

March 4, 1880.

THE PRESIDENT in the Chair.

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

In pursuance of the Statutes, the names of Candidates for election into the Society were read, as follows:—

Alderson, Henry James, Col. R.A.	Hannington, John Caulfield,
Allbutt, Thomas Clifford, M.A.,	Major-General.
M.D., F.L.S.	Heaton, John Deakin, M.D.,
Attfeld, Prof. John, Ph.D., F.C.S.	F.R.C.P.
Ayrton, Prof. William Edward.	Hughes, Prof. David Edward.
Blanford, Henry Francis, F.G.S.	Jeffery, Henry M., M.A.
Bristowe, John Syer, M.D.,	Kempe, Alfred Bray, B.A.
F.R.C.P.	Lee, John Edward, F.S.A.,
Christie, William Henry Mahoney,	F.G.S.
M.A., Sec. R.A.S.	Liversidge, Prof. Archibald,
Creak, Ettrick William, Staff	F.G.S., F.C.S., F.L.S.
Commander R.N.	M'Coy, Prof. Frederick, F.G.S.
Creighton, Charles, M.D.	McLeod, Prof. Herbert, F.I.C.,
Dallas, William Sweetland,	F.C.S.
F.L.S.	Miller, Francis Bowyer, F.C.S.
Dallinger, Rev. William Henry.	Moulton, J. Fletcher, M.A.
Day, Francis.	Niven, Prof. Charles, M.A.,
Dobson, George Edward, M.A.,	F.R.A.S.
M.B., F.L.S.	Palgrave, Robert Henry Inglis,
Douglass, James Nicholas,	F.S.S.
M.I.C.E.	Phillips, John Arthur.
Dyer, William Turner Thiselton,	Preece, William Henry, C.E.
M.A., F.L.S.	Priestley, Prof. William Overend,
Godman, Frederic Du Cane,	M.D., F.R.C.P.
F.L.S., F.G.S., M.E.S.	Rae, John, LL.D.
Godwin-Austen, Henry Haver-	Ranyard, Arthur Cowper,
sham, Lieut.-Col.	F.R.A.S.
Goodeve, Prof. Thomas Minchin,	Rawlinson, Robert, C.B., M.I.C.E.
M.A.	Reinold, Prof. Arnold William,
Grantham, Richard Boxall, F.G.S.,	M.A.
M.I.C.E.	Rennie, George Banks, C.E.
Graves, The Right Rev. Charles,	Reynolds, Prof. J. Emerson,
Bishop of Limerick.	M.D.

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Spiller, John, F.C.S.

Thudichum, John Louis William,  
M.D., F.R.C.P.

Tilden, William A., D.Sc.

Tribe, Alfred, F.C.S.

Walsingham, Thomas, Lord.

Ward, James Clifton, F.G.S.

Watson, Rev. Henry William, M.A.

Wilson, Sir Samuel.

Wright, Charles R. Alder, D.Sc.

Wright, Edward Perceval, M.A.,  
M.D., F.L.S.

The following Papers were read:—

- I. "Fired Gunpowder. Note on the Existence of Potassium Hyposulphite in the Solid Residue of Fired Gunpowder."  
By Captain NOBLE (late R.A.), F.R.S., &c., and F. A. ABEL,  
C.B., F.R.S., V.P.C.S. Received February 24, 1880.

In our second memoir on fired gunpowder we have discussed in detail that part of M. Berthelot's friendly criticism of our first memoir which relates to the potassium hyposulphite found by us, in variable proportions, in our analyses of the solid products obtained by the explosion of gunpowder in the manner described. While pointing out that we had taken every precaution in our power to guard against the production of hyposulphite, by atmospheric action upon the potassium sulphide, during the removal of the hard masses of solid products from the explosion vessel, and had effectually excluded air from them, when once they were removed until they were submitted to analysis, we admitted the impossibility of guarding against the accidental formation of some hyposulphite during the process of removal, especially in some instances in which the structure of the residue had certainly been favourable to atmospheric action, and in which a more or less considerable development of heat had afforded indications of the occurrence of oxidation.

