The Variations of Electromotive Force of Cells Consisting of Certain Metals, Platinum, and Nitric Acid

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VIII. *The Variations of Electromotive Force of Cells consisting of certain Metals, Platinum, and Nitric Acid.*

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Introduction.

The experiments described by one of us in another paper have established that the necessary condition for the chemical reactions between nitric acid and the metals copper, mercury, and bismuth, is the presence and continuous formation of nitrous acid. These results confirm the previous observations of Russell in the case of the metal silver. Further, it has been shown that when these metals are introduced into purified nitric acid, no apparent change takes place at first, but after some time gas bubbles are seen to rise from the surface of the metal, and the liquid then contains an amount of nitrous acid which can be detected by the more delicate reagents. The amount of this acid increases up to a maximum and constant point, while concomitantly the amount of metal dissolved per unit of time equally increases to a maximum and constant value. It seemed, therefore, desirable to ascertain if these phenomena determined by the balance are correlated with any alteration of electromotive force. To avoid any misunderstanding, however, it would be advisable at the outset to state that this paper is separated from that of one of us " On the Condition of Chemical Change between certain Metals and Nitric Acid," rather on account of division of labour than of difference of subject. The idea of measuring the electromotive force of cells consisting of platinum, certain metals, and nitric acid occurred to the latter of us, while the apparatus and method of measurement finally adopted are due solely to the former.

Previous Investigations.

Many years ago Faraday* pointed out that neither nitrogen peroxide nor nitric acid are conductors when pure, but that the addition of water to the former, or of nitrous acid to the latter, produces the property of conductivity " in a very high degree among electrolytes." Thus the presence of nitrous acid is the necessary

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* 'Experimental Researches,' series xvi., 1815–1818.

condition that nitric acid should become an electrolyte. Again, FARADAY[*] proved that the electric position of certain pairs of metals in nitric acid is varied according to the conditions of concentration and temperature; in fact, experiments on this point were considered by him to be of especial importance in confirming the chemical and disproving the contact theory of the voltaic cell.

POGGENDORFF gives one determination of the E.M.F. of a cell consisting of copper, nitric acid (sp. gr. = 1·222, with nine times its volume of water), and platinum; the value found, taking the E.M.F. of a Daniell's cell at 1070 millivolts, is calculated out as 660 millivolts.

THOMSEN[†] alludes to the various reactions occurring in the combinations zinc / H_2SO_4, 100 H_2O/fuming nitric acid/carbon, as also zinc/H_2SO_4, 100 H_2O/HNO_3, 7H_2O / carbon; the chemical changes taking place in these cells are shown to vary with the concentration of the acid and the chemical energy produced. In the latter cell there is a reduction of the hydrate of nitric acid to nitrogen peroxide, which dissolves without evolution of gas, but with more dilute acid nitric oxide is formed and evolved. The E.M.F. observed of these combinations is substantially in accord with that calculated from the chemical energy developed, expressed in heat units, an agreement which, as ARMSTRONG has pointed out, is the more remarkable considering the gradual accumulation of the products of decomposition of the nitric acid within it, and the effects liable to be produced thereby.

OSTWALD,[‡] in the course of his investigations on contact electricity, measured the difference of potential between metals and aqueous solutions of various electrolytes by the dropping electrode method; amongst other results he gives values for the E.M.F. of certain metals in nitric acid of three different degrees of concentration. He regards, however, his determinations as uncertain, as the metals were strongly attacked by the acid liquid.

But in all these investigations no especial care seems to have been taken to purify the nitric acid from the nitrous acid, which is almost invariably present, neither are details given as to any variation of E.M.F., conditions of temperature and concentration remaining the same. These variations form the principal subject of the present enquiry.

Preliminary Experiments.

Certain preliminary experiments made with the aid of a quadrant electrometer showed that the E.M.F. of a copper-platinum couple dipping in nitric acid of 28 per cent. concentration gradually increased from the moment of contact of the metal with the acid for about two minutes, when it reached its maximum value. But if a small trace of a nitrite were added to the pure nitric acid this maximum E.M.F. was reached

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[*] 'Experimental Researches,' series xvii.

[†] 'WIEDEMANN, Annalen,' vol. 11, 1880, p. 263; also 'Thermochem. Untersuch.,' vol. 3, p. 437.

[‡] 'Zeits. Phys. Chem.,' vol. 1, 1887, p. 602.

at the moment of immersion of the metals; while, on the other hand, the addition of a small trace of urea caused this phenomenon of the increase of E.M.F. to be delayed for a greater interval of time.

This method, however, presented the disadvantage, that, owing to the long period of the vibrations of the needle of the quadrant electrometer, the E.M.F. could not conveniently be determined at the very moment of immersion of the metals. It was, therefore, thought desirable to construct some form of apparatus, which should permit of immediate measurement, and should also ensure that no current passed in the galvanic cell, whereby the proportion of nitrous acid and, consequently, the E.M.F. might be increased.

It was decided to use the capillary electrometer, as the quickest in its action of all instruments for measuring differences of potential; secondly, to balance the E.M.F. of the platinum-copper couple from first to last against a difference of potential, which could be varied at will, and its amount at any given moment automatically recorded; and, finally, to interpolate in the circuit a resistance sufficiently great to make the movements of the mercury of the electrometer sluggish to some degree, so as to minimise the quantity of electricity which would pass while the operator was balancing the E.M.F. of the cell, and at the same time to preserve the instrument from damage.

The Apparatus.

