, 262, and 266; a large number of additional ones might be obtained by the same method. The amounts of decrease are for a difference of temperature of 100°, ranging from 60° to 160° F.

Table XV.—Influence of Temperature on Voltaic Potential.

Metals.	Liquids.	Volt.
Pb + and Ni —	in MgSO ₄ (weak solution)	·1876 decrease.
Mg+ " Cd—	" KHO "	·2046 "
Mg+ " Sn—	" KCy "	·2518 "
Al + " Ag—	" KHO (strong solution)	·2484 "
Cd + " Sn—	" KI "	·2998 "
Mg+ " Ag—	" KF "	·3028 "
Mg+ " Sn—	" Na ₂ HPO ₄ "	·5894 "

The instances were selected because they were conspicuous ones. The results are probably in some cases partly due to extremely thin films of insoluble matter formed upon the metals (see pp. 255, 261, 270, 278); this assumption of the existence of films will not, however, explain many of the cases in Tables I and IV, when non-corroded metals were rendered negative by being heated. Fifty-six cases of relative diminution of volta-electric potential by rise of temperature are included in the cases of reversal in Table X (see p. 266).

Similar results to the above were arrived at by a more direct method. The chemico-electric potential of each pair of metals was first determined (by the method of balance) at 60° and then at 160° F., by suddenly immersing the pair in the previously prepared liquid. The following were the results:—

Table XVI.—Influence of Temperature on Voltaic Potential.

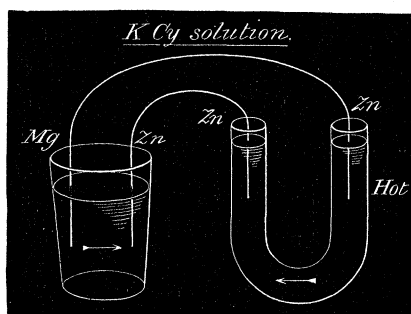
Metals.	Liquids.		Volts at 60° F.		Volt at 160° F.	
Pb+ and Ni—in	MgSO ₄ (weak solution)	·3447	·2364	= ·1083 decrease.
Mg " Cd "	KHO (" " ")	·6189	·4485	= ·1704 "
" Sn "	KCy (" " ")	1·0070	·0842	= ·9229 "
Al " Ag "	KHO (strong " ")	1·5083	1·2245	= ·2838 "
Cd " Sn "	KI (" " ")	·3313	·2912	= ·0401 "
Mg " Ag "	KF (" " ")	·8064	·6032	= ·2032 "
" Sn "	Na ₂ HPO ₄ (" " ")	1·1087	·2758	= ·8329 "
" Ni "	MgSO ₄ (weak " ")	1·3469	1·3722	= ·0253 increase.

Remarks.—While each of these determinations except the last one agrees with the former ones in being a case of decrease of electric potential by equal rise of temperature, the amounts of decrease for the corresponding pairs of metals differ very considerably in the two tables, probably in consequence chiefly of the circumstance that in each of the experiments of the former determinations the metals in mutual contact were the same, but at different temperatures, whilst in the latter they were dissimilar ones at the same temperature. When heating a voltaic pair, the heat is applied to two metals, both of which are previously electro-polar by contact with each other, as well as by contact with the liquid; but when heating one junction of a liquid and metal thermo-couple, the metal has not been previously rendered electro-polar by contact with a different one, and is therefore in a somewhat different electric state. Faraday observed similar cases ("Experimental Researches," 1923), viz., that by either heating one or two pieces of silver or of platinum in a cold mixture of 1 part of sulphuric acid and 80 of water, little or no electric current was manifest, but on heating the silver or platinum alone of a voltaic pair of those metals in that liquid, in each case a current occurred. Heating the platinum made it strongly negative, and heating the silver made it weakly positive. These cases illustrate the necessity of considering the effect of voltaic contact, as well as that of chemico-

electric influence, when examining thermo-electric actions of metals in liquids. Additional instances are given on pp. 281, 288.

With the object of ascertaining the electric potential of voltaic currents from pairs of metals in the "cold" columns of liquid of Table X in thermo-electric terms of one of the same metals; the current of two of those metals (contiguous or as near to each other as could be obtained) in one of those liquids at atmospheric temperature, was balanced by a thermo-electric one from two pieces of one of the same metals in a second portion of the same liquid, in a bent glass tube, as shown in the annexed sketch (fig. 2),* and the

FIG. 2.



difference of temperature between the two pieces ascertained at which the balance occurred. Usually, however, the bent tube alone (as in fig. 1, p. 251, but provided with a hot water-bath), containing the two metals, was used. The temporary portion of current was in every case allowed to subside before applying the heat. Cases in which the voltaic current from two contiguous metals was too strong to be balanced by the only applicable thermo-electric one were excluded. The electric potentials at 60° F. of most of the voltaic pairs employed were subsequently determined. The following are the results :—

Table XVII.—Thermo-electric Balance of Chemico-electric Action.

