Extracts from the papers of Sir Charles Wheatstone

WHEATSTONE 2: Material relating to experiments designed to measure electromotile forces and electric potential, [1834-1875]

K/PP107/2/4/1-314

[1871-1875]

Working notes compiled by Charles Wheatstone comprising measurement of the electro-motive force between electrodes coated with films of sulphides, bromides and iodides, elements including zinc, mercury, cobalt and rubidium, and between electrodes of various alloys; measurement of electric potential of compound circuits; observations on the manufacture of amalgams; calculation of the weights of products of electrophoresis; the phenomenon of 'passivity'; employment in electric cells of peroxides and teroxides.

The Papers of Charles Wheatstone

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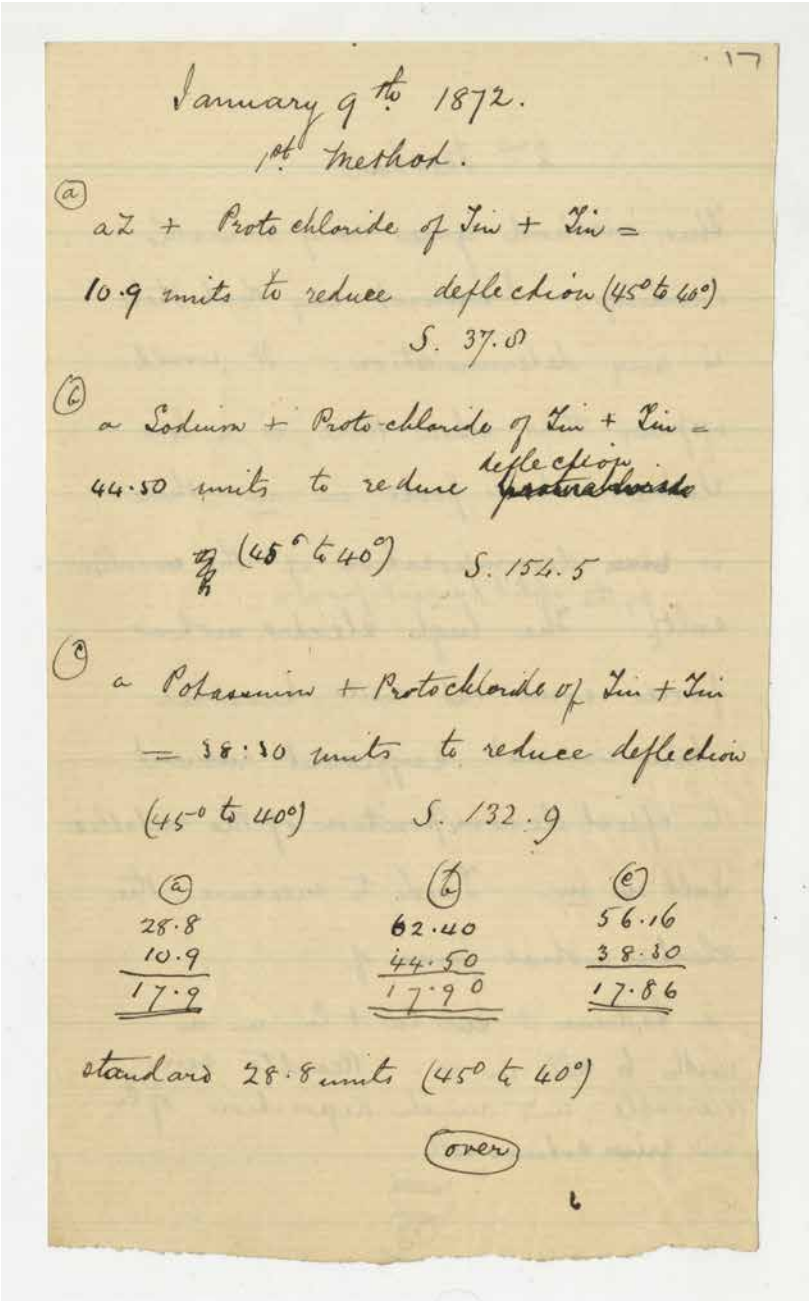

17

January 9th 1872.

1st Method.

(a) aZ + Proto chloride of Tin + Tin =

10.9 units to reduce deflection (45° to 40°)

S. 37.0

(b) a Sodium + Proto chloride of Tin + Tin =

44.50 units to reduce ~~proto chloride~~ deflection

(45° to 40°) S. 154.5

(c) a Potassium + Proto chloride of Tin + Tin

= 38.30 units to reduce deflection

(45° to 40°) S. 132.9

(a)	(b)	(c)
28.8	62.40	56.16
10.9	44.50	38.30
17.9	17.90	17.86

standard 28.8 units (45° to 40°)

over

K/PP107/2/4/17

Notes by Richard William Mellingford Higgs describing methodology for measuring the electromotive forces zinc to mercury, 1872 Jan 9, page 1.

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2nd Method

This method gives very variable readings. I cannot say that there is any determination. It would appear that when there is a low electro motive force in m there is ~~[illegible]~~ decomposition of the metallic salt by the split current from n. The high electro motive forces come out well because there is not sufficient current to effect decomposition of the metallic salt in m. Tried to measure the electromotive force of a Sodium + Sul Cu + Cu in m with 6 cells in n. Results very variable; and much deposition of Cu on ~~[illegible]~~ sodium cell.

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41

Thallium and its Peroxide.

January 31st 1872.

Standard = 28·8 units (45° to 40°).

a Z + Nitrate of Thallium + a Thallium

= 14·28 units (45° to 40°). S. 49.5

a Sodium + Sulphate of Thallium + a Thallium

= 47·8 units (45° to 40°). S. 165.9

a Potassium + Sulphate of Thallium + a Tl

= 41·5 units (45° to 40°). S. 140.9

a Thallium + Sulphate of Copper + Cu

= 14·5 units (45° to 40°). S 50.3

a Thallium + Sulphuric Ac: + peroxide

of lead = 51·0 units (45° to 40°). S. 177.1

a Thallium + Sulphuric Ac: + peroxide

of Thallium = 53·3 units (45° to 40°) S 185.0

a Thallium + Chloride of platinum

+ Platinum = 24·0 units S 83.3

a Z + Sulphuric Ac: + Peroxide of

Thallium = 67.5 units (45° to 40°). S 234.3

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Measurements of the electromotive force between thallium and its peroxide, by Richard William Mellingford Higgs and annotated by Wheatstone, 1872 Jan 31.

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44

Niobium or Columbium:

March 8th, 1872.

Metallic Niobium reduced from the chloride upon platinum and upon copper wire, as a black deposit easily removed by the touch.

a Z + Solution of Niobic acid + Niobium = 16 units (45° to 40°). S. 55.5

a Sodium + Solution of Niobic acid + Niobium = 49·5 units (45° to 40°). S. 171.0

a potassium + solution of Niobic acid + Niobium = 43·3 units (45° to 40°). S. ~~153·3~~ 150·3

Niobium + sulphate of Copper + Copper = 12·8 units (45° to 40°). S. 44.4

Niobium + chloride of platinum + platinum = 22·2 units (45° to 40°). S. 77.0

Niobium + sulphuric acid + peroxide of lead = 49·3 units (45° to 40°). S. 171.1

K/PP107/2/4/44

Measurement of the electromotive force on niobium or columbium probably by Richard William Mellingford Higgs, 1872 Mar 8.

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81

Aluminum. Pure Chemicals. ?

January 20th. 1872.

Standard = 28.8 units (45° to 40°).

aZ + ~~[illegible]~~ Chloride of Alumina + Alum^m

= 10 units S' 34.7

Aluminum + Chloride of Copper + Cu

= 16 units. S. 55.5

aZ + al = 10

al + Cu = 16.8

26.8

This is the best measure I can obtain. The action of the acid of the chloride upon the aluminum is so Energetic and so much gas is Evolved that the measure is very unreliable. In the case where the aluminum is the negative metal, the

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Measurements of electromotive forces on aluminum by Richard William Mellingford Higgs, 1872 Jan 20, page 1.