We contended, however, that the method of analysis, and the precautions adopted by us in carrying it out, precluded the possibility of accidental formation of hyposulphite at this stage of our investigations. With respect to the precautions, we could, and still do, speak with perfect confidence; and we certainly have believed ourselves fully justified in being equally confident with respect to the process adopted by us for the determination of the proportions of sulphide and hyposulphite, inasmuch as we accepted and used in its integrity the method published in 1857 by Bunsen and Schischkoff in their classical memoir on the products of explosion of gunpowder, and adopted since that time by several other investigators who have made the explosion of gunpowder the subject of study, and whose results are referred to in our first memoir.

Imposing implicit confidence in the trustworthiness of this method

of analysis, emanating as it did from one of the highest authorities in experimental research, we considered ourselves fully justified in maintaining that the very considerable variations in the amount of hyposulphite found in different analyses, carried out as nearly as possible under like conditions, and the high proportion of sulphide obtained in several of those analyses, afforded substantial proof that accidental oxidation during the collection and analysis of the residues was not sufficient to account for all but the very small quantities of hyposulphite, which, in M. Berthelot's view, could have pre-existed in the powder residues. Other facts established by the exhaustive series of experiments detailed in our first memoir, were referred to by us in our second memoir in support of the above conclusion (from which we have still no reason whatever to depart). At the same time we described a series of supplementary experiments which had been instituted by us, with a view to obtain, if possible, further decisive evidence as to the probable proportions of hyposulphite and sulphide actually existing in the residues furnished by the explosion of gunpowder in closed vessels.

In the first place, the residues obtained by the explosion of charges of R.L.G. and pebble powders were submitted to special treatment. Portions of each, consisting exclusively of large masses, were very speedily detached and removed from the explosion vessels, and sealed up in bottles freed from oxygen, having been exposed to the air only for a few seconds. Other portions of the same residues were very finely ground and exposed to the air for 48 hours. As was stated in our recent memoir, the portions of the residues treated in the last-named manner contained very large proportions of hyposulphite (although in one of them there still remained about 3 per cent. of sulphide) while those portions which had been for only a brief period exposed to air (and which presented but small surfaces) were found to contain from 5 to 8·5 per cent. of hyposulphite. As, throughout our entire series of previous experiments, no accidental circumstances had occurred which even distantly approached the special conditions favourable to the oxidation of the sulphide presented in these particular experiments, we considered ourselves fully justified in concluding that the non-discovery of any sulphides in the analyses of residues furnished by the fine grain powder in three out of the whole series of experiments, was not due to accident in the manipulations; and that in those instances, in our several series of experiments, in which large quantities of hyposulphite were found, the greater proportion of that substance must have existed before the removal of the residues from the explosion vessel.

Not suffering the question to rest there, however, we proceeded, in the second place, to adopt new precautions, in two special experiments, for guarding against the possible formation of hyposulphite in

the removal of the residues from the explosion vessel, and their preparation for analysis.

Distilled water, carefully freed from air by long continued boiling, was syphoned into the vessel when it had cooled after the explosion, and thus no air was ever allowed to come into contact with the solid products. When the vessel was quite filled with water it was closed, and, after having been left at rest for a sufficient time to allow the residue to dissolve completely, the solution was rapidly transferred to bottles which had been freed from oxygen. These, when completely filled with the liquid, were hermetically sealed until the contents were submitted to analysis in accordance with the usual method, when they furnished respectively 4 and 6 per cent. of hyposulphite. These results corresponded closely to others obtained by the analysis of seven residues obtained in experiments with P., R.L.G., and L.G. powders, in which there were no peculiarities assignable as a possible reason why the proportions of hyposulphite should be so much lower, in these cases, than in other experiments carried out with the same powders under as nearly as possible the same conditions.

By the results obtained under the various conditions pointed out in the foregoing, we were forced to the conclusion that the discovery of a small or a larger proportion of hyposulphite by the analysis of the powder residue, obtained as described, is consequent upon some slight variation (apparently not within the operator's control) attending the explosion itself; but that hyposulphite does exist, though generally not to anything like the extent we were at first led to believe, as a normal and not unimportant product of the explosion of powder in a closed space.