Solution.	Chemico-electric				Thermo-electric				Difference in F. degrees.	Volt.	
	Positive.	Negative.	F.		Positive.	F.	Negative.	F.			
KCy	Mg	to Zn	at 54°	=	Zn	at 167°	to Zn	at 54°	=	113	= ·1811
"	Ni	" Pb	" 58	=	Pb	" 210	" Pb	" 58	=	152	= ·0060
"	Ag	" Ni	" 56	=	Ni	" 74	" Ni	" 56	=	18	= ·0898
"	Pb	" Pd	" 58	=	Pd	" 88	" Pd	" 58	=	30	= ·1192
"	Pd	" Fe	" 60	=	Fe	" 178	" Fe	" 60	=	110	= ·0720
KF	Al	" Mg	" 58	=	Mg	" 82	" Mg	" 58	=	24	
"	Zn	" Al	" 56	=	Al	" 90	" Al	" 56	=	34	= ·5083
"	Cd	" Sn	" 56	=	Sn	" 120	" Sn	" 56	=	64	= ·0651
"	Cd	" Fe	" 54	=	Fe	" 194	" Fe	" 54	=	140	= ·1235
"	Pd	" Pt	" 60	=	Pt	" 202	" Pt	" 60	=	142	= ·0209

* One leg of the bent tube was surrounded by a water-bath, which could be heated gradually.

Table XVII—(continued):

Solution.	Chemico-electric				Thermo-electric				Difference in F. degrees.	Volt.
	Positive.	Negative.	F.		Positive.	F.	Negative.	F.		
KBr	Al	Sn	58	=	Sn	184	Sn	58	=	126 = '1456
"	Cd	"	58	=	Al	160	Al	58	=	102 = '0979
"	Al	Fe	60	=	Fe	105	Fe	60	=	45 = '0616
"	Sn	Ni	60	=	Ni	180	Ni	60	=	120 = '3058
"	Ag	Pd	60	=	Ag	180	Ag	60	=	120 = '0814
KNO ₃	Cd	Fe	52	=	Fe	140	Fe	52	=	88 = '0634
"	Pb	Sn	60	=	Sn	162	Sn	60	=	102 = '1428
"	Sn	Al	58	=	Al	72	Al	58	=	14 = '0396
"	Ni	Cu	54	=	Cu	90	Cu	54	=	36 = '0785
"	Cu	Ag	56	=	Ag	160	Ag	56	=	104 = '0577
"	Cu	Au	44	=	Au	200	Au	44	=	156 = '1344
K ₂ CO ₃	Mg	Al	56	=	Al	140	Al	56	=	84
"	Sn	Pb	56	=	Pb	190	Pb	56	=	134
"	Pb	Zn	56	=	Zn	108	Zn	56	=	52
"	Zn	Cd	58	=	Cd	168	Cd	58	=	110
"	*Pd	Au	40	=	Au	160	Au	40	=	120 = '0562
"	*Au	Pt	42	=	Pt	134	Pt	42	=	92 = '0112
"	*Pt	Ag	42	=	Ag	190	Ag	42	=	148
Na ₂ HPO ₄	Cd	Sn	56	=	Sn	120	Sn	56	=	64 = '1595
"	Sn	Al	56	=	Al	94	Al	56	=	38 = '0666
"	Al	Fe	56	=	Fe	145	Fe	56	=	89
"	Cu	Ni	56	=	Ni	170	Ni	56	=	114
"	*Pd	Pt	44	=	Pt	190	Pt	44	=	146 = '0198
"	*Pd	Au	42	=	Au	170	Au	42	=	128 = '0481
KI	Pb	Al	56	=	Al	80	Al	56	=	24 = '0605
NaCl	Al	Fe	56	=	Fe	202	Fe	56	=	146 = '1261
"	Fe	Sn	56	=	Sn	184	Sn	56	=	128 = '1512
"	*Pd	Pt	43	=	Pt	95	Pt	43	=	52 = '0821
KCl	Cu	Ni	56	=	Ni	148	Ni	56	=	92 = '06859
"	Pb	Fe	56	=	Fe	74	Fe	56	=	18
HCl	Au	Pt	56	=	Au	56	Au	134	=	78 = '0792
K ₂ SO ₄	Pb	Sn	50	=	Sn	173	Sn	50	=	123 = '0809
"	Al	Ni	58	=	Ni	202	Ni	58	=	144 = '5135
"	*Pb	Al	33	=	Al	162	Al	33	=	129
"	*Pd	Pt	40	=	Pd	40	Pd	60	=	20 = '0109
KHO	Cd	Fe	54	=	Fe	180	Fe	54	=	126 = '0056
"	Fe	Cu	50	=	Cu	72	Cu	50	=	22 = '4187
H ₂ SO ₄	Sn	Pb	54	=	Pb	154	Pb	54	=	100 = '1108
"	Cd	Al	56	=	Al	182	Al	56	=	126 = '1761
"	Pb	Ni	50	=	Ni	164	Ni	50	=	114 = '1729
"	*Au	Pt	40	=	Pt	118	Pt	40	=	78 = '0785
Na ₂ SO ₄	Cd	Fe	56	=	Fe	192	Fe	56	=	136 = '1613
"	Pb	Sn	54	=	Sn	120	Sn	54	=	66 = '0368
"	*Ni	Cu	42	=	Cu	180	Cu	42	=	138 = '0735
"	*Ag	Pd	40	=	Ag	40	Ag	110	=	70
"	*Pt	Au	44	=	Au	180	Au	44	=	136
"	*Pd	Pt	42	=	Pd	42	Pd	134	=	92 = '0742
HNO ₃	Fe	Al	54	=	Al	108	Al	54	=	54 = '2046
"	Sn	Ni	50	=	Ni	190	Ni	50	=	140 = '2439
"	Ag	Pt	50	=	Ag	50	Ag	180	=	180
HClO ₃	Cd	Al	48	=	Al	144	Al	48	=	96 = '1947
"	Fe	Sn	50	=	Fe	50	Fe	176	=	126 = '0126
"	Sn	Pb	50	=	Sn	50	Sn	168	=	118 = '0498
"	Ag	Au	49	=	Ag	49	Ag	154	=	105 = '0516
"	*Pd	Pt	36	=	Pd	36	Pd	163	=	127
MgSO ₄	Zn	Al	48	=	Al	132	Al	48	=	84 = '4420
"	*Cu	Au	48	=	Cu	48	Cu	190	=	142 = '0814
"	*Pd	Pt	42	=	Pd	42	Pd	128	=	86 = '0552
K Alum.	Pb	Al	48	=	Al	120	Al	48	=	72 = '0232
"	Al	Sn	48	=	Sn	120	Sn	48	=	72 = '0320
"	*Au	Ag	38	=	Au	38	Au	100	=	62
"	*Pt	Pd	40	=	Pt	40	Pt	60	=	20
Am Alum ...	Fe	Al	48	=	Al	102	Al	48	=	54 = '0264
"	Pb	Sn	52	=	Sn	98	Sn	52	=	46 = '0478
"	*Au	Pt	40	=	Au	40	Au	160	=	120