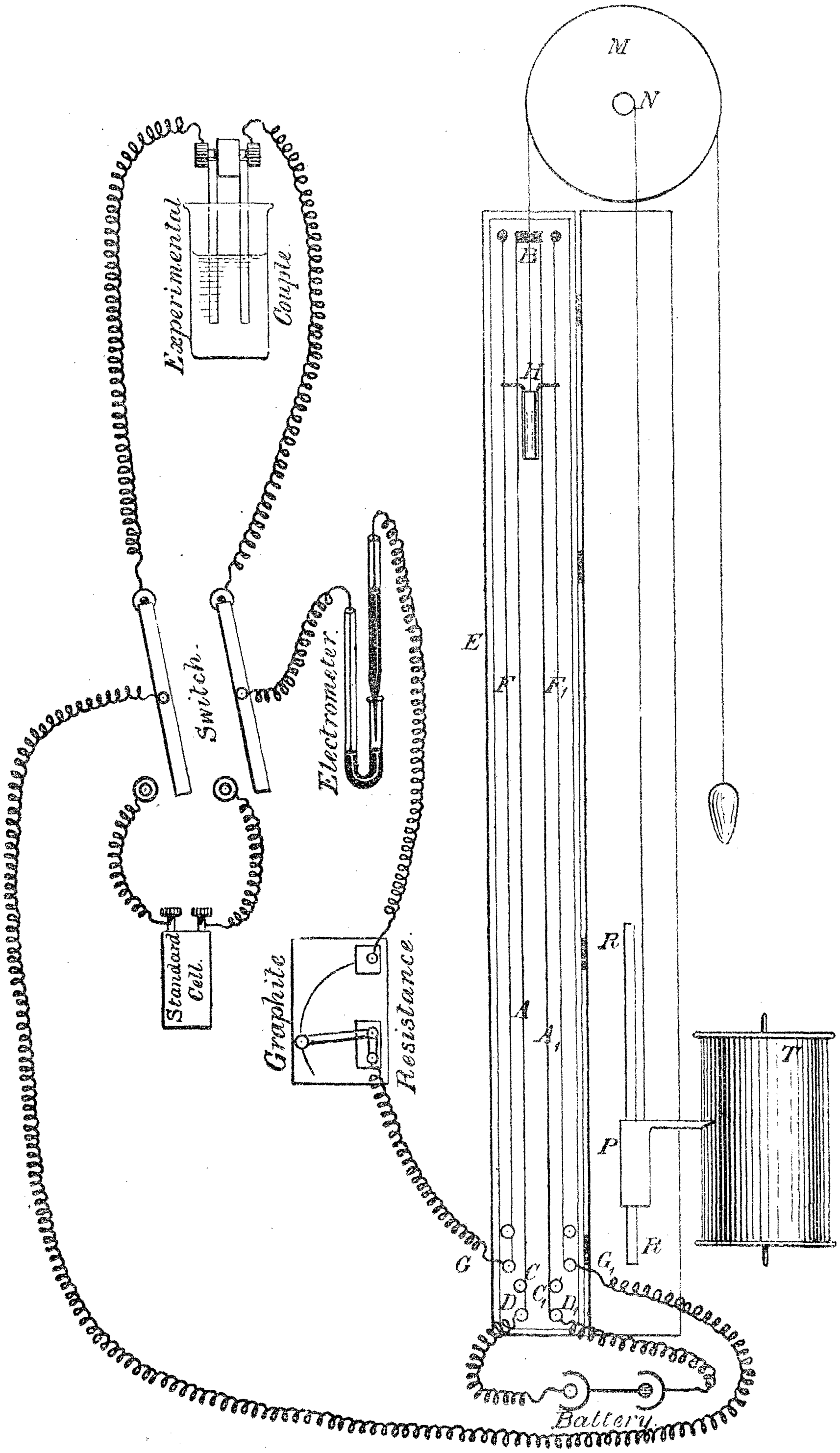
In balancing the E.M.F. of the experimental cell a rheochord (fig. 1), designed by one of us, was employed. A, A′ is a German silver wire 4·5 metres long, and of 20 ohms resistance, which is soldered by the middle to the brass yoke B, the resistance of which is practically zero. The two ends of the wire are attached to springs C, C′, which keep it stretched, and through these to the terminals D, D′.

The yokes, springs, and terminals are cemented to varnished glass pegs in the wooden trough E, which is at the same time the baseboard and the box of the instrument. Two stouter wires, F, F′, insulated from each other and parallel to A, A′, are attached in a similar manner to the terminals G, G′. A heavy rider, H, carries two pairs of spring jaws, made also of German silver, which pinch the wires so as to make electrical connection between A and F and between A′ and F′. Two Daniell's cells are connected with the terminals D and D′, and the terminals G and G′ of the derived circuit are connected with the platinum-copper couple through the electrometer.

The difference of potential thus introduced to balance the E.M.F. of the experimental cell is proportional (errors of calibration excepted) to the distance of the rider H from the yoke-piece B.

The edge of the trough E is graduated in millimetres, so that the position of the rider can be read off. The movement of the rider during an experiment is automatically recorded as follows:—

Fig. 1.



The rheochord.

On the end of the trough E, which for this purpose is fixed in a vertical position, is a flanged wheel, M, 7·5 inches in diameter, on which is wound a thin gut line attached to the rider. Another line, with a counterpoise, is also wound on the same wheel so that the rider may be kept, by the slight friction of its jaws on the rheochord wire, in any position in which it may be placed. On the axle of the wheel is a flat-bottomed groove, N, ·75 inch in diameter, on which also a gut line is wound in such a manner that the weight, P, attached to it may rise when the rider is pushed downward and *vice versâ*, the movement of the weight, P, being only one-tenth of that of the rider. The weight works in a slide, R, attached to the lid of the box or trough, which is held open when in use by the clamps by which the instrument is fastened to the bench.

The weight, P, carries a light arm, on the end of which is a style for the purpose of writing on the smoked paper upon the recording-cylinder, T, which is driven by clock-work in the usual manner. Thus the position of the rider throughout each experiment is recorded on a diminished scale.