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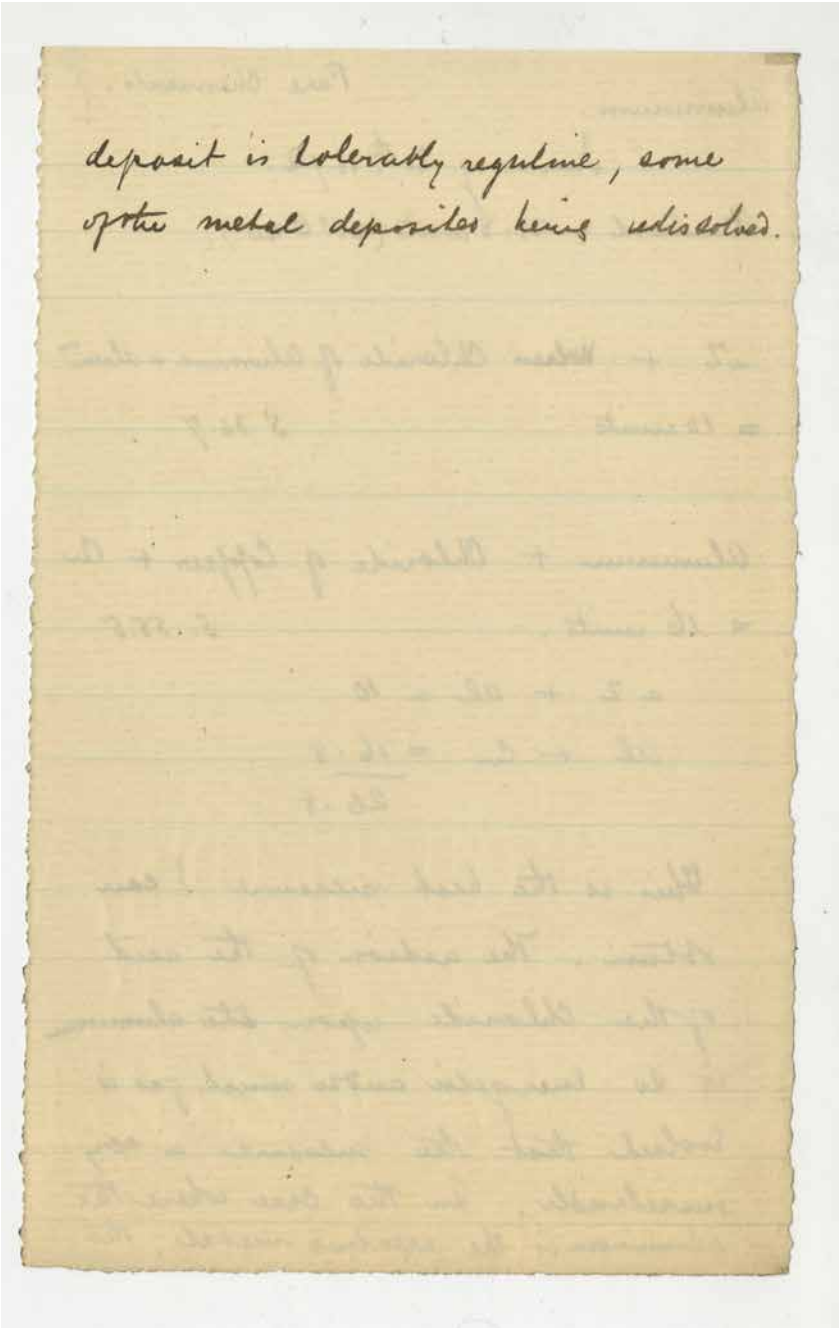

deposit is tolerably regular, some
of the metal deposited being redissolved.

K/PP107/2/4/81
Measurements of electromotive forces on aluminum by Richard William Mellingford Higgs, 1872 Jan 20, page 2.

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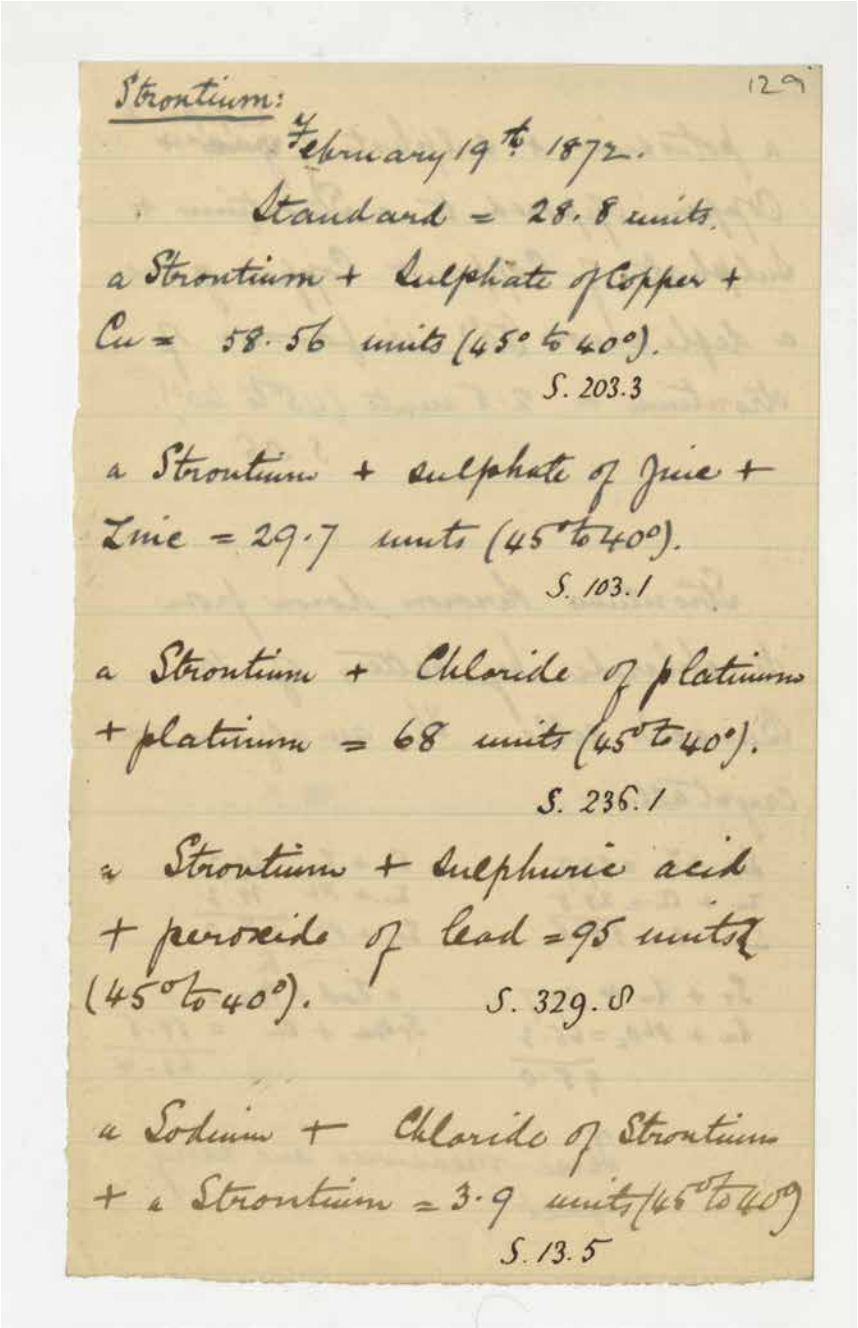

129

Strontium:

February 19th 1872.

Standard = 28.8 units.

a Strontium + Sulphate of Copper + Cu = 58.56 units (45° to 40°).

S. 203.3

a Strontium + sulphate of Zinc + Zinc = 29.7 units (45° to 40°).

S. 103.1

a Strontium + Chloride of platinum + platinum = 68 units (45° to 40°).

S. 236.1

a Strontium + Sulphuric acid + peroxide of lead = 95 units (45° to 40°).

S. 329.8

a Sodium + Chloride of Strontium + a Strontium = 3.9 units (45° to 40°)

S. 13.5

K/PP107/2/4/129

Measurements of electromotive forces on strontium, by Robert William Mellingford Higgs, 1872 Feb 19, page 1.

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a potassium + sulphate of Copper + Copper opposed to a Strontium + Sulphate of Copper + Copper gave a deflection (50°) in favour of strontium = 2·5 units (45° to 40°).

S. S. 6

Strontium thrown down from its chloride by battery of 10 Bunsen's cells. The amalgam was crystalline.

Sr + Zn = 29·7	Sr + Zn 29·7
Zn + Cu = 28·8	Zn + Pt 38·3
Sr + Cu 58·5	Sr + Pt 68·0
Sr + Zn = 29·7	a Sod + Sr = 3·9
Zn + PbO_2 = 65·3	Sr + Cu = 58·5
95·0	62·4

These measures are very exact.