Remarks.—The thermo currents produced by solutions of potassic carbonate and sodic phosphate were usually strong, and so also were those with aluminium, tin, and iron, and yielded many balances; whilst those from solutions of oxalic, formic, and tartaric acids were too feeble to balance the corresponding voltaic ones. In obtaining balances with the noble metals, the voltaic currents were so very small that the Thomson's reflecting galvanometer had to be employed; these cases are indicated by an asterisk.

By means of a separate experiment it was ascertained that the amount of error caused by the voltaic current producing polarisation before the thermo current had time to balance it was small, even in the cases where the former current was comparatively strong, as with a solution of potassic cyanide.

A number of thermo-electric reversals occurred during the making of these determinations: thus, in a solution of potassic nitrate, gold was thermo-electro-positive below and negative above 200 F., and platinum behaved similarly below and above 180°. Aluminium in solution of potassic carbonate became less thermo-positive above 140° F. Lead in sodic chloride and magnesium in potassic hydrate was thermo-positive below 170° and negative above it. In sodic sulphate nickel was thermo-negative below 110° and positive above that temperature. In dilute nitric acid lead was negative below and positive above 180°, and tin similarly below and above 150°. In dilute chloric acid iron was positive up to 150° and negative above it. In potassic alum nickel was positive below and feebly negative above 164° F. In ammoniac alum aluminium was negative below and positive above 150°, and nickel was positive below and negative above 170° F. In magnesian sulphate cadmium behaved singularly; whilst it was chemico-negative to zinc and positive to aluminium at 60° F., by heating it alone (the zinc being in the cold part of the liquid) it became more negative, but with aluminium in the place of zinc, the cadmium became more positive by being heated. This experiment was repeated and similar results obtained; it is probably a case of the kind mentioned on pp. 279 and 288.

On comparing these reversals with the positions of the same metals in the same liquids in Table I, it will be observed that some of them do not agree in thermo-electric sign in the two cases. These apparent discrepancies may be partly accounted for by the circumstance that in the experiments of Table I, the metals were suddenly immersed in the hot and cold portions of liquid, whilst in the present ones they were immersed in the two cold portions, and one of them then gradually heated; they may also be partly explained by the circumstance observed that the balance obtained during a rising of temperature was frequently at a somewhat higher point than one obtained whilst the temperature was falling (compare also p. 272 for

effect upon reversal point by gradually heating the liquid). This difference of effect during a rising and falling of temperature is probably due to some hindrance to change of molecular movements analogous to that of supersaturation of a liquid by a salt.