Some time after the submission of our second memoir to the Royal Society, we received a communication from Professor Debus, which has led us to institute a further series of experiments bearing upon this question of the existence of hyposulphite, and the results we have arrived at have led us so greatly to modify our views on this point, that it is our duty to communicate them without loss of time to the Royal Society.

As introductory to these, it is necessary to repeat the account, given in our first memoir, of the method pursued by us for determining the proportions of potassium monosulphide and hyposulphite in a powder residue.

The solution of the residue, prepared by the several methods already described, was separated by filtration, as rapidly as possible, from the insoluble portion, the liquid being collected in a flask in which it was at once brought into contact with pure ignited copper oxide. The solution and oxide were agitated together, from time to time, in the closed flask, the two being allowed to remain together until the liquid

was perfectly colourless. In a few instances the oxide was added in small quantities at a time, in others the sufficient excess was added at once, with no difference in the result obtained. The only points in which this method differed from that described by Bunsen and Schischkoff in their memoir, was in the employment of a flask well closed with an india-rubber bung for the stoppered cylinder which was employed by them; and in occasionally curtailing somewhat the prescribed period (two days) for which the liquid and the copper oxide were allowed to remain together, the operation being considered complete when the solution had become colourless. Bunsen and Schischkoff prescribed that the liquid when separated by filtration from the mixed copper oxide and sulphide obtained in the foregoing treatment, is to be divided into seven equal volumes, in one of which the amount of hyposulphite may be most simply estimated by acidifying it with acetic acid, and then titrating with a standard iodine solution. This course was adopted by us, and it will therefore be seen that we departed in no essential point whatever from the method of Bunsen and Schischkoff, which we had considered ourselves fully warranted in adopting, without questioning its trustworthiness.

We were informed, however, last July by Dr. Debus, that in submitting potassium polysulphides to treatment with copper oxide, he had found much hyposulphite to be produced, even when air was perfectly excluded, it having been in the first instance ascertained that the several polysulphides experimented with did not contain any trace of hyposulphite. We proceeded at once to confirm the correctness of his observations, by submitting potassium polysulphides to treatment with copper oxide, proceeding exactly according to the method prescribed by Bunsen and Schischkoff for the treatment of powder residues. In one experiment we obtained as much as 87.1 per cent. of potassium hyposulphite (calculated upon 100 parts of potassium monosulphide). Even in an experiment with pure potassium monosulphide, we obtained 11.6 per cent. of hyposulphite upon its treatment for the usual period with copper oxide.

We next proceeded to convince ourselves that by substituting zinc chloride solution for copper oxide, the sulphur existing in solutions of potassium mono- and poly-sulphides might be abstracted, according to the usual method of operation, without producing more than the very small quantities of hyposulphite ascribable to the access of a little air to the sulphides before or during the method of treatment.

Having confirmed the validity of Dr. Debus' objection to Bunsen and Schischkoff's method, and established the trustworthiness of a modification of that method (zinc chloride being substituted for copper oxide), we proceeded to submit to precisely similar treatment with these two reagents portions of solutions obtained by dissolving, with total exclusion of air (in the manner described in our last memoir

and the present note), the residue furnished by special experiments with P., R.L.G., and F.G. powders, exploded under the usual conditions obtaining in our researches, and in quantities ranging from 4,200 to 35,000 grs. (272·2 grms. and 2,268 grms.). The following is a tabulated statement of the results obtained by the two modes of treatment, and of the differences between the proportions of hyposulphite obtained by treatment of portions of one and the same residue with the two different reagents under conditions as nearly alike as possible :—

Table I.

No. of experiment.	Description of powder.	Quantity used.		Density of charge.	Amount of hyposulphite furnished by 100 parts of powder with employment of—		
		Grains.	Grams.		Zinc chloride.	Copper oxide.	Difference.
245	P.	3,396	220·05	0·3	·12	1·93	1·81
241	P.	5,660	366·76	0·5	·07	2·46	2·39
246	R.L.G.	4,200	272·16	0·4	·05	1·43	1·38
244	R.L.G.	5,250	340·19	0·5	·06	1·58	1·52
243	F.G.	4,523	293·41	0·4	·07	1·56	1·49
242	F.G.	6,300	408·23	0·6	·27	2·26	1·99
247	P.	35,000 (5 lb.)	2,267·97	0·23	·78	2·82	2·04

For purposes of comparison, we subjoin a statement of the lowest proportions of hyposulphite furnished by 100 parts of the three powders used in our general series, and also the proportions, similarly expressed, which were obtained in the experiments with sporting and mining powder, the residues of which were dissolved with the same special precautions adopted in the case of the experiments given in Table I.