The Standard of Electromotive Force.

The standard of E.M.F. to which all the measurements were ultimately referred was a Clark's cell, made up according to the directions given by Lord Rayleigh.[*] The form adopted was a U-shape, the limb containing the mercury being of a greater diameter than that of the limb containing the zinc pole; in fact, the cell was made of a disused pipette, one end of which was cut off and the delivery tube bent round. It was supported by passing the limbs through a cork fitted with a wide-mouthed bottle, and this was filled with water in which a thermometer was immersed. It was thought that the temperature of the cell could thus be more easily ascertained and would be less liable to variation.

Before and after each experiment the Daniell's cells were balanced against the Clark's cell and the position of the rider noted. It has been shown by one of us that, with a capillary electrometer arranged in this way, the quantity of electricity allowed to pass in the process of balancing need never be more than sufficient to charge ·25 microfarad to ·005 volt.

The Capillary Electrometer.

The capillary electrometer was of the form introduced by one of us, and gave a measurable excursion with a difference of potential of ·001 volt.[†] The working pressure was about 6·5 cms. of mercury, and the meniscus was very rapid in its movements. A micrometer scale was used in the eye-piece of the observing microscope to ensure accuracy in balancing the E.M.F., and connection was made with the circuit by a double-make key which was closed only at the moment of the observation.

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[*] 'Phil. Trans.,' 1885, p. 781.

[†] A more sensitive instrument would have been unmanageable.

The Interpolated Resistance.

The resistance interpolated in the circuit to prevent damage to the electrometer was a streak of graphite upon ground glass. By a simple arrangement the effective length of the streak could be adjusted, varying the resistance from zero to about a million ohms. In practice, 750,000 ohms was found to be ample. It may be noted that even this amount of resistance does not affect the sensitiveness of the electrometer if the insulation is good, but simply makes the movement of the mercury slower.

The Materials Used.

The purest electrotype copper procurable, and metallic silver of the degree of purity known as test metal, were supplied to us by Messrs. JOHNSON and MATTHEY; for the mercury, which had been distilled twice *in vacuo*, we are indebted to Mr. F. J. SMITH.

The nitric acid was purified according to the method described by one of us; it was sufficiently free from nitrous acid to give no colouration with metaphenylene diamine; the proportion of this impurity was, therefore, probably less than one part in two or three millions. For each separate experiment the metallic strips were thoroughly washed and cleansed, the success of the experiments depending upon the care bestowed on this point.

The Experimental Cell.

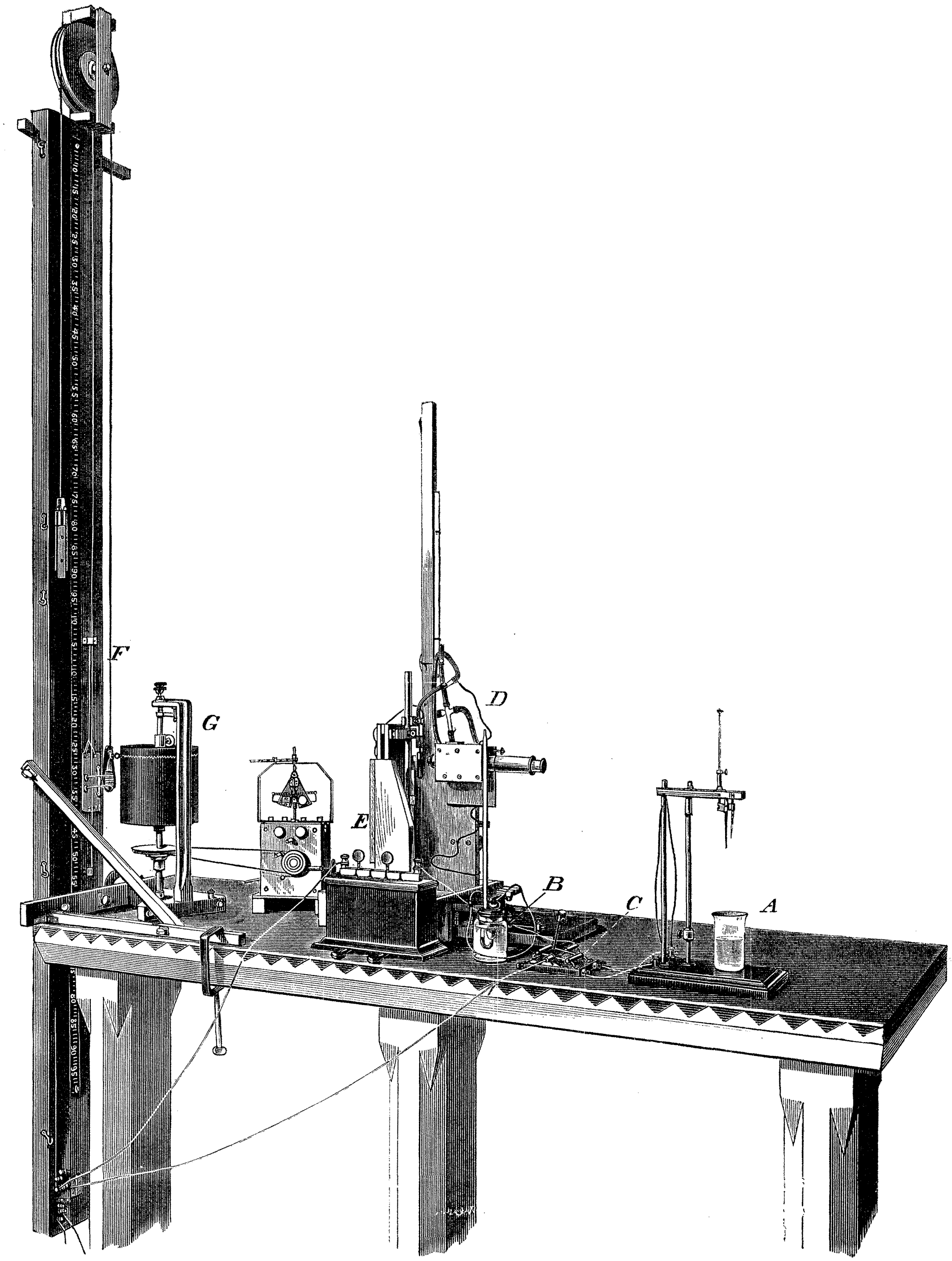
The copper and the platinum strips were fixed vertically in insulated brass screw-clamps, the lower end of each strip passing through a glass tube and projecting about a centimetre beyond it, the purpose of this arrangement being to prevent the possibility of the strips coming in contact with one another, or of the acid with the clamps. An ebonite bar which carries the clamps slides freely on a rod, and is prevented from twisting on it by a guide rod, at the top of which is a catch to fix the bar while everything is being prepared. On the rod is an adjustable stop to regulate the depth to which the copper and platinum strips can be immersed. The acid is contained in a beaker enclosed in a jacket supplied with water, the temperature of which remained constant in the interval of time required for an experiment.