A series of experiments were made to determine whether the difference in potential, caused in a voltaic cell by rise of temperature, is usually completely accounted for by the electromotive forces produced by the same rise of temperature of the same metals separately in the same liquids. The electric potentials in Table XVIII of the voltaic elements (A) at 60° F. (B) and 160° F. (C) were separately ascertained by means of the thermo-piles (p. 257); and those of the separate metals in the form of thermo-elements (D and E) as produced by a difference of from 60° to 160° F. were also separately determined in the same manner, and by the aid of the bent tube apparatus, &c. (see pp. 251 and 257). The liquids employed were of the same quality and strength as those mentioned on p. 252. The following table exhibits the results. The arrows represent the direction of the current at the heated junction:—

Table XVIII.

A Elements.		Potentials in volts of voltaic elements.			Potentials in volts of thermo-elements.		
		B At 60° F.	C At 160° F.	Differ- ence.	D At 60° and 160° F.	E At 60° and 160° F.	Total potentials.
Neg.	Pos.				Pos. Cu	Neg. Pt	
1. Pt	Cu in dilute solution of NaCl	·1760	·2106	·0346	→ ·044	no current	·0440
2. Pt	Sn in dilute solution of KCl	·4769	·6533	·1764	→ ·0594	→ ·1244	·1838
3. Pt	Pb in dilute HClO ₃ ...	·5648	·5850	·0202	→ ·0201	→ ·0317	·0518
4. Pt	Sn in dilute solution of Am alum ...	·6008	·6740	·0732	→ ·0655	→ ·0515	·1170
5. Cu	Sn in ditto.....	·3735	·4796	·1061	→ ·0615	→ ·0381	·0996
6. Pt	Sn in dilute HCl	·6998	·7726	·0728	→ ·1945	→ ·0100	·2045
7. Pt	Sn in dilute H ₂ SO ₄ ...	·4866	·8051	·3185	→ ·2912	→ 0·216	·3128

Remarks.—These results show a considerable percentage of excess in four and a small one of deficiency in two of the cases; and indicate that the difference of potential produced in a voltaic cell by rise of temperature is not in all cases equal to the sum of the potentials produced by heating the two metals separately.

One of the objects of the research being to examine the relation of ordinary chemical corrosion to the thermo- and chemico-electric actions of metals in electrolytes, the rates of corrosion of as many as possible of the different metals employed (see Table I, p. 253), wholly immersed in an equal number of separate portions of the same liquid, were ascertained, with one liquid at a time, in order to compare the series thus arrived at with the orders of the same metals in the same liquid in the thermo- and chemico-electric series.

In carrying out this object, obstacles arose which prevented complete corrosion series being obtained to correspond with the thermo- and chemico-electric ones. In some cases the metals became covered with a film of gas, or with a solid coating, each of which altered the rate of corrosion; these cases were entirely rejected. In other cases the liquids contained traces of impurity which caused a solid film upon the metal; this was overcome by repeatedly immersing the metal in the liquid until the impurity was wholly removed, and then reimmersing it several times during longer periods, until concordant rates of corrosion were obtained. And in other instances the metal itself contained small amounts of impurity, which by exciting electric polarity, increased the corrosion. In addition to these and other influences, the rate of corrosion must have been affected by the unequal degrees of adhesion of the soluble products of corrosion to the corroding surface, and the unequal rates of diffusion of those substances into the surrounding liquid; these influences were reduced to a minimum by employing either very dilute solutions of the corroding agents, or such liquids as corroded but slowly. All these circumstances had to be considered, and each combination of metal and liquid treated in such a manner as to ensure the most attainably accurate result; but even under the most carefully prepared conditions, rate of corrosion is a very variable phenomenon.

With silver, palladium, gold, and platinum, it was necessary to use much larger sheets and stronger solutions, and to continue the experiments during a longer period. The solutions of the two alums were four times, and those of potassic cyanide, sulphuric, hydrochloric, nitric, and chloric acids were of ten times, and the remainder of the usual strength. The silver was immersed in dilute nitric and chloric acids during one month and the other metals during three months. Most of the liquids corroded silver very slightly, and the metal acquired an adherent insoluble coating. The rates of loss are given in the table, but are separated from those in the weak liquids by horizontal lines.

The action was in no case allowed to continue longer than was sufficient to exhaust about 10 or 20 per cent. of the corroding substance. After excluding all doubtful cases, a sufficient number remained for the purposes intended. The rates of loss by corrosion

in all cases are given in grains per square inch per hour. The following are the orders of the degrees of rapidity of corrosion of the metals at 60° F.

Table XIX.—Simple Corrosion Series at 60° F.