Table II.

Number of experiment.	Nature of powder.	Amount of hyposulphite in 100 parts of gunpowder used.	Remarks.
7	Pebble.	2·06	{ Lowest proportions furnished by the respective powders.
44	R.L.G.	1·75	
17	F.G.	3·04	
196	Curtis & Harvey No. 6.	2·28	{ Special precautions taken in collecting the residue.
194	Mining powder.	2·77	

In reference to the foregoing numerical statements, we have to offer the following observation :—

1. Substituting zinc chloride for copper oxide as the precipitant of the sulphur which existed in the form of sulphide in solutions of powder residues to which air had not had access at all, until the time of its treatment with the zinc chloride, the amount of hyposulphite existing in solution after such treatment was found to range from 0.05 to 0.78 in 100 parts of gunpowder, while the treatment of portions of the same solutions with copper oxide, in the precise manner adopted in our series of experiments, yielded proportions ranging from 1.38 to 2.39 per 100 of powder used. Comparing the results furnished by the two modes of treatment, it will be seen that in the case of the parallel experiments (245), which exhibited the least considerable difference in the amount of hyposulphite found, that existing after the copper oxide treatment was about sixteen times greater, while in the case of the highest difference (Experiment 241) it was about thirty-four times greater than that found after the treatment with the zinc chloride.

2. It would appear from these results that, in four or five out of seven experiments, no hyposulphite, or at any rate only minute quantities, existed in the residues previous to their solution, and although it would seem to have existed in very appreciable amount in two out of seven residues, the highest proportion found after the zinc chloride treatment was less than one-half the lowest proportion found in our complete series of analyses in which the copper oxide treatment was adopted.

3. A comparison of the results among each other leads, therefore, to the conclusion that potassium hyposulphite cannot be regarded as a normal constituent of powder residue (obtained in experiments such as those carried out by us), and that M. Berthelot is correct in regarding this salt as an accidental product, which, if existing occasionally in appreciable amount in the solid matter previous to its removal from the explosion vessel, is formed under exceptional conditions, and then only in comparatively small proportions.

While submitting this as the conclusion to be drawn from our most recent experiments, we are of opinion that the following points deserve consideration in connexion with the question whether hyposulphite may not, after all, occasionally exist, as the result of a secondary reaction, in comparatively large proportion in the explosion vessel before the residue is removed.

It will be observed that although the copper oxide treatment, when applied to the sulphide in the pure condition (*i.e.*, undiluted with the other potassium compounds found in powder residue), gave rise to the production of very large proportions of hyposulphite, when polysulphides were used, the highest proportion of that substance

found, after the treatment of the particular residues used in the experiments given in Table I, only amounts to 2.82 per cent. upon the gunpowder (pebble powder) employed, which corresponds to about 14.5 per cent. of the average proportion of monosulphide existing in the residue furnished by that powder. In observing this, it must be borne in mind that the sulphide existing in powder residue is always present, in part, and sometimes to a considerable extent, in the form of polysulphide, also, that the experiments with the sulphides were conducted precisely according to the method pursued in the treatment of the powder residues. It would appear, therefore, as though the mixture of the sulphide with a very large proportion of other salts in solution rendered it less prone to oxidation by the copper oxide than when the undiluted sulphide is submitted to its action.

In comparing with the results furnished by the zinc chloride those obtained by the copper oxide treatment, in the special experiments given above, it is observed that, omitting one exceptional result (No. 241) for which we do not attempt to account, the highest proportions of hyposulphite are furnished by those residues which also gave the highest with the zinc chloride, the differences between the results furnished by the two treatments being likewise the highest in these three cases; so also the lowest proportions furnished by the copper oxide treatment, correspond to the lowest obtained with the zinc oxide, and the differences between the results furnished by the two methods are in the same manner the lowest in these. It would almost appear, therefore, as though the existence of a very appreciable proportion of hyposulphite in the solution of the residue had some effect in promoting the production of hyposulphite when the residue is submitted to treatment with copper oxide.