The Circuit.

The general arrangement of the apparatus is shown in fig. 2 (from a photograph).

A = the experimental cell.
B = the standard cell.
C = the switch by means of which either the experimental cell or the rheochord can be put into the circuit.
D = the electrometer.

Fig. 2.



The apparatus.

E = the graphite resistance (represented by a resistance box).
F = the rheochord.
G = the recording cylinder, driven by clockwork (the Daniell's cells are omitted).

A diagram of the circuit showing the connections is given in fig. 1.

The Method of Experiment.

The method of conducting an experiment was as follows:—The copper and platinum strips were fixed in the clamps, and the beaker containing the acid placed beneath them. The rider of the rheochord was then set as nearly as possible in the position in which the E.M.F. of the derived circuit would balance the initial E.M.F. of the experimental cell, this having been determined by a preliminary experiment; the driving-clock was set going at such a rate as would bring the expected duration of the more important part of the experiment well within one revolution of the recording cylinder. At a given signal, one operator released the catch, and the bar carrying the clamps was dropped, suddenly immersing the metal strips in the acid. At the same instant the other observer pressed the contact key of the electrometer, which had up to that time been short-circuited and disconnected. If there was any movement of the mercury, he brought it back to zero as quickly as possible by shifting the rider of the rheochord up or down as might be required.

If, however, the position of the rider had been well chosen, there was no movement of the meniscus of the mercury, which remained at zero for a longer or shorter time, till the E.M.F. of the experimental cell began to rise. When this took place, the difference of potential derived from the rheochord being no longer sufficient to balance it, the meniscus commenced to move slowly down. The movement was checked by drawing the rider gently down, and thus increasing the balancing E.M.F.; and this was continued so long as the electrometer showed any change, the level of the mercury being kept constantly at zero.

When the E.M.F. of the experimental cell had become steady it was disconnected, and the standard cell put into the circuit instead by means of the switch. The rider was shifted until the E.M.F. of the standard cell was exactly balanced by that of the rheochord circuit, and its position was noted.* A line was next marked round the cylinder corresponding to some known position of the rider, generally at 1000 mm., and a series of short marks, corresponding to intervals of 100 mm., was added to serve as a scale of reference.

In addition to the record on the drum, the position of the rider was read off on the scale attached to the rheochord at the beginning and end of each experiment.

The curves were measured by a sliding T ruler, the vertical portion of which was graduated in millimetres and ended in a point, the zero of the scale, while the horizontal portion was provided with a vernier graduated into fifths of a millimetre.

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* If the rider is set at 1438 mms., and the standard cell balanced by altering the resistance of the battery circuit, the rheochord readings are in decimals of a volt.

Thus the height of the curve above any arbitrary base line could be determined for each second of time, and by means of the recorded data the scale-readings could be directly converted into millivolts, the value of the Clark's cell being taken as 1·438 volt.

Copper / Nitric Acid / Platinum.

In the earlier experiments the platinum and copper strips were heated *in vacuo*, to eliminate traces of occluded gases; but in the later experiments, as the required apparatus was not available, this precaution was omitted.

In the succeeding Table the values are given for each interval of five seconds (unless there was no alteration) from the moment of immersion of the copper-platinum strips in the acid.

TABLE I.

Concentration of acid = 29·2 per cent. Temperature 15°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	54	50	214	105	448
5	93	55	234	110	450
10	114	60	266	115	468
15	133	65	297	125	470
20	155	70	341	130	480
25	167	75	374	145	482
30	177	80	413	175	490
35	189	90	422	185	494
40	198	95	434	205	512*
45	200	100	441		

In Table II. the results are given of another experiment conducted under precisely similar conditions.

TABLE II.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	47	40	272	120	524
5	92	45	389	130	527
10	117	50	475	155	533
15	122	55	491	190	535
20	134	75	503	225	539
25	148	90	507	265	543
30	175	95	513		
35	215	105	518		

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* It is probable that the final values given in Tables I. and II. do not represent the maximum attainable, as our subsequent experience showed that this is only reached after the lapse of a number of minutes.