	1 KCy.*	2 H ₂ SO ₄ .	3 HCl.	4 HNO ₃ .	5 KCl.	6 Am Alum.
	Grain.	Grain.	Grain.	Grain.	Grain.	Grain
1.....	Al ·0095	Mg 1·0000	Mg ·1581	Zn ·6130	Cd ·00036	Mg ·13770
2.....	Zn ·0054	Fe ·0189	Zn ·0490	Cd ·3780	Zn ·00030	Zn ·00101
3.....	Cu ·0053	Cd ·0026	Fe ·0118	Sn ·3750	Fe ·00026	Cd ·00066
4.....	Ag ·0016	Pb ·0018	Cd ·0026	Mg ·1570	Sn ·00025	Pb ·00060
5.....	Cd ·0014	Sn ·0009	Pb ·0023	Fe ·1406	Cu ·00012	Fe ·00059
6.....	Pd ·0012	Cu ·0006	Cu ·0018	Pb ·0250	Al ·00006	Cu ·00038
7.....	Au ·0009	Ni ·0005	Sn ·0017	Ni ·0030	Ni Trace	Ni ·00025
8.....	Sn ·0006	Al ·0004	Ni ·0004	Cu ·0008	Ag Less	Sn ·00013
9.....	Ni ·0005	Pd None	Pd None	Ag ·00022	Pd None	Ag ·00000032
10.....	Fe Trace	Au „	Au „	Pd None	Au „	Au None
11.....	Pt None	Pt „	Pt „	Au „	Pt „	Pd „
12.....	Pt ·00000036	Pt „	...	Pt „

	7 HClO ₃ .	8 KBr.	9 K Alum.	10 KI.	11 NaCl.	12 K ₂ SO ₄ .
	Grain.	Grain.	Grain.	Grain.	Grain.	Grain.
1...	Mg ·3164	Cd ·00058	Mg ·0038	Zn ·00025	Fe ·00026	Pb ·00060
2...	Fe ·1068	Zn ·00050	Zn ·00047	Fe ·00020	Pb ·00012	Fe ·00048
3...	Sn ·0480	Cu ·00029	Fe ·00046	Cd ·00015	Cu ·00006	Zn ·00040
4...	Ni ·0079	Fe ·00026	Cd ·00041	Ag ·00005	Sn ·00005	Sn ·00036
5...	Pb ·0074	Pb ·00022	Ni ·00022	Sn Trace	Ni ·00001	Cd ·00028
6...	Cd ·0040	Al ·00010	Cu ·00018	Ni Less	Ag Trace	Ag None
7...	Cu ·0008	Ni None	Sn ·00005	Pd None	Au None	Au „
8...	Ag ·000026	Au None	Ag ·00000032	Au „	Pd „	Pd „
9...	Au None	Pd „	Pd None	Pt „	Pt „	Pt „
10...	Pd „	Pt „	Au „
11...	Pt „	...	Pt „

Remarks.—These series and numbers show, 1st, that the order of rapidity of corrosion differed with every different metal and in every different solution; 2nd, the rates of corrosion of each metal varied in nearly every separate liquid; 3rd, in each solution also it differed with every different metal; 4th, the most chemically positive metals were usually the most quickly corroded; and 5th, the corrosion of metals was usually the fastest in the most acid liquids. These results indicate that the rate of corrosion depends both upon the metal and upon the liquid, probably most upon the former. With regard to the effect of chemical composition of the liquid, the differences of order between the series with a solution of potassic cyanide and with

* This sample was found by analysis to contain 89·14 per cent. of actual cyanide.

dilute sulphuric acid at 60° F. were found to be greater than those between the series with potassic bromide and chloride.

Comparisons of the order of the corrosion series at 60° F., with the thermo-electric ones of the same liquids of Table I (p. 253), and the chemico-electric ones of the "cold" columns in Table X (p. 265) show that the order of simple corrosion differs largely from that of chemico-electric, and still more largely from that of thermo-electric action. In no one pair of the twelve corresponding series of Tables X and XVIII did the order of metals entirely agree, the least agreeing ones were those in potassic cyanide and bromide. The degree of chemico- or thermo-electric potential therefore does not vary in the same order as that of rapidity of simple corrosion in any of the liquids examined. These different degrees of relative divergence of order of the three tables indicate a greater degree of complexity of thermo-electric than of chemico-electric action of metals in liquids in the given cases, and a less dependence of the former than of the latter upon simple corrosion. As real thermo-electric action of metals in liquids does not necessarily include corrosion, the latter when it occurs with the former is not the cause of it.

With regard to the relation of voltaic action to corrosion, Poggen-dorff published ("Phil. Mag.," 1840, vol. xvi, pp. 495 and 537) a number of experiments showing that the chemico-electromotive force was not the strongest in those liquids where the corrosion of the metal was apparently the most rapid, but he does not appear to have actually verified the relative losses of weight by weighing the metals; nor to have excluded from his tables those metals which became coated with a film of insoluble matter.

In order to ascertain whether rise of temperature caused every metal to corrode faster, or had always the effect of making only those metals corrode faster which by it were rendered more chemico-electro-positive, and those more slowly which were rendered negative, series of corrosion experiments were made with most of the same metals and liquids (see p. 252) at 160° F. as were employed in the thermo-electric experiments of Table I, care been taken to keep the metals wholly immersed, and the liquids from altering in strength by evaporation. The length of time during which it was necessary to continue the experiment varied from five minutes to eight hours. Table XX (p. 286), shows the rates of loss in grains per square inch per hour. The proportionate rates of increase for 100° F. rise of temperature, as calculated from the numbers on Table XIX, p. 284, are also given for comparison.