In a recalculation of the results of our analyses of the powder residues upon the assumption that the whole of the hyposulphite obtained existed originally as monosulphide, it is found that, in several instances in which the proportion of hyposulphite was high, the analytical results are much less in accordance with each other than when it is assumed that the hyposulphite found, or at any rate a very large proportion of it, existed as such in the residue before removal from the explosion vessel. Thus, taking the F.G. series, in which the *mean quantity* of hyposulphite actually found is about double of that obtained either from the pebble or R.L.G. powders, selecting from this series the three experiments which gave the highest proportions of hyposulphite, and calculating in the manner described in our first memoir the total quantities both of solid and gaseous products, first from the basis of the analysis of the solid products, secondly from the basis of the analysis of the gaseous products, and further on the assumption that the hyposulphite found existed as hyposulphite

either as a primary or secondary product prior to removal from the explosion vessel, we have as follows:—

Experiment No. 40, F.G. powder. Density '6, hyposulphite found, 18·24 per cent.

	Calculated solid products. grms.		Calculated gaseous products. grms.
From analysis of solid products . . . .	170·268	..	125·220*
From analysis of gaseous products ..	172·509*	..	122·979

Experiment No. 42. F.G. powder. Density '7, hyposulphite found, 18·36 per cent.

	Calculated solid products. grms.		Calculated gaseous products. grms.
From analysis of solid products . . . .	200·191	..	144·547*
From analysis of gaseous products ..	200·220*	..	144·520

Experiment No. 47. F.G. powder. Density '8, hyposulphite found, 19·95 per cent.

	Calculated solid products. grms.		Calculated gaseous products. grms.
From analysis of solid products . . . .	231·652	..	162·335*
From analysis of gaseous products ..	229·392*	..	164·595

Calculating now in the same manner the quantities of solid and gaseous products on the assumption that the hyposulphite found was, prior to removal from the explosion vessel, in the form of mono- or poly-sulphide, we have from the same experiments:—

#### Experiment No. 40.

	Calculated solid products. grms.		Calculated gaseous products. grms.
From analysis of solid products . . . . .	157·273	..	133·842
From analysis of gaseous products ..	168·136	..	122·979

#### Experiment No. 42.

From analysis of solid products . . . . .	185·914	..	155·722
From analysis of gaseous products ..	197·118	..	144·520

#### Experiment No. 47.

From analysis of solid products . . . . .	211·462	..	176·694
From analysis of gaseous products ..	223·561	..	164·595

\* Water included.

Lastly, we still think that the following facts, given in our second memoir, must not be overlooked in considering the question of possible occasional existence of considerable proportions of hyposulphite, viz., that "the production of high proportions of hyposulphite was but little affected by any variations in the circumstances attending the several explosives (*i.e.*, whether the space in which the powder was exploded were great or small), excepting that the amount was high in all three cases when the powder was exploded in the largest space; on the other hand, a great reduction in the size of grain of the gunpowder used appeared to have a great influence upon the production of hyposulphite, as when passing from a very large grain powder (P. or R.L.G.) to a fine grain powder (F.G.). Thus, the production of hyposulphite exceeded 20 per cent. (on the solid residue) in only 3 out of 9 experiments with P. powder, in 3 out of 10, with R.L.G., and in 7 out of 9 with F.G.; while it was below 10 per cent. in 4 out of 9 experiments with P. powder, in 5 out of 10 with R.G.L., and in only 1 out of 9 with F.G. powder." The experiments made with these several powders followed in no particular order, and no circumstance existed in connexion with them to which these great differences in the results obtained could be ascribed.

We append a recalculation of the mean results of our three series of analysis, adding the values of the hyposulphite found, as monosulphide, to the amount of sulphide actually found, and we hope to be allowed to add to our second memoir a similar recalculation of the whole of our analyses.