It will be seen, not only from these results, but more clearly from the recorded curve, that the initial E.M.F. of the cell Pt / HNO_3 dil. / Cu, under these conditions is at first very small, and that it rises at first slowly, then more or less rapidly, and finally very slowly until it becomes nearly constant. This last stage is necessarily very protracted as the curve more nearly approaches its asymptote; thus, in the results given in Table II. the alteration of E.M.F. during the last two minutes was only 19 millivolts. It is also worthy of note in these and succeeding experiments that although the general shape of the curve representing the rise of E.M.F. is fairly regular, yet indications are not wanting that there are minor irregularities in the rise, which may be described as secondary oscillations. The explanation of this almost unique case of an increase of E.M.F. is doubtless as follows: the E.M.F. at the start is that (or nearly so) of the combination platinum / nitric acid / copper, while that at the conclusion is that of the combination platinum / nitrous acid / copper. The rate of rise is due, other conditions remaining the same, to the number of molecules of nitric converted into nitrous acid. If the containing vessel was not perfectly clean, if the strip of copper contained a trace of oxide, or even was touched with the finger, or if the strip of platinum was moistened with a drop of liquid used in a previous experiment, then the rise of E.M.F. was almost instantaneous. The initial value depends upon the degree upon which these conditions of purity have been fulfilled, and also upon the success attending the somewhat difficult process of the purification of the nitric acid.

If, then, this alteration of E.M.F. is dependent upon the conversion of nitric to nitrous acid, the presence of a substance, such as urea, which would destroy the nitrous acid, would cause the phenomenon to be protracted. Accordingly an experiment was conducted under precisely the same conditions as before, except that ·25 grm. of urea was added to the 25 c.c. of nitric acid.

TABLE III.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	85	420	287	610	425
5	105	430	301	630	429
Constant	for 87″	450	314	640	437
95	150	460	327	660	448
105	160	470	345	670	450
120	166	480	356	680	460
Constant	for 45″	490	358	690	472
165*	171	510	368	710	483
330	235	520	371	750	494
340	243	540	379	780	515
360	249	560	382	790	519
390	252	570	393	810	527
400	266	580	412	895	542
410	272	590	414	915	550

* At this point there was a failure in the recording of the style.

On comparing the results given in Tables II. and III., it will be evident that in the latter case a much greater interval of time is required before the maximum value is reached, the numbers being 265 and 915 seconds respectively. This last interval is probably the measure of time required for the complete decomposition of the urea added, by the nitrous acid formed. These results were also confirmed by another pair of observations.

Table IV.—Conditions as before.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	109	55	370	115	542
5	297	60	404	135	548
10	233	65	437	155	555
15	—	70	453	160	568
20	257	75	476	200	575
25	270	80	492	240	581
30	288	85	503	280	584
35	302	90	510	320	586
40	313	95	516	360	592
45	332	100	523		
50	350	110	534		

The experiment was then repeated with introduction of ·25 grm. urea as in the case of Table III.

Table V.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	255	25	348	85	368
5	307	30	350	105	372
10	329	45	354	271	372
15	332	55	360		
20	341	65	364		

The difference in the rate of rise of the E.M.F. in the two cases is very evident, and confirms, in every respect, the previous observations. Other series of experiments were conducted, in order to determine the effects produced by alterations of conditions, such as concentration of acid, temperature, and addition of nitrous acid.

Effect of Concentration.

A sample of nitric acid was purified as before, and made up to a concentration of 15 per cent., *i.e.*, nearly one-half the strength of that used in the preceding experiments.

Table VI.—Concentration of Acid = 15 per cent. Temperature = 16°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	369	135	498	868	746
5	386	255	516	898	789
15	411	315	531	958	795
35	421	Interval	of 213″	988	800
45	428	528	588	1018	816
55	435	558	603	1048	820
65	446	588	622	1078	828
75	448	618	644	1108	832
85	462	668	648	1168	839
95	465	718	674	1198	846
105	477	778	679	1228	858
125	496	808	—		

If these numbers be compared with those of Table IV., it will be seen that the effect produced by decreasing the concentration is to lengthen out to a considerable degree the phenomenon of the increase of E.M.F., for to reach the same point, viz., 592 millivolts, 360″ were required in the one and about 540″ in the other case.

The higher initial value is probably due to a greater proportion of nitrous acid present initially in the nitric acid, as our experience has shown us that a difference of a very few parts per million makes a considerable alteration not only in the rate of chemical change, but also in the variations of electromotive force; it is also probably conditioned by the amount of occluded gases in the metallic strips.

Decrease of concentration also seems to increase to a slight extent the final value of the E.M.F., which is doubtless influenced to a greater degree by the proportion of nitrous acid, but to a less degree by the quantity of metallic salt dissolved per unit volume of the acid.

The experiment was then repeated under the same conditions, except that a small quantity of sodium nitrite was added to the nitric acid; a maximum value of 711 millivolts in one case and 727 in another was reached *at once.* This result shows that the increase of E.M.F. observed is due for the most part to the *production of nitrous acid.* The slightly lower final value of the E.M.F., when the nitrous acid has been added as such, is in accordance with the observations of one of us, that nitrous acid ready formed is not so active a material as nitrous acid in the alternative process of formation and decomposition.

As a confirmation of the above values the results are given below of one preliminary set of determinations made by a different method and by means of a Thomson's quadrant electrometer; the values were compared with another Clark's cell of different construction to that used by us.

TABLE VIA.—Concentration of Acid = 26 per cent. Temperature = 16°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	648	100	738	200	808
10	648	110	748	220	814
20	642	120	760	240	822
30	656	130	768	280	828
40	668	140	774	340	828
50	685	150	783	370	858
60	689	160	783	430	853
70	705	170	794	550	863
80	724	180	801		
90	732	190	808		

On comparison of these results with those given in Table VI., it will be seen, as before, that the time required to reach the maximum value of the E.M.F. is less with more concentrated acid. The experiment was then repeated with addition of 1 per cent. of sodium nitrite; a value of 755 millivolts was reached at once, and there was no further increase. Other preliminary experiments gave nearly identical results, but it is not thought necessary to quote them.