Remarks.—By comparing these results with those obtained at 60° F., as shown in Table XIX, p. 284, it will be seen that in nearly every case rise of temperature increased the rate of corrosion. The only exception in the total fifty-seven cases was zinc in dilute nitric acid,

Table XX.—Simple Corrosion Series at 160° F.

	KCy.			HCl.		HClO ₃ .		Am Alum.				
			Increase from 1 to—		Increase from 1 to—		Increase from 1 to—		Increase from 1 to—			
1.....	Al	·4940	52	Mg	1·2106	7·65	Mg	1·4507	4·58	Mg	·3520	2·55
2.....	Cu	·1258	23·7	Zn	·2090	4·26	Fe	·6140	5·84	Fe	·0732	124·00
3.....	Zn	·0495	9·1	Fe	·1370	11·6	Cu	·2573	321·6	Zn	·0382	37·80
4.....	Au	·0282	31·3	Al	·0273	...	Zn	·2160	...	Pb	·0138	23·00
5.....	Ag	·0070	4·4	Pb	·0231	10·0	Pb	·1940	26·20	Cd	·0073	11·00
6.....	Pd	·0051	4·2	Cu	·0156	8·66	Sn	·1690	3·52	Al	·0071	...
7.....	Cd	·0046	3·3	Cd	·0096	3·7	Cd	·1070	26·70	Sn	·0060	46·10
8.....	Sn	·0042	7·0	Sn	·0078	4·6	Ni	·0474	6·00	Cu	·0032	8·42
9.....	Pb	·0031	...	Ni	·0039	9·7	Al	·0215	...	Ni	·0014	5·60
10.....	Ni	·0027	5·4	Ag	·0026	...	Pt	·00015	...	Ag	Trace	...
11.....	Fe	·0010
12.....	Pt	None
	Average...		20·0	Average...		7·52	Average...		56·35	Average...		32·31

	HNO ₃ .			H ₂ SO ₄ .			K Alum.		
			Increase from 1 to—			Increase from 1 to—			Increase from 1 to—
1.....	Mg	·8853	5·64	Mg 4·0426	4·04	Mg ·1226	32·21		
2.....	Cd	·8176	2·16	Zn ·2510	...	Fe ·0821	178·00		
3.....	Zn	·6040	·98*	Fe ·2493	13·20	Zn ·0386	82·10		
4.....	Fe	·6000	4·26	Al ·0284	71·00	Pb ·0138	...		
5.....	Sn	·5666	1·51	Pb ·0196	10·90	Al ·0090	...		
6.....	Pb	·2155	8·62	Sn ·0115	12·80	Sn ·0080	160·00		
7.....	Al	·0260	...	Cd ·0091	3·50	Cd ·0077	18·80		
8.....	Ni	·0151	5·03	Cu ·0062	10·30	Cu ·0028	15·55		
9.....	Cu	·0133	16·60	Ni ·0057	11·40	Ni ·0022	10·00		
	Average...	5·60	Average...	17·14	Average...	70·95			

and this was a very feeble one. The increases of rate of corrosion under the influence of heat were extremely variable, whilst that of tin in dilute nitric acid was increased 1·5 times, that of copper in hydrochloric acid was increased 321·6 times; both these metals and acids were very pure, and not a trace of oxide appeared upon the tin. The total average increase for the entire series was 29·98. The changes produced in the orders of the series by difference of temperature were least in dilute hydrochloric acid. The results contained in Tables XIX and XX show that when metals are rendered thermo-electro-negative in liquids by being heated, their electric change is not attended by diminished rapidity of corrosion. It was found by comparing Table XIX with Table I that the proportion of cases in which the metal most corroded was more thermo-

* This was the only case of decrease, and was verified by means of a repetition experiment.

positive or less negative to that in which it was less positive or more negative, was 384 to 199 (= 65·87 per cent.), or as 1·93 to 1; also by similarly comparing Table XX, that the proportion in which the metal most corroded at 160° F. was most positive or less negative to that in which it was the reverse, was 338 to 151 (= 69·12 per cent.), or as 2·24 to 1.

And with regard to the relation of corrosion to voltaic state, it has been assumed "that in all these cases the positive electricity sets out from the more oxidable metal, and traverses the liquid towards the less oxidable one;" but comparisons of Tables X, XIX, and XX show that this is not entirely correct; with twelve different liquids at 60° F. the most chemico-electro-positive metal was also the most corroded one in 337 cases, and the least corroded in 62—a proportion of 5·43 to 1, or 84·44 per cent.; and with seven liquids at 160° F. the numbers were respectively 248 and 59—a proportion of 4·20 to 1, or 80·77 per cent. Neither volta-positive nor negative state, therefore, is always proportionate to degree of ordinary corrosion, either in cold or hot liquids. These figures show also that by a rise of temperature of 100° F. the proportion of cases in which the negative metal was the most corroded, increased from 15·56 to 19·23 per cent. of the entire number of cases. Comparison of the above proportions with those of the relation of corrosion to the thermo-electric states of metals in liquids, viz., 1·93 to 1 and 2·24 to 1 (see above), shows that corrosion usually influenced in a much greater degree the chemico- than the thermo-electric properties of such combinations.