K/PP107/2/4/129

Measurements of electromotive forces on strontium, by Robert William Mellingford Higgs, 1872 Feb 19, page 2.

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March 8th 1872. 147

Didymium: (not known in metallic state).

Reduced didymium into mercury from nitrate: metal not ~~easily~~ reduced upon platinum or copper (~~otherwise~~ perhaps not sufficient salt).

Standard = 28·8 units (45° to 40°).

a Didymium + sulphate of zinc + zinc = 13 units (45° to 40°). S. 45.2

a Di + sulphate of Copper + Copper = 41·8 units (45° to 40°). S 145.2

a Di + chloride of platinum + platinum = 51·2 units (45° to 40°). S. 177.7

a Di + sulphuric acid + peroxide of lead = 78·3 units (45° to 40°). S. 271.8

a Sodium + nitrate didymium + a Di = 20·5 units (45° to 40°). S. 71.1

a Potassium + nitrate didymium + a Di = 14·3 units (45° to 40°). S. 49.6

K/PP107/2/4/147

Measurements of electromotive forces on didymium 'not known in metallic state' [originally thought to be an element], by Richard William Mellingford Higgs, 1872 Mar 8.

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February 10th 1872. 148

Dr. Frankland's Lithium amalgam.

Standard = 28.8 units (45° to 40°)

a Lithium + Sulphate Copper + Copper = 40.32 units (45° to 40°). S. ~~152~~ 140

a Lithium + Chloride of platinum + platinum = 49.8 units (45° to 40°) S. 172.9

a Lithium + Sulphuric acid + peroxide of lead = 76.8 units (45° to 40°). S. 266.5

a Lithium + Sulphate of zinc + zinc = 11.5 units (45° to 40°). S. 39.9

a Sodium + Chloride of Lithium + amal. Lithium = 22.0 units (45° to 40°). S. 76.3

a Potassium + Chloride of Lithium + a Lithium = 15.8 units (45° to 40°). S. 54.0

The lithium oxidises out of the mercury most rapidly; it has now (5 minutes after making measures) Entirely

K/PP107/2/4/148

Measurements of electromotive forces on 'Dr [Edward] Frankland's [(1825-1899), chemist] lithium amalgam', by Richard William Mellingford Higgs, 1872 Feb 10, page 1.

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disappeared. The first measure gave sodium, the next measure gave the number recorded which remained constant.

a Li + Cu = 40.32
a Sod + Li = 22.00
a Sod + Cu = 62.32
Error = 0.18

a Li + a Zn = 11.5
a Zn + Cu = 28.8
a Li + Cu = 40.3

a Li + a Zn = 11.5
a Zn + PbO_2 = 65.3
a Li + PbO_2 = 76.8

a Pot + Li = 15.8
a Li + Cu = 40.32
a Pot + Cu = 56.12
Error = 0.04

a Li + a Zn = 11.5
a Z + Pt = 38.3
a Li + Pt = 49.8

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Standard = 28·8 units (45° to 40°). 159

January 29th 1872.

Indium:-

a Zinc + Sulphate of Zinc + Indium (Indium being slightly + to Zinc). = 1·2 units (45° to 40°).

S. 4.1

a Sodium + Chloride of Indium + Indium = 32·4 units (45° to 40°).

S 111.0

a Potassium + Chloride of Indium + Indium = 26·2 units (45° to 40°).

S. 90.9

Indium + Sulphate of Copper + Cu = 30 units (45° to 40°).

S. 104.1

a Sod + Indium	=	32·4
Indium + Copper	=	30·0
a Sod + Cu	=	62·40
a Potassium + I	=	26·2
Indium + Cu	=	30·0
		56·2

Error 0·04

K/PP107/2/4/159

Measurements of the electromotive force of indium by Richard William Mellingford Higgs, annotated by Wheatstone, 1872 Jan 29.

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160

April 5th 1872.

Indium is deposited from its chloride upon cadmium and zinc, but not upon tin. Every care was taken to ensure clean surfaces.

a Sodium + Chloride of Indium + Indium

units (45° to 40°).

gave 32.3 1st trial

32.0 2nd " S 111.1

33.0 3rd "

32.5 4th "

32.5 5th " S. 112.0

32.5 6th "

Indium + sulphate Copper + Copper gave 30. 29. 30. 2. 30. 30. 30 units for 6 trials.

K/PP107/2/4/160

Measurements of the electromotive forces of indium, by Richard William Mellingford Higgs, annotated by Wheatstone, 1872 Apr 5.

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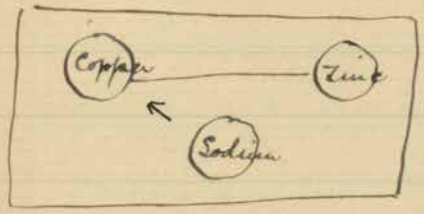
174

Compound Circuits

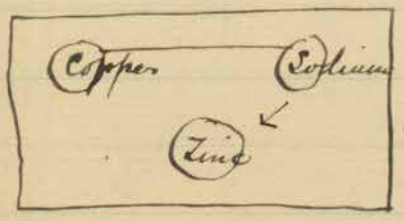
March 11th 1872.

Standard = 28.8 units (45° to 40°).



Electro-motive force = 62.40 units (45° to 40°).

S. 216.6
216.9 S+C



Electro-motive force = 33.6 units (45° to 40°).

S. 116.6

Electro-motive force = 62.40 units (45° to 40°).

S. 216.6
216.9 S+C

K/PP107/2/4/174

Measurement of electromotive forces of compound circuits by Richard William Mellingford Higgs with annotated by Wheatstone, 1872 Mar 11.

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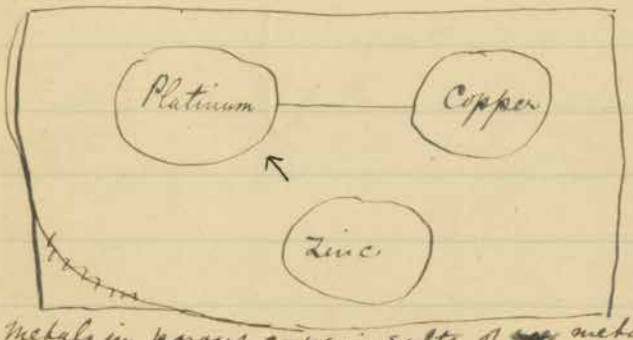
K/PP107/2/4 - Papers relating to the development of the electric telegraph

Compound Circuits:- 175

March 11th 1872.

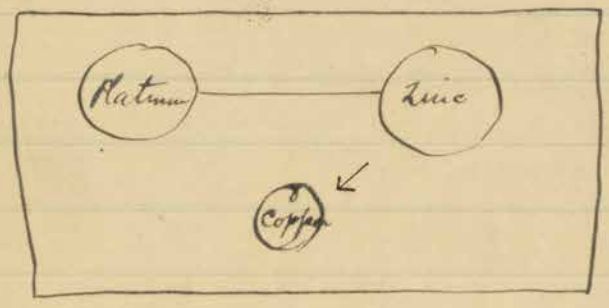
Standard = 28.8 units (45° to 40°).



Metals in porous cups in salts of ~~cop~~ metals; porous cups in dilute sulphuric acid

S. 132.9 38.3

Electromotive force = ~~[illegible]~~ units $\left(\frac{45°}{40°}\right)$



Electromotive force = 28.8 units (45° to 40°). S. 100

K/PP107/2/4/175

Measurements of the electromotive force of compound circuits by Richard William Mellingford Higgs, 1872 Mar 11.

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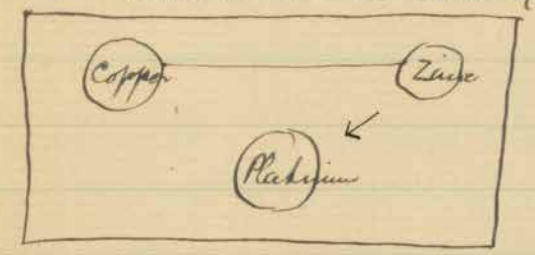
Compound circuits: 176

March 11th 1872

Standard = 28·8 units (45° to 40°).



Electro-motive force = 38·3 units (45° to 40°).