Effect of Temperature.

To determine the effect produced by variation of temperature, two experiments were conducted with the same acid as that used above, but heated in a jacket of water.

TABLE VII.—Concentration of Acid = 15·0 per cent. Temperature = 36°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	600	40	779	120	860
5	636	45	807	140	866
10	648	50	815	150	898
15	700	70	821	After 2′	862
20	712	80	834	,, 5′	848
25	742	90	845	,, 7′	846
30	768	100	859		

TABLE VIII.—Concentration of Acid = 15·0 per cent. Temperature = 50°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	634	6	858	14	884
2	755	8	870	Constant at	864
4	811	10	874		

It will be evident that an increase of temperature causes a more rapid rise of the E.M.F., a result due to the more rapid solution of the copper, and consequent production of nitrous acid; it is probable from other experiments that, if the conditions could be kept absolutely fixed, the rise of E.M.F. per unit of time would be found to be a logarithmic function of the temperature. As a comparison, the times required for the rise of E.M.F. between the same limits, viz., 634 and 858 millivolts, are 840, 75, and 6 seconds respectively.

Another point is worthy of observation, namely, that at the higher temperatures the E.M.F. reaches a maximum value, and then slowly, but somewhat irregularly, decreases until it reaches a constant value; this may be due to the vapour of water either oxidising the surface of the metal above the acid, or carrying up bubbles of oxides of nitrogen which attack the metal, and thus produce a temporary increase.

In conclusion, the value of the E.M.F. in water for the copper-platinum strips used in the above experiments was determined. It was found to be 410 millivolts (and after 3 hours 441), which is practically the initial value given in Table IV., thus showing that the E.M.F. of the combination copper / water / platinum is not very different from that of copper / dilute nitric acid / platinum, while it is even probable that the still lower value obtained with more concentrated acid is due to an immediate formation of oxide.

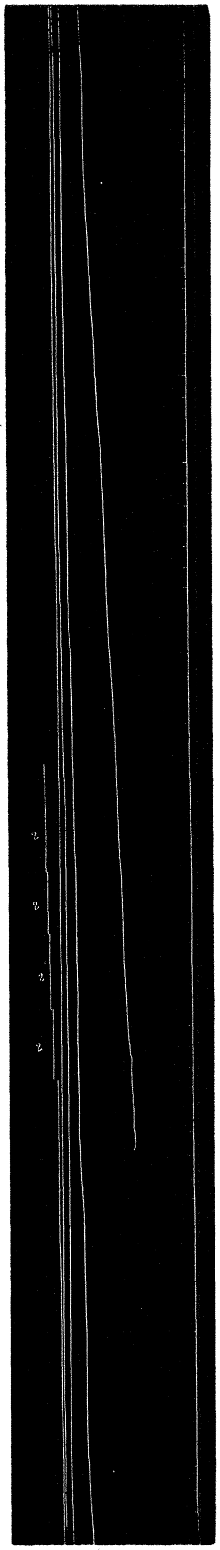
A characteristic curve is given of the rise of E.M.F. in one experiment, in which the abscissæ represent the time in seconds from the start, while the ordinates are reduced rheochord readings which are functions of the E.M.F. The same remarks apply in the case of the curves for other metals.

Silver / Nitric Acid / Platinum.

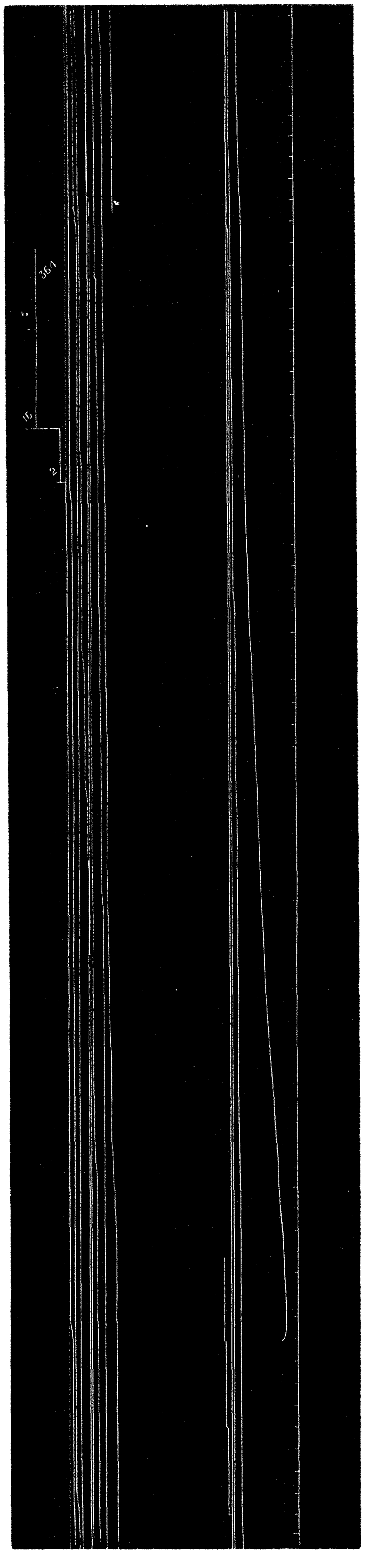
Precisely similar experiments to those described above were conducted with metallic silver, which showed the same general results of rise of E.M.F.; this will be evident from the results given in the following Tables :—

TABLE IX.—Concentration of Acid = 15·0 per cent. Temperature = 15°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	319	90	414	240	560
10	325	110	442	250	572
20	350	120	446	280	577
30	355	130	465	300	600
40	364	140	474	370	619
50	377	150	484	440	629
60	395	180	491	560	650
70	400	190	506	680	674
80	409	200	525	800	681



Characteristic curve of Copper / Nitric Acid / Platinum. Temp. 16°. Acid, 15 per cent.