Not only was the relative number of cases in which the volta-negative metal was the most corroded increased by rise of temperature, but also the average relative loss by corrosion of the negative one to that of the positive was more than doubled.

The following appear to be cases in which contact influenced the thermo-electric currents of metals in liquids. With each instance, in the first part of the experiment the metal was suddenly immersed in the hot liquid; and, in the second part, the same metal and liquid were gradually heated. In a solution of potassic bromide, copper alone was thermo-positive, but when gradually heated in contact with tin it was thermo-negative; in one of potassic nitrate platinum alone was thermo-positive, but in contact with gold it was rendered slightly more negative during a slight elevation only of temperature; in potassic hydrate magnesium alone was thermo-negative, but in contact with lead it was rendered more positive by heat up to 170° F.; in sodic sulphate nickel alone was thermo-positive, but in contact with tin it was more negative up to 110° F.; in dilute nitric acid lead alone was thermo-positive, but in contact with iron it was more negative up to 180° F.; in the same liquid tin alone was thermo-negative, but in contact with nickel it was more positive up to 160° F.;

and in dilute chloric acid iron alone was thermo-negative, but in contact with tin it was more positive up to 150° F. These cases were observed whilst making experiments to determine the balance points of Table XVII (p. 279), but were not included in that table because they did not yield balances.

In each of these causes the electric effect of heat upon the same metal in the same liquid was opposite to its usual thermo-electric one in that liquid. In each case also its effect was to increase, within the limits of a moderate rise of temperature, the strength of the already existing voltaic current. These changes may be explicable by supposing that the additional irregularities of electric potential introduced by the second metal at its two points of contact with the liquid and original metal altered the electric condition of the subsequently heated metal. The pre-existing voltaic currents also were so feeble that these unusual effects of heat do not appear to have been due to chemical changes of the liquid at the heated electrode; such changes, and the degrees of polarisation due to them, must also have been small in comparison with those already produced by ordinary chemical corrosion.

In a separate communication "On some Relations of Chemical Corrosion to Voltaic Currents," "Proc. Roy. Soc.," vol. 36, p. 331, I have examined the amounts of external voltaic current produced by the corrosion of known weights of various metals at atmospheric temperature.

The general conclusions drawn from the experiments described in the present paper may be found in the "Abstract," "Proc. Roy. Soc.," vol. 36, p. 50.

The fact that the mere contact of the metal and liquid of a thermo-electric pair is attended by electric polarity, and that either heating the one junction or cooling the other of such a couple produces an electric current, may be regarded as evidence that at all times, whilst no heat or cold is being applied to either of these joinings, the molecular actions at the two points of union tend to produce a current, but as these tendencies are opposite in direction and equal in strength, no current occurs. Each of these junctions may also be regarded as a surface of contact previously possessing a tendency to alter in temperature, and this view is supported by the discovery of Pouillet, that even when non-corrodible metals touch liquids, a slight change of temperature occurs ("Annal. de Chimie," 1822, pp. 141-162).

In support of this view, it may be observed that amongst the instances composing the chemico-electric series of Table X are many the currents of which are at the most of doubtful chemical origin. Of these, are the cases in which currents are produced by non-corroded metals, such as platinum, gold, palladium, and silver, in feebly corrosive liquids, including solutions of neutral salts. A suitable

instance of this kind is silver and platinum in a strong solution of potassic fluoride. The electromotive force of this combination was found to be .0477 of a volt (see Table XII, p. 273).

In order to test the inference "that at all times, whilst no heat or cold is being applied to either of the junctions of the thermo-electric couple, the molecular actions at the two points of union tend to produce a current," I suspended, by means of a pure silver wire, a sheet of pure silver, $2\frac{1}{2}$ inches wide and 3 inches deep, between two sheets of platinum, 3 inches wide and 6 inches deep, in a glass cell, containing a solution of pure potassic hydrate, 10 grains per ounce of water, the platinum being immersed 4 inches, and the silver wholly, in the liquid, and the two metals united outside by the wire. At the outset, the platinum was positive to the silver, about 5° deflection being produced of the needle of a galvanometer of 100 ohms resistance, and after a few hours 1° , and permanently half a degree; it then remained constant at that point, as shown by occasional testing during about four months, when, by concentration of the liquid by evaporation, the current was feebly reversed. After diluting the liquid to its original strength, the platinum was again positive half a degree, and continued so during a further period of one year. In a similar previous experiment with smaller plates similar results were obtained.

To ascertain whether the platinum was corroded, two electrodes—one of sheet silver and one of platinum—each about 1 inch wide and 3 inches deep, were partly immersed in a similar solution of the hydrate, and a current from two Smee's cells passed through the liquid, the platinum being the anode, during several weeks. The plates were then reweighed; the platinum had not perceptibly diminished in weight, and the silver had lost less than .01 grain.