S. 132·9
133·3 P+Z

There are three cases. 1 When the single metal is more positive than the other two, in which case the emf is that between the highest and the lowest. 2 When the single metal is ~~is high~~ more negative than the other two, in which case also the emf is between the highest and lowest. 3 When the single metal is more positive than one and more negative than the other of the combination, in which case the emf is that of the two lowest

K/PP107/2/4/176

Notes and measurements of electromotive forces on compound circuits by Richard William Mellingford Higgs with additional notes by Wheatstone, 1872 Mar 11.

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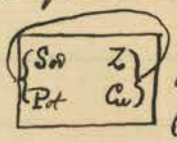
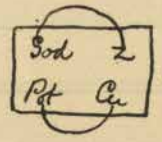
February 6th. 1872. 177

Standard = 28.8 units (45° to 48°)

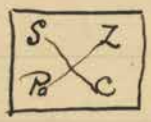
Place four porous cells in the same vessel with dilute sulphuric acid, and ascertain the electromotive force of the three following orders:-



Emf: = 61.9 (45° to 40°)
(Sodium + Cu nearly)
S. 214.9



Emf: = 62.3 (45° to 40°)
(Sod + Cu nearly)
S. 216.3



Emf: = 32.0 (45° to 40°)
? Sod + Zn
S. 111.1

In the last case an immense quantity of hydrogen was generated at the copper plate.

K/PP107/2/4/177
Diagrams, notes and measurements of the electromotive forces of compound cells by Richard William Mellingford Higgs with annotation by Wheatstone, 1872 Feb 6.

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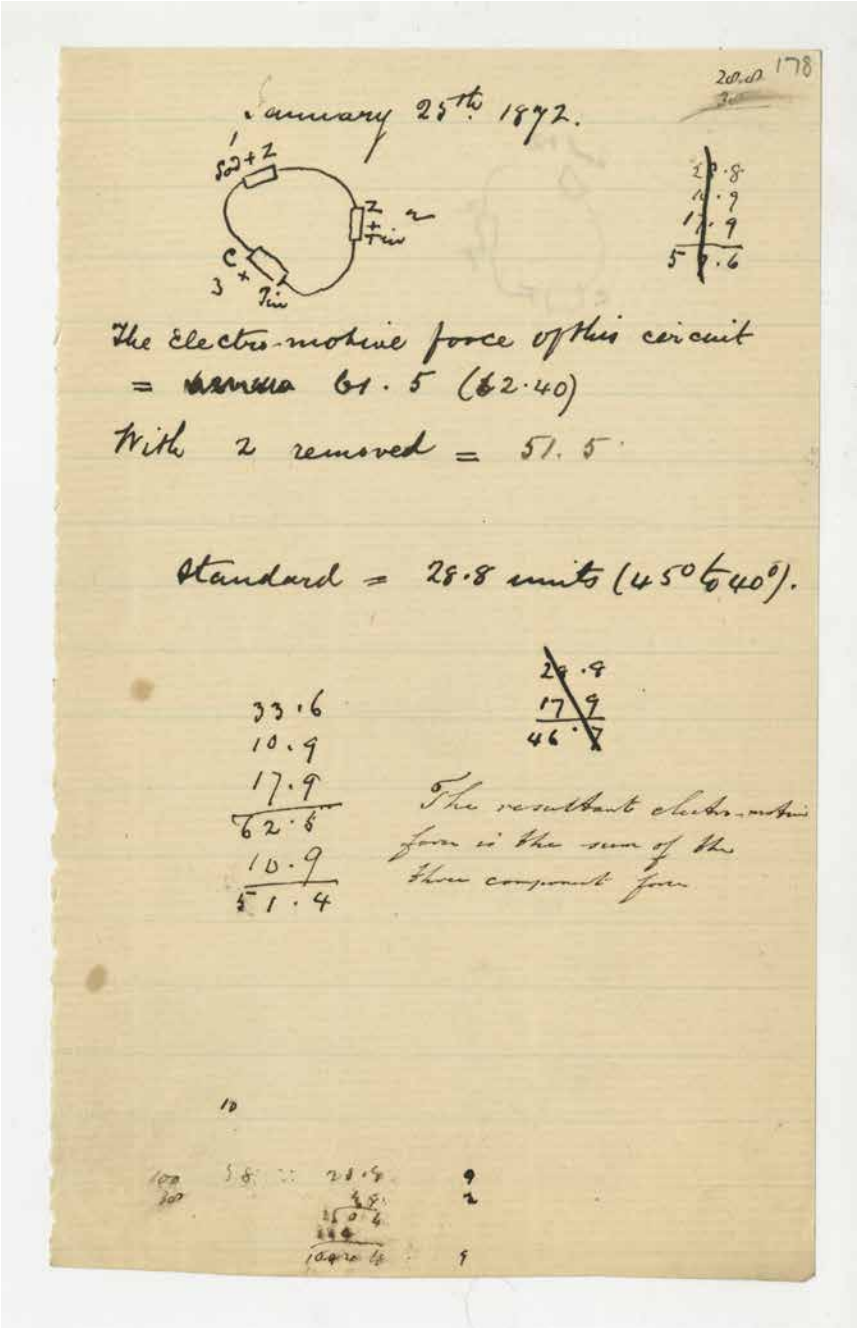
K/PP107/2/4 - Papers relating to the development of the electric telegraph



January 25th 1872.

The Electro-motive force of this circuit = 61.5 (62.40)

With 2 removed = 51.5

Standard = 28.8 units (45° to 40°).

33.6
10.9
17.9
62.6
10.9
51.4

The resultant electro-motive force is the sum of the three component forces

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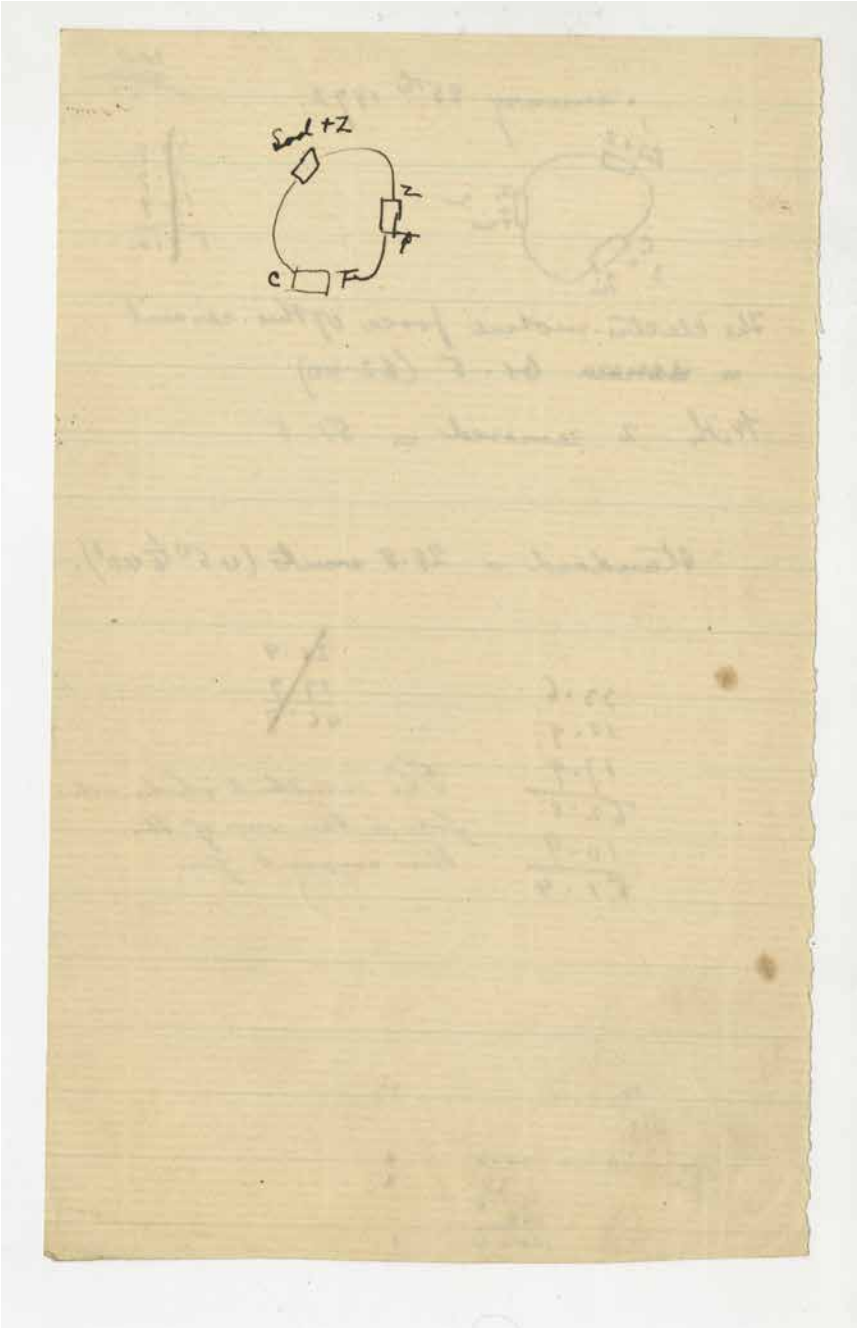

K/PP107/2/4/178
Notes, diagrams and measurements of the electromotive force of compound cells by Richard William Mellingford Higgs with annotations by Wheatstone, 1872 Jan 25, page 2.