Characteristic curves of Silver / Nitric Acid / Platinum. α at temp. 29°; β at temp. 16°.

The curve representing the variation of E.M.F. rises at first with uniform regularity, but in the *later stages*, in an irregular or staircase form ; this is not due to instrumental error, but is the actual record of a periodic change in the experimental cell.*

There can be but little doubt, considering the results obtained from a chemical standpoint by RUSSELL, that in the case of this metal also the initial E.M.F. is that of silver / nitric acid / platinum, while the final is that of silver / nitrous acid / platinum. But to meet the possible objection that the rise of E.M.F. is the effect of that cause to which we attribute it, and not to some gradual formation of oxide or, it may be, of metallic nitrate, on the surface of the metal above the level of the acid liquid, the experiment above was repeated under precisely the same conditions, except that the metallic surface above the liquid was coated over with vaseline to protect it from acid fumes and oxides of nitrogen.

TABLE X.—Conditions as in Table IX.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	267	100	349	320	450
10	303	110	356	390	456
20	305	120	367	400	487
30	319	130	374	410	499
40	322	150	399	480	508
60	332	220	402	490	520
80	338	300	426	610	552
90	345	310	435	1570	680

On a comparison of the results given in Tables IX. and X., the values for the initial and final E.M.F.'s are seen to be within the limits of experimental error ; the form of the curves in the two cases is the same, and in many parts of their course they are superposable. This shows, therefore, that the rise of E.M.F. is not due to any alteration of the metallic surface above the acid liquid.

Effect of Temperature.

The experiments were repeated, the one condition of temperature being varied ; the results obtained are given below.

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* It was noticed that if the graphite resistance was cut out and the rider allowed to remain in one position for a few seconds, the mercury of the electrometer did not always rise steadily, but frequently moved with a series of rapid oscillations, which apparently coincided with the evolution of bubbles larger than usual. This was seen also in the case of copper.

TABLE XI.—Concentration of acid = 15·0 per cent. Temperature 29°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	260	60	485	250	547
10	314	70	503	390	569
20	388	80	509	410	579
30	427	100	519	531	594
40	455	110	524	Probably not complete.	
50	479	180	538		

TABLE XII.—Concentration of acid = 15·0 per cent. Temperature 39°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	360	40	636	90	664
10	522	50	643	120	668
20	563	60	651	130	680
30	597	70	660		

A fourth experiment was conducted at 41°, but the rise of E.M.F. was too rapid for correct observation.

The results obtained with silver confirm in every particular those obtained with copper, viz.: that increase of temperature produces a more rapid rise, but does not appreciably alter the final value of the electromotive force.

Bismuth / Nitric Acid / Platinum.

The metal used for these determinations was cast into a small cylinder, 6 inches long and $\frac{1}{6}$ inch diameter; between each operation the coating of black oxide, formed by the immersion of the metal in the acid, was carefully removed.

TABLE XIII.—Concentration of acid = 15 per cent. Temperature 16°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	685	60	946	190	995
10	760	70	—	220	1024
20	810	80	956	310	1055
30	850	90	971	490	1058
40	875	100	982		
50	896	120	986		

On repetition of the above experiment, under precisely the same conditions, the following values were obtained.

TABLE XIV.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	737	40	913	80	1006
10	809	50	940	90	1014
20	872	60	944	160	1040
30	902	70	985	Constant.	

Thus the behaviour of a circuit consisting of bismuth, platinum, diluted nitric acid is precisely similar to those containing the metals copper and silver. The net result obtained was to be expected from the observations of one of us, that no chemical reaction takes place between bismuth and nitric acid, save in the presence of nitrous acid. As in the previous example, the initial value of the E.M.F. is approximately that of bismuth / nitric acid / platinum, while the final value is that of bismuth / nitrous acid / platinum.

Effect of Temperature.

The above experiments were repeated with alteration of the one condition of temperature. In the two following tables the results are given of experiments conducted at 34° and 66° respectively.

TABLE XV.—Temperature 34°.

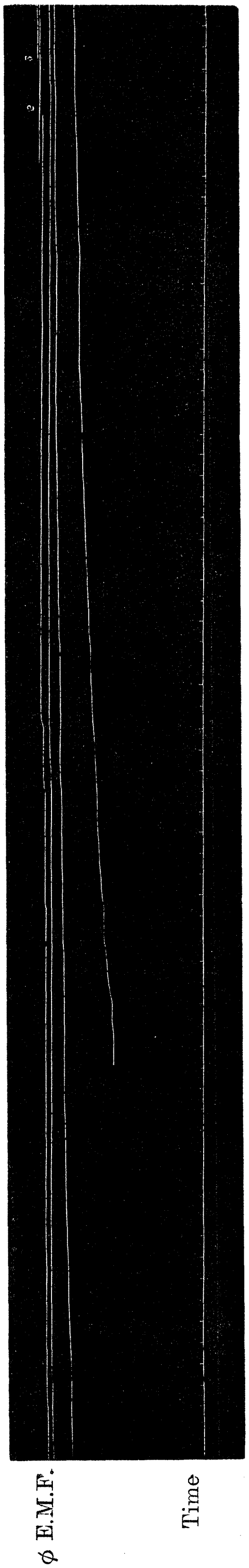
Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	884	40	996	120	1033
10	896	50	1011	Constant.	
20	950	80	1058		
30	950	110	1045		

TABLE XVI.—Temperature 66°.