As an additional example, when gold and platinum produce an electric current in a solution of neutral potassic sulphate, gold being positive (see Table X, p. 266), the solution does not corrode them (see p. 283), and the current is therefore not due to chemical corrosion.

In each of such cases there are three points of heterogeneous contact:—1st. Where the liquid A touches the metal B; 2nd. Where it touches the metal C; and 3rd. Where the metals B and C touch each other. At each of these points the substances are rendered electro-polar by molecular action, and as a feeble current occurs the polarities thus produced do not balance each other. As also a less degree of electric potential is necessary to make a current pass through a suitable electrolyte than to cause a refractory metal such as gold or platinum to corrode, the current is produced without corrosion of metal. This current at once begins to produce the usual effect of raising obstacles to its own continuance, by causing polarisation at the electrodes, and becomes more feeble. As a portion of the current, however, continues permanently, producing the usual effect

upon a galvanometer needle, a permanent source of power must exist; and as corrosion of metal does not occur, this source of power must be different from that of the voltaic current; such currents have been attributed to capillary action.

“Report to the Solar Physics Committee on a Comparison between apparent Inequalities of Short Period in Sun-spot Areas and in Diurnal Temperature-ranges at Toronto and Kew.” By BALFOUR STEWART, M.A., LL.D., F.R.S., and WILLIAM LANT CARPENTER, B.A., B.Sc. Communicated to the Royal Society at the request of the Solar Physics Committee. Received April 21. Read May 1, 1884.

1. It has been known for some time, through the researches of Sabine and others, that there is a close connexion between the Inequalities in the state of the sun's surface as denoted by sun-spot areas and those in terrestrial magnetism as denoted by the diurnal ranges of oscillation of the declination magnet; and moreover, the observations of Baxendell, Meldrum, and various other meteorologists have induced us to suspect that there may likewise be a connexion between solar inequalities and those in terrestrial meteorology.

This latter connexion, however, assuming it to exist, is not so well established as the former—at least if we compare together Inequalities of long period. Attempts have been made to explain this by imagining that for long periods the state of the atmosphere, as regards absorption, may change in such a manner as to diminish or even cloak the effects of solar variation by increasing the absorption when the sun is strongest and diminishing the absorption when the sun is weakest.

On this account it has seemed to us desirable to make a comparison of this kind between short-period Inequalities, since for these the length of period could not so easily be deemed sufficient to produce a great alteration of the above nature in the state of the atmosphere.

The meteorological element which we have selected for comparison with sun-spots has been the diurnal range of atmospheric temperature—an element which presents in its variations a very strong analogy to diurnal declination-range.

2. There are two ways in which a comparison might be made between solar and terrestrial Inequalities. We might take each individual variation in sun-spot areas and find the value of the terrestrial element corresponding in time to the maximum and the minimum of the solar wave. If we were to perform this operation for every individual solar Inequality and add together the results, we might

FIG. 1.

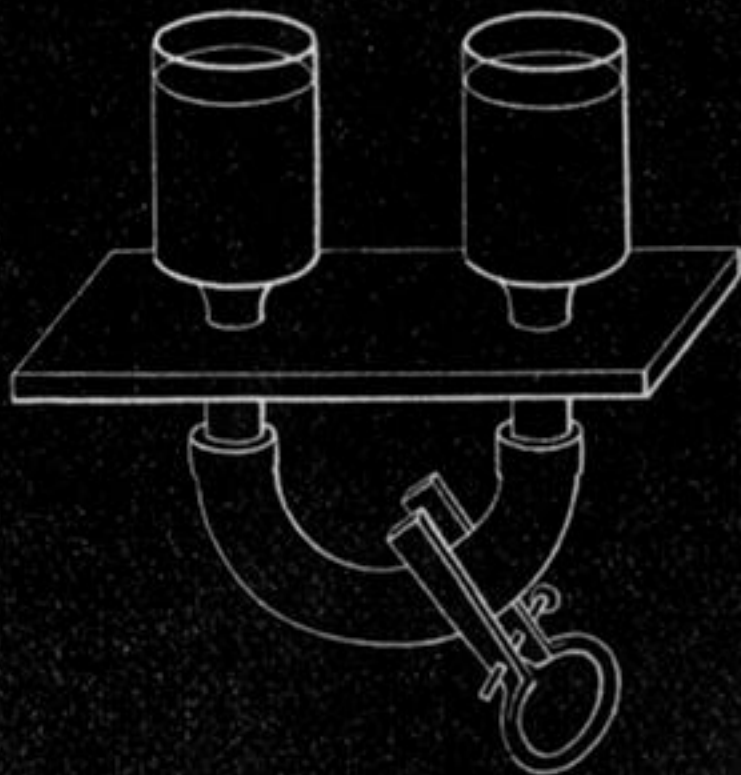


FIG. 2.

K Cy solution.