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179

(57)

Ex 1. See Paper of Monday.

Ex 2. Standard cell gave 100 turns.

1st With a broken 99
2d With b broken 213
3d With a and b completed 212
} turns.

in 100
25 215.1

The variation in the sodium measure seems to be somewhat due to the deposit of a green salt on the porous cell. This deposit when it once sets in is very rapid, and a cell giving a measure of 216 and 217 turns after 10 minutes only gave 167 and 173. The variation does not appear to be due to the oxidation of the sodium, as by transferring the amalgam to a clean porous cup, the highest electromotive force (viz 217 turns) is obtained. The experiments to-day have been made with an amalgam of the consistency of paste, ie semi-solid; but the electro-motive force I find remains constant (measure 217 turns) with results as well for only 1.5 per cent sodium (This my own experiments). With less I have not tried, as I have not here the means of an accurate lower measure.

My method of measuring the per-centage of sodium is as follows:— I make the amalgam, then select a small quantity, weight it carefully. I then wash it and allow it to stand in water: the difference of weight is the weight of the sodium.

Description of experiments to measure the electromotive force of compound cells, probably by Richard William Mellingford Higgs, [1871-1875].

King's College London Archives

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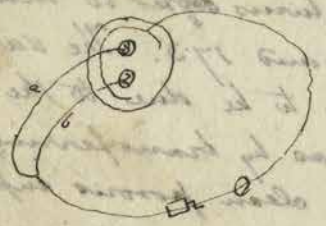
K/PP107/2/4 - Papers relating to the development of the electric telegraph

July 10. 1871

1 Ascertain the E.M.F. of Sodium & Potass (compared with Z) by the 2d method taking care to have the mercury properly charged with sodium.

2 Place two porous pots, one charged with amal of Z, the other with amal of S, in the standard cell with sul of c and C'; thus



Measure the E.M.F. 1st a broken. 2d b broken 3d a & b completed.

3. Measure the E.M.F. of the following:

Amal of Z ... Acetate of Lead – Lead

Do Do Platinum

2 Standard cells + (P – Acet of L[illegible])

Observe the substances deposited at each electrode.

4 Measure the contrary E.M.F. of

1 A cell of P + sul of cop + P

2 P + acet of lead + P

3 C' + sulp of cop + C'

4 L + acet of lead + L

K/PP107/2/4/179

List of experiments to measure the electromotive force of compound cells, 1871 Jul 10.

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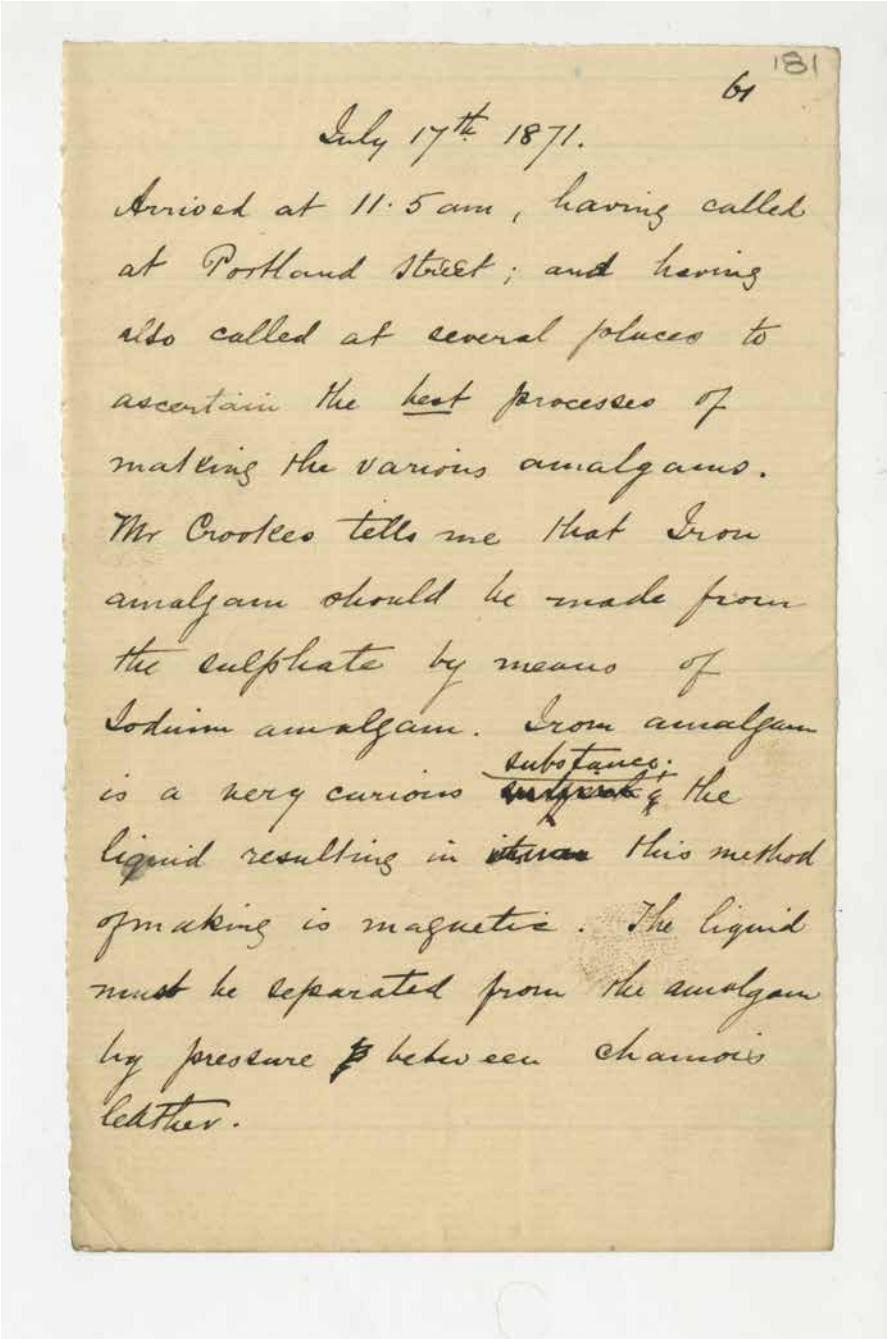

181

July 17th 1871.

Arrived at 11·5 am, having called at Portland Street; and having also called at several places to ascertain the best processes of making the various amalgams. Mr Crookes tells me that Iron amalgam should be made from the sulphate by means of Sodium amalgam. Iron amalgam is a very curious substance; & the liquid resulting in this method of making is magnetic. The liquid must be separated from the amalgam by pressure between chamois leather.

K/PP107/2/4/181

Note by Richard William Mellingford Higgs describing his attempt to ascertain best processes of making various amalgams including from Mr Crooke's [possibly William Crookes (1832-1919), chemist and physicist], 1872 Jul 17.

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186

75.) Lead amal + Chloride of Copper + Copper gives 32, 33, and 33 turns for the three experiments.

The failure of Saturday's experiment it seems is due to the amalgam. I first tried the amalgam made last week, and obtained 20 as my result. I then tested the amalgam, and found large quantities of copper. ~~It was~~ It was made with Guffin's lead, but the copper must have been deposited during the measurement. The above results are to-day obtained with an amalgam of pure lead.

K/PP107/2/4/186

Notes by Richard William Mellingford Higgs relating to the preparation of metals including lead amalgam and chloride of copper, [1871-1872].