This recalculation develops (as we pointed out in our second memoir must necessarily be the case) a more or less considerable deficiency of oxygen in the total products of explosion; there is, however, in every instance, also a deficiency of hydrogen, and it may, therefore, be reasonably concluded that the deficiencies in the total quantities of the oxygen and the hydrogen in the powder used, which are unaccounted for in the products found, on the assumption that variable proportions of the total hyposulphite found actually existed in the residues as *sulphide*, are properly accounted for by assuming that the missing quantities of these elements actually existed among the products as water, the amount of which it was obviously impossible to determine.

In conclusion, we have to state that we considered it right, in consequence of the error discovered in the method adopted for the examination for hyposulphite, to repeat the experiments described in our first memoir as having been made by us, with the view of ascertaining whether hyposulphite could exist at temperatures approaching those to which the solid products of explosion were actually subjected in the explosion vessels in our experiments.

To test this point we submitted, for between ten minutes and a

Table III.—Showing the mean composition by weight of the products of combustion of 1 grm. of gunpowder of the undermentioned natures when the whole of the hyposulphite found is supposed originally to have existed in the form of sulphide.

Nature of powder.	Proportions by weight of gaseous products.						Proportions by weight of solid products.										Water.		
	Carbonic anhydride.	Carbonic oxide.	Nitrogen.	Sulphydric acid.	Marsh gas.	Hydrogen.	Oxygen.	Potassium carbonate.	Potassium sulphate.	Potassium monosulphide.	Potassium sulphocyanide.	Potassium nitrate.	Potassium oxide.	Ammonium sesquicarbonate.	Sulphur.	Charcoal.			
Pebble .....	·2685	·0480	·1122	·0111	·0006	·0006	·	·3258	·0710	·1042	·0014	·0013	·	·0005	·0445	·0008	·4409	·5496	·0095
R.L.G. ....	·2630	·0422	·1117	·0109	·0008	·0009	·0002	·3415	·0844	·0787	·0013	·0015	·	·0004	·0495	·0004	·4298	·5593	·0111
F.G. ....	·2689	·0355	·1123	·0101	·0004	·0007	·0003	·2861	·1252	·0999	·0007	·0009	·0056	·0003	·0381	·	·4282	·5569	·0148

quarter of an hour, to the highest heat (about  $1,700^{\circ}$  C.) of a Siemens regenerative furnace, two platinum crucibles, one filled with powder residue, the other with potassium hyposulphite. At the conclusion of the exposure, and while the crucibles were still red hot, they were plunged into water, deprived of air by long-continued boiling, and at once sealed. The powder residue was found still to contain 1.27 per cent. of hyposulphite, while the crucible with the pure salt consisted of a mixture of sulphate and sulphide, but with an amount of 2.1 per cent. of hyposulphite.

It is probable that, if the exposure had been still longer continued, the hyposulphite would have altogether disappeared, and the experiment can only be taken as proving that the hyposulphite, especially if mixed with other salts, is neither quickly nor readily decomposed, even at very high temperatures.

II. "On the Dynamo-Electric Current and on certain Means to Improve its Steadiness." By C. WILLIAM SIEMENS, D.C.L., LL.D., F.R.S. Received March 1, 1880.

(Abstract.)

The author, after alluding to the early conception by Dr. Werner Siemens of the dynamo-electric or accumulative principle of generating currents, makes reference to the two papers on the subject presented, the one by Sir Charles Wheatstone and the other by himself, to the Royal Society in February, 1867. The machine then designed by him, and shown in operation on that occasion, is again brought forward with a view of indicating the progress that has since taken place in the construction of dynamo-electrical machines, particularly those by Gramme and Siemens-von Alteneck. The paper next points out certain drawbacks to the use of these machines, both of them being subject to the disadvantage that an increase of external resistance causes a falling off of the current; and that, on the other hand, the short circuiting of the outer resistance, through contact between the carbon electrodes of an electric lamp, very much increases the electric excitement of the machine, and the power necessary to maintain its motion, giving rise to rapid heating and destructive sparks in the machine itself.

An observation in Sir Charles Wheatstone's paper is referred to, pointing to the fact that a powerful current is set up in the shunt circuit of a dynamo-electric machine, which circumstance has since been taken advantage of to some extent by Mr. Ladd and Mr. Brush, in constructing current generators.

The principal object of the paper is to establish the conditions under