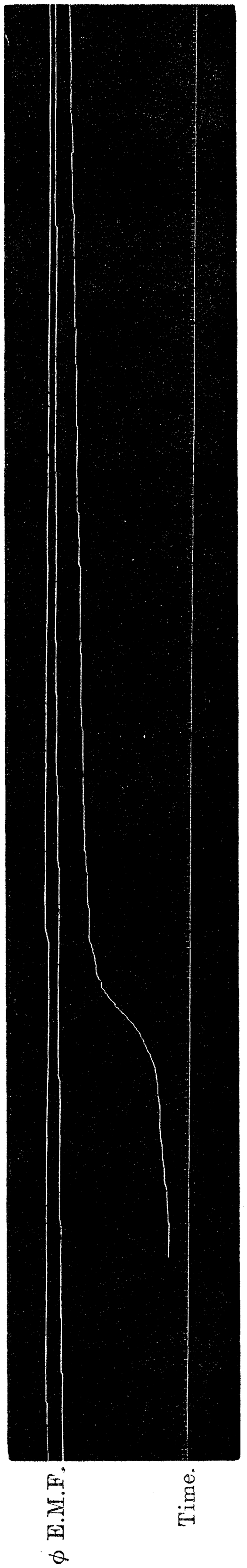
Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	682	15	1128	30	1091
5	999	20	1123	55	1061
10	1020	25	1112	Constant.	

As in the case of copper and silver, so also in that of bismuth, increase of temperature produces a more rapid rise of E.M.F.; and, in fact, at a temperature of 66°

Characteristic curve of Bismuth / Nitric Acid / Platinum. Temp. 16°. Acid, 15 per cent.



Characteristic curve of Mercury / Nitric Acid / Platinum. Temp. 15°. Acid, 29·1 per cent.



it was almost too sudden for correct observation; the final value, however, is not affected. It will be seen that at the higher temperatures the E.M.F. rises to a maximum and then falls slightly to the value at which it remained constant for several minutes. The possible reasons for this phenomenon have been discussed above.

Mercury / Nitric Acid / Platinum.

The mercury was introduced into the acid by means of a small U-tube having limbs of unequal length, in the shorter one of which, the acid came in contact with the metal, while down the longer, a platinum wire passed serving as a connection with the rest of the apparatus. In the use of mercury there is, however, this disadvantage, that there is a difference of potential due to capillarity, which produces an accidental but permanent charge in the instrument, and diminishes or increases, as the case may be, the readings by a constant amount. In the particular experiment quoted, the readings were diminished; and the values given below are intended merely to illustrate the similarity of the behaviour of mercury to that of the other metals discussed above.

TABLE XVII.—Concentration of acid = 29·2 per cent. Temperature 16°.

Time.	E.M.F.	Time.	E.M.F.	Time.	E.M.F.
seconds.	millivolts.	seconds.	millivolts.	seconds.	millivolts.
0	0 + x	90	260 + x	195	305 + x
10	13 ,,	100	262 ,,	215	307 ,,
20	29 ,,	105	266 ,,	235	315 ,,
30	41 ,,	115	271 ,,	255	317 ,,
40	103 ,,	125	279 ,,	295	331 ,,
50	225 ,,	145	281 ,,	335	335 ,,
60	239 ,,	155	285 ,,	355	339 ,,
70	248 ,,	165	291 ,,	420	361 ,,
80	255 ,,	175	301 ,,		

Other experiments conducted in the same manner gave precisely similar results with different errors due to capillarity, so that in this case also it is probable that the final E.M.F. is that of the combination mercury / nitrous acid / platinum.

Conclusion.

I. The experiments detailed above show that when the metals, copper, silver, bismuth, and mercury are introduced into purified nitric acid of varying degrees of concentration, and a couple made with platinum, the electromotive force of such a cell increases considerably until it reaches a constant and (in most cases) a maximum value.

This rise of E.M.F. is attributed to the production of nitrous acid by the decomposition of the nitric acid, and the final value is considered to be due to the former acid only, while the initial value is due for the most part to the latter acid, though it is affected to a remarkable degree by the amount of impurity of nitrous acid either initially present or produced by minute and unavoidable uncleanliness of the metallic strips and the containing vessel.

II. If nitrous acid has been previously added to the nitric acid then the maximum E.M.F. is reached at once.

III. If the conditions, namely, increase of temperature, of impurity, and of concentration of acid, are such as could favour a more rapid production of nitrous acid, then the rise of E.M.F. is concomitantly more rapid.

IV. Conversely, if the conditions are unfavourable to the production of nitrous acid the rise of E.M.F. is less rapid.

V. If any substance, such as urea, be added, which would tend to destroy the nitrous acid as fast as it may be formed, then the rise of E.M.F. is extremely slow, being dependent upon the number of molecular impacts of nitrous acid upon the surface of the metal. Thus the results obtained by the electrometer and of the chemical balance are in every way confirmatory, the one of the other. These results open out the further question as to whether the E.M.F. of batteries, in which concentrated nitric acid forms an ingredient, is dependent not upon the nitric acid *per se*, as hitherto supposed, but upon the nitrous acid present in the fuming nitric acid, and formed also by the reduction of the acid by the hydrogen, which would otherwise be given off from the zinc and sulphuric acid.

Also since recent investigations have tended to show that the products of electrolysis of sulphuric acid are instrumental in effecting the solution of zinc, it is probable that the E.M.F. of a combination zinc / sulphuric acid / platinum may exhibit variations similar to those of combinations, wherein nitrous acid, one of the products of electrolysis of nitric acid, is continuously being formed.

To these problems we hope at no distant date to direct our attention.

Finally, we would express our thanks to Mr. F. J. SMITH, of Trinity College, for kind assistance and advice; to Mr. H. G. MADAN, of Queen's College, for taking photographs of our apparatus; and especially to Professor BURDON SANDERSON for kindly placing at our disposal the apparatus from his department.

The experiments were conducted partly in the Chemical Department of the Museum, and partly in a private laboratory.