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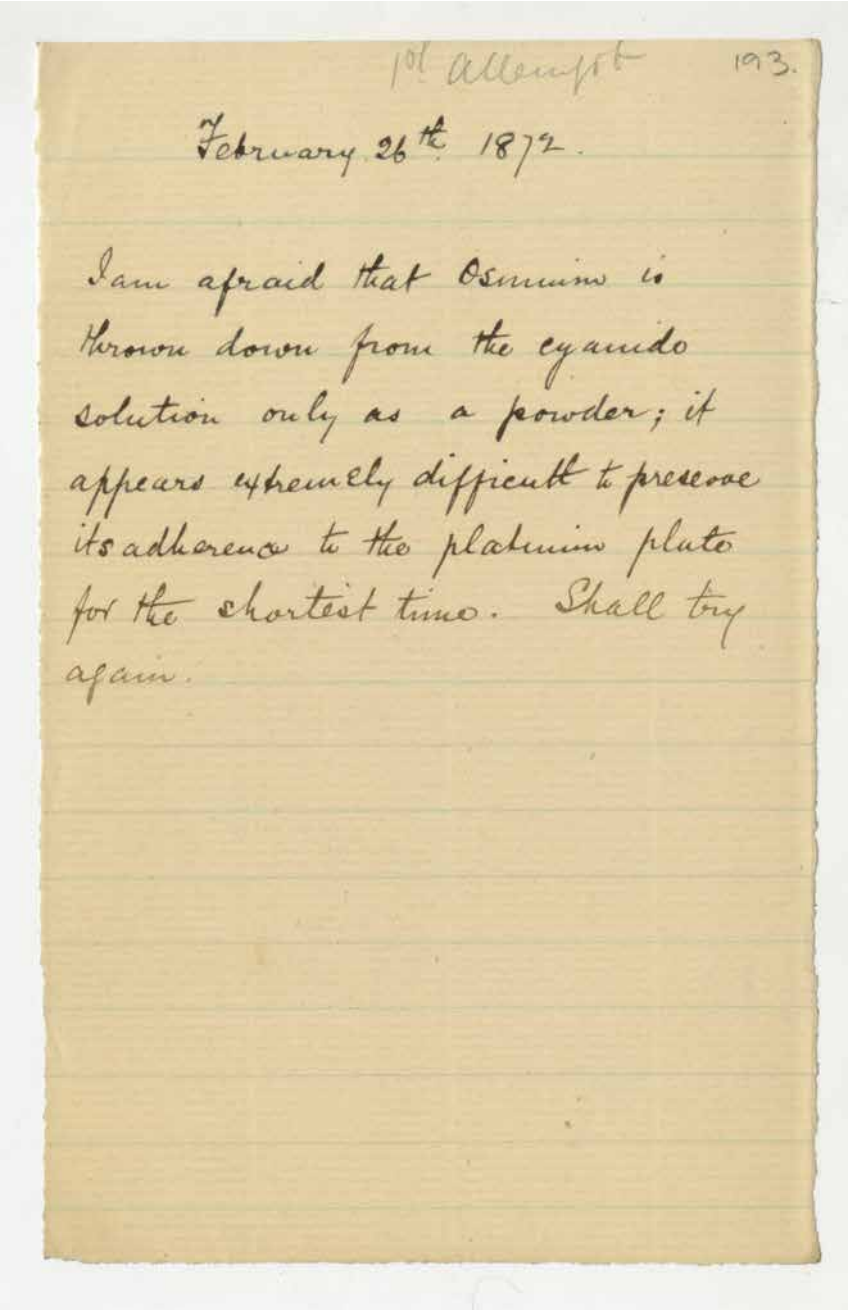

1st attempt 193.

February 26th 1872.

I am afraid that Osmium is thrown down from the cyanide solution only as a powder; it appears extremely difficult to preserve its adherence to the platinum plate for the shortest time. Shall try again.

K/PP107/2/4/193

Note by Richard William Mellingford Higgs outlining the difficulty of preparing osmium cyanide compound, 1872 Feb 26.

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204

February 10th 1872.

Placed in circuit with 4 Smee's cells a decomposing cell of acetate of lead, and allowed it to remain till the solution became perfectly clear. A quantity of lead was found deposited at one electrode = ·38 grms, and peroxide = ·44 grms at the other*. The solution contained acetic acid only.

It wd. be interesting to so prepare a salt (in pure state) as to be able to ~~deduct~~ ascertain the proportion of acid remaining in solution to the acid originally present in the salt.

* Taking O = 8; Pb = 103·5; PbO_2 = 103·5 + 16 = 119·5

119·5 : 103·5 :: ·44 : ·381 +

K/PP107/2/4/204

Description of decomposing cell of lead acetate by Richard William Mellingford Higgs, 1872 Feb 10.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

207

Grove has made the following interesting experiment. A gold wire dipped either in nitric acid or hydrochloric acid separately is unattacked, but if the two liquids communicate with each other, and a gold wire dipped in each and the circuit be completed with a galvanometer, a current is there proceeding from the attacked wire. I will not here reproduce the explanation which he has given in accordance with the chemical theory, but will proceed to some experiments which I think will tend to the true elucidation of the point. But first I will give my theory on the subject.

The wire is unattacked by hydrochloric acid but is so by nitric acid, it however instantly receives a polarization which prevents further action; this polarization is removed by hydrochloric acid, so that a mixture of these two acids act energetically on the wire. When Grove's circuit is arranged we have passive platinum against clean platinum and an e m f is developed which sets up a current from the latter to the former. Now for the experiments:

Platinum if it becomes passive when dipped into nitric acid certainly does not remain so long after being exposed to the air; but if immediately it is removed from the nitric acid and plunged into nitrate

K/PP107/2/4/207

Description of an experiment by William Robert Grove (1811-1896), natural philosopher, [1871-1875], page 1.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

acid forming part of a circuit, an instantaneous current is produced from the to the . If the wire be dipped first in sulphuric acid, and afterwards in ~~the~~ nitric acid in the circuit, no effect is produced. This is a proof of polarization by nitric acid, for if the current were owing to the action of the two liquids on each other, a current should be produced in both cases.

To prove this explanation the following experiment was made. In a ~~cell~~ vessel containing nitric acid a stationary and a rotating plate of platinum were placed. When a circuit was formed and both were stationary, no current was shown because both plates were equally polarized; but when one plate was set in motion a current set out from the ~~stationary to the~~ moving to the stationary plate. In the latter case the polarization on one plate ~~plate~~ was removed, and if the e m f could be measured it would probably be that of platinum and one of its oxides.

K/PP107/2/4/207
Description of an experiment by William Robert Grove (1811-1896), natural philosopher, [1871-1875], page 2.

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K/PP107/2/4 - Papers relating to the development of the electric telegraph

212

Passive Thallium:

February 22nd. 1872.

Standard = 28·8 units (45° to 40°).

a Z + sulphuric acid + passive thallium = 67·4 units (45° to 40°).

S. 232.0

a Sodium + sulphuric acid + passive thallium = 101 units (45° to 40°).

S. 350.6

Evidently from appearance the peroxide.

K/PP107/2/4/212

Notes on passive thallium, by R William Higgs annotated by Wheatstone, 1872 Feb 22.

218

February 22nd 1872.

Platinum undergoes no change when subjected to the action of the battery with nitric acid, or to nitric acid without the battery.

Gmelin and other chemists say that platinum is not oxidised by nitric acid.

The peroxide can be obtained by fusion of the metal with nitre, or with the battery, employing a nitro-hydrochloric acid. The measure of the peroxide has been made.

King's College London Archives

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

February 22nd 1872. (2) 219

with the single cell or with the battery. If with the battery and a solution of normal (undiluted) Chloride of platinum the ~~st~~ current should be too strong, the metal is thrown down in laminæ, but gives, when arranged as a single cell, the full electromotive force = 38.3 units (45° to 40°). S. 132.9

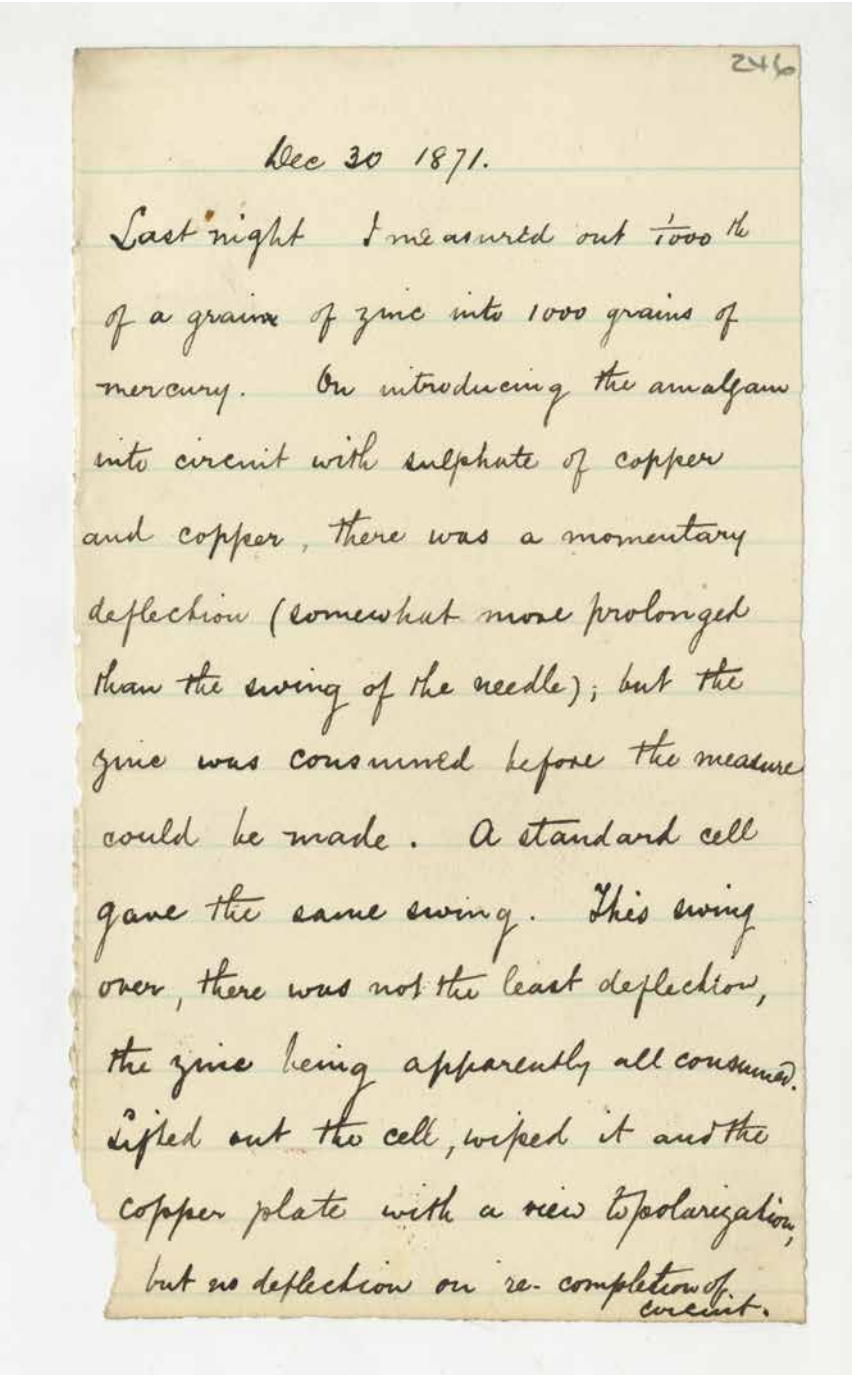
Spongy platinum prepared ~~from~~ by igniting the chloro-platinate of ammonium behaves precisely as platinum black and gives (at + chloride of platinum + spongy platinum) an electro-motive force = 16.8 units (45° to 40°). S. 58.3

K/PP107/2/4/219

Notes by Richard William Mellingford Higgs describing the passivity of platinum, 1872 Feb 22, page 2.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph



246

Dec 30 1871.

Last night I measured out $\frac{1}{1000}$th of a grain of zinc into 1000 grains of mercury. On introducing the amalgam into circuit with sulphate of copper and copper, there was a momentary deflection (somewhat more prolonged than the swing of the needle); but the zinc was consumed before the measure could be made. A standard cell gave the same swing. This swing over, there was not the least deflection, the zinc being apparently all consumed. Lifted out the cell, wiped it and the copper plate with a view to polarization, but no deflection on re-completion of circuit.

K/PP107/2/4/246

Description of experiment using an amalgam of zinc and mercury by Richard William Mellingford Higgs, 1871 Dec 30, page 1.

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K/PP107/2/4 - Papers relating to the development of the electric telegraph

247

Dec 30 1871.

Electromotive force of alloy of lead and zinc in atomic proportions + dilute sulphuric acid + Cu = 60 turns (45° to 40°) (standard = 60 (45° to 40°)). Polarization sets up very quickly. When bubbles of gas appear plentifully at Cu plate, there is considerably diminution of electro-motive force (= 20 turns).

Alloy of Zinc and Lead in equal parts by weight + Sul. Ac. + Cu = 60 turns; and 14 after 2 minutes.

K/PP107/2/4/247

Description of experiment using an amalgam of zinc and mercury by Richard William Mellingford Higgs, 1871 Dec 30, page 2.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

248

Dec 28th 1871.

Last night I weighed out 1000 grains of mercury and tested it. There was no deflection. I then weighed into the mercury 1/100th of a grain of zinc, and allowed the amalgam to stand all night. This morning I measured out the amalgam into two equal portions, carefully ascertaining the electro-motive force of each with Cu + Sulph Cu. Each gave precisely the same electro-motive force as the standard cell – (100 on my coils; 60 between 45° and 40° on the rheostat).

K/PP107/2/4/248

Description of an experiment using alloys and mixed amalgams including mercury and zinc by Richard William Mellingford Higgs, 1871 Dec 28.

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K/PP107/2/4 - Papers relating to the development of the electric telegraph

255

Dec. 26. 1871.

* Standard (45° to 40°)	=	60	turns	100
† Sodium "	=	130	"	216.5
Potassium "	=	117	"	195.0

* The standard measure came out well. † The Sodium measure was taken with amalgam carefully prepared at home and kept in hydrogen till immediately before the measure. I obtained the same measure (or other terms) on my own galvanometer and res: coil. I do not think an experiment could have been made more carefully. The measures made here with the amalgam (kept in H. all night and part of yesterday) and that made at my own place agree perfectly.

Measured (the cup of) a mixed amalgam of Na + K + Zn.

First measure	=	129	turns. (Na)
Second "	=	117	turns (K)
Third "	=	59	turns (Zn)

Towards the end of the experiment cut copper was deposited. I obtained the results by carefully watching the needle; but clearly the Sodium oxidises out more quickly than Potassium.

K/PP107/2/4/255

Notes on measurements of the electromotive force of various amalgams by Richard William Mellingford Higgs, 1871 Dec 26.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

Myrtle Cottage,
Hammersmith, W.
February 5th 1872.

Sir Charles Wheatstone,

Dear Sir,

I hope the enclosed numbers will be of use to you. I find that when acid instead of a salt is employed there is so much polarization that the results are too anomalous to record: thus Zn + Sulphuric Acid + Brass gave readings varying between 2° and 80° – between 0 units and 95°. Your own experiments have shown that an alloy employed as a positive metal gives the electro-motive force of the most positive metal of the alloy.

Very faithfully yours,
Richard Higgs.

Sir Charles Wheatstone,
&c &c.

K/PP107/2/4/260

Letter from Richard William Mellingford Higgs regarding the problems with the results when acid is used instead of salt and a table showing the electromotive force of alloys of several metals, 1872 Feb 5, page 1.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

Electro-motive force of Alloys of Several Metals employed as the negative plate of a Voltaic Element.
Standard = 100

Positive Metal	Salt in Solution	Negative plate. Alloy of	Electro motive force B.A. units (45° to 40°). (a)		(b)
† Zinc.	1. Tri chloride of Gold 2. Chloride of Zinc. 3. Together	Gold and Zinc.	139	—	0
Zinc.	Substituting chloride of Zinc.	Gold and Zinc.	139	—	38
Zinc.	" Salt of Bismuth.	Gold and Bismuth.	139	—	66.7
Zinc.	" Salt of Antimony.	Gold and Antimony.	139	—	93.7
Zinc.	" Salt of Cobalt.	Gold and Cobalt.	139	—	77
† Zinc.	1. Salt of Silver 2. " Zinc 3. Together	Silver and Zinc.	123.5	—	0
Zinc.	Substituting salt of lead.	Silver and Lead.	123.5	—	41.6
Zinc.	" " Tin	Silver and Tin.	123.5	—	38
Zinc	" " Bismuth	Silver and Bismuth	123.5	—	66.7
Zinc	" " Antmy	Silver and Antimony	123.5	—	93.7
† Zinc	1. Sulphate of Copper 2. " Zinc 3. Together	Copper and Zinc.	100	—	0
Zinc.	Substituting salt of Tin	Copper and Tin.	100	—	38
Zinc.	" " Palladium	Copper and Palladium.	133	—	100
Zinc.	" " Bismuth	Copper and Bismuth.	100	—	66.7
Zinc.	1. Chloride of lead. 2. " Antimony. 3. Together	Lead and Antimony.	93.7	—	41.6
		Platinum and Molybdenum.	Not successful.		
Zinc.	No salt yields Ms. well. 1. Nitrate of Palladium 2. " " Bismuth 3. Together.	Palladium and Bismuth	133	—	66.7
		Gold and Lead.	Not successful.		
		Gold and Iridium.	Not successful.		
Zinc.	1. Chloride of Gold 2. Salt of Nickel 3. Together.	Gold and Nickel.	139	—	86.8
Zinc.	1. Chloride of Tin 2. " " Lead 3. Together	Tin and Lead.	41.6	—	38
		Tin and Palladium	Not thrown down well.		
Zinc.	1. Chloride of Tin 2. " " Antimony. 3. Together.	Tin and Antimony.	93.7	—	38
		~~Tin and Zinc~~			
Zinc.	1. Salt of Tin. 2. " Bismuth 3. Together	Tin and Bismuth.	66.7	—	38
† Zinc.	1. Chloride of Zinc 2. Chloride of Antimony 3. Together	Zinc and Antimony.	93.7	—	0
		~~Zinc and Tin~~			
+ Zinc.	1. chloride of Zinc 2. " Tin 3. Together	Zinc and Tin	38	—	0

† There were also tried with Sodium: in every case the increase of electro-motive force was that of Sodium + Zinc.

R. Higgs

In the case of Molybdenum and Iridium the failure was due to an insufficiency of the salt.

K/PP107/2/4/260

Letter from Richard William Mellingford Higgs regarding the problems with the results when acid is used instead of salt and a table showing the electromotive force of alloys of several metals, 1872 Feb 5, page 2.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

260

Remarks.

The galvanometer employed was a small reflecting instrument of some delicacy, shunted so as to give 100 units as the unit introduced to diminish the deflection 5° from 45° with a cell of aZ + Sulphate of Copper + Copper.

The measures were taken on an Elliott's resistance box showing $\frac{1}{100}$ths of ~~an~~ a B. A. units.

The salts were those sold as 'pure', recrystallised or purified according to the methods given in Watt's 'Chemical Dictionary'

The alloys were thrown down on ~~to~~ graphite plates; it having been first ascertained with ~~sig~~ alloys that the electro-motive force was not subject to any alteration consequent upon the use of electrolytically deposited metals instead of metals alloyed by fusion.

Results

It will be seen from the annexed table—

That the electromotive force was that of Zinc + the ~~[illegible]~~ most electronegative metal reduced from the salt. It need scarcely be said that every care was taken with the mixed salts to see that both metals were reduced.

The last column of the table shows the result with the (a) ~~most~~ salt of the ~~most~~ more electro-negative, and (a) with the mixed salts (these giving invariably the same electro-motive force) and (b) with the salt of the more positive metal of the alloy. In cases where as in Gold and Zinc, zinc became opposed to zinc by reduction there was a momentary deflection, or swing of the needle before reduction took place. When the negative salt had reduced out, and reduction ~~[illegible]~~ of the positive metal had commenced, the emf was that of the latter.

Deduction.

It would appear that:—

The electro-motive force depends upon the ~~salts~~ metal reduced from the solution, the number being always that of an element formed simply of the most electro-negative metal and its salt.

The metals employed gave singly the following electromotive forces:—

aZ + Gold = 139.	aZ + Palladium = 133.	aZ + Nickel = 86.8.
aZ + Silver = 123.5.	aZ + Tin = 38.	
aZ + Copper = 100.	aZ + Bismuth = 66.7.	
aZ + Lead = 41.6	aZ + Antimony = 93.7.	
aZ + Platinum = 134.	aZ + Cobalt = 77.	

a Zinc + a Sodium = 33.5.

K/PP107/2/4/260

Letter from Richard William Mellingford Higgs regarding the problems with the results when acid is used instead of salt and a table showing the electromotive force of alloys of several metals, 1872 Feb 5, page 3.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

272 a

March 30th 1872.

Standard = 28.8 units ($\frac{45°}{40°}$).

It wd. appear from the following experiments that a peroxide cannot be reduced to a protoxide, when employed as a positive element:

peroxide of lead + {dilute hydro-chloric acid + teroxide of gold = 54.5 units (45° to 40°). This measure remained constant for nearly an hour, the plates being undisturbed. Suddenly the needle fell to nearly zero, rebounded and when quiet gave 1.5 units (45° to 40). The teroxide of gold was upon a gold, the peroxide of lead upon a platinum plate.

K/PP107/2/4/272

Notes relating to the peroxide of lead by Richard William Mellingford Higgs, 1872 Mar 30.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

February 16. 1872 276

I have not recorded experiments made with a series of elements in comparison with the amount of peroxide deoxidised, because I find it extremely difficult to ascertain the precise moment of the complete disappearance of the peroxide. If I weigh proportionate loss with the peroxide I bring to bear the error consequent upon a second drying of a thin film of peroxide. With the peroxide of platinum and teroxide of gold serious errors would also be introduced from the reduction of the oxides by even a moderate amount of heat. Once drying the deposited peroxide before weighing has no injurious Effect.

K/PP107/2/4/276

Notes by Richard William Mellingford Higgs on experiments using peroxide of platinum and teroxide of gold, 1872 Feb 16.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

277

1.

– Dec.r 11th 72 –

The electromotive force of peroxide of lead & zinc amalgam compared with that of zinc amalgam & copper by old method of reducing deflection from 45 to 40.

zinc amalgam & oxide of lead

0 —— -- 260 + 5.5 = 265.5

0 - - - - - 260 = 260

0 – – - - 205 = 205

The electromotive force then went down rapidly, & on putting a small projecting part of the oxide of lead below the surface, the electromotive force rose, but soon fell as the oxide was expended.

Zinc a_1 + Cu + $CuSO_4$ = 14 - — 133.5 = 119.5

K/PP107/2/4/277

Notes on the electromotive force of peroxide of lead and zinc amalgam by John Rymer Jones (1851-[1919]), chemist and later electrical engineer at the India Rubber Gutta Percha and Telegraph Works (son of Thomas Rymer Jones (1810-1880), Professor at King's College London), 1872 Dec 11, page 1.

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

278

2.

— Decr. 11th 72 —

A fresh plate of platinum covered with oxide of lead was then put up with a porous cell with zinc amalgam, as in the last experiment with the following results.

Zinc amalgam + oxide of lead

0 —— 260 + 13·5 = 273·5

Standard (zinc a + Cu + $CuSO_4$) cell

53 — — — — 173·25 = 120·25

171·5 — — — — 51 = 120·5

2 / 240·75

Turns = 120·37

30 : 68 :: 120·5 : 272

Calculated = 272 } Turns
Experimental = 273·5 }

the oxide

K/PP107/2/4/278

Notes on the electromotive force of peroxide of lead and zinc amalgam by John Rymer Jones (1851-[1919]), chemist and later electrical engineer at the India Rubber Gutta Percha and Telegraph Works (son of Thomas Rymer Jones (1810-1880), Professor at King's College London), 1872 Dec 11, page 2.

King's College London Archives

The Papers of Charles Wheatstone

K/PP107/2/4 - Papers relating to the development of the electric telegraph

288

February 2nd. 1872

a Z + Permanganate of Potash + Platinum
= 76 units (45° to 40°). S. 263.8

Peroxide (MnO_2) of manganese is thrown down of platinum plate. Probably metallic manganese is first reduced and immediately oxidised to teroxide of manganese (Mn_3O_4 or manganic acid). The latter being very unstable is probably immediately reduced to the bi-oxide.

[I advised the use of permanganate of potash as an oxidising agent instead of chromic acid in the chromate battery (in the Journal of the American Technology — 1869-1870), and several American firms made some batteries on this principle. They were found to work well
P.T. over

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K/PP107/2/4 - Papers relating to the development of the electric telegraph

where a succession of contacts were made, but not with a continued or prolonged contact. R.H.]