

February 23, 1882.

THE PRESIDENT in the Chair.

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

THE BAKERIAN LECTURE on the "Chemical Theory of Gunpowder," was delivered by Professor H. DEBUS, Ph.D., F.R.S. Received February 8, 1882.

The following is an Abstract:—

1. Dr. Jebb* mentions a manuscript as existing at Oxford, entitled "Liber ignium ad comburendos hostes," by Marcus Græcus, probably written in the eighth century, wherein the preparation of gunpowder is accurately described, and Bellani reports that the English used cannon at the Battle of Crecy. Gunpowder, therefore, has been known more than a thousand years, and its use for the purposes of war more than five hundred, nevertheless, no chemical theory of the combustion of gunpowder has hitherto been proposed which will enable us to calculate the quantity of each of the chief products of combustion from the known composition of a given weight of powder, or the amount of heat generated during its metamorphosis. A theory which can solve these problems I have the honour to submit in the present paper to the Royal Society.

2. The constituents of gunpowder—saltpetre, charcoal, and sulphur—are transformed during combustion into the following products:—Potassic carbonate, potassic sulphate, potassic disulphide, potassic sulphocyanate, carbonic acid, carbonic oxide, nitrogen, sulphuretted hydrogen, marsh-gas, ammonia, hydrogen, and water.

The hydrogen compounds—sulphuretted hydrogen, ammonia, and marsh-gas, the free hydrogen and potassic sulphocyanate—do not, as a rule, amount together to more than about two per cent. of the weight of the powder from which they have been produced; and as their formation is not the direct result of the reactions which cause the explosion of the powder, they are regarded as secondary products and not considered in a discussion of the chemical metamorphosis of gunpowder.

Besides the potassium salts mentioned, potassic hyposulphite has been found as one of the constituents of the solid residue left by powder after its explosion. According to experiments by the author, which have been confirmed by Noble and Abel, this salt is formed in considerable quantities from potassic sulphide during the analysis of

* Poggenдорff, "Geschichte der Physik," 87.

the residues according to Bunsen and Schischkoff's method; and as it is decomposed at 225° C., it cannot be considered as one of the chief products of the combustion of gunpowder.

3. With regard to the products, potassic carbonate, potassic sulphate, potassic disulphide, carbonic acid, carbonic oxide, and nitrogen, the following problems have to be solved:—

(a.) To determine the reactions which cause the formation of these substances and the order in which they succeed each other, and to represent the *complete* combustion of gunpowder by one chemical equation.

(b.) To calculate from the known composition of a given weight of powder the volume of gas and the amount of heat generated during its combustion, and to ascertain the relative energies of powders of different composition.

The solution of each of these problems is described in the paper.

4. Noble and Abel* describe the quantitative relations of the products of combustion of a given weight of powder of known composition in the following words:—

“(a.) The proportions in which the several constituents of solid powder residue are formed are quite as much affected by slight accidental variations in the conditions which attend the explosion of one and the same powder in different experiments, as by decided differences in the composition as well as in the size of grain of different powders.

“(b.) The variations in the composition of the products of explosion furnished in close chambers by one and the same powder under different conditions, as regards pressure, and by two powders of similar composition under the same conditions, as regards pressure, are so considerable, that no value whatever can be attached to any attempt to give a general chemical expression to the metamorphosis of gunpowder of normal composition.

“(c.) Any attempt to express, even in a comparatively complicated chemical equation, the nature of the metamorphosis which a gunpowder of average composition may be considered to undergo, when exploded in a confined space, would therefore only be calculated to convey an erroneous impression as to the simplicity or the definite nature of the chemical results and their uniformity under different conditions, while it would, in reality, possess no important bearing upon an elucidation of the theory of explosion of gunpowder.†

“(d.) Very small-grain powder, such as F.G. and R.F.G., furnish decidedly smaller proportions of gaseous products than a large-grain powder, R.L.G.: while the latter again furnishes somewhat smaller proportions than a still larger powder, P, though the difference between the gaseous products of these two powders is comparatively inconsiderable.”

* “Phil. Trans.,” clxv (1875), p. 137.

† *Ibid.*, p. 85.

Noble and Abel exploded successively portions of powder of the same description in their apparatus, and found considerable fluctuations in the relative quantities of the products of explosion in different experiments. These fluctuations they do not explain, but state that "*slight accidental variations in the conditions which attend the explosion,*" have as much influence on the relative quantities of the constituents of the solid powder residue as decided differences in the composition of the different powders. And as the exact nature of these "*slight accidental variations in the conditions which attend the explosion*" is not known, they conclude that the metamorphosis cannot be represented by a chemical equation.

The author of this abstract has described in the paper the causes of the variations in the relative quantities of the products of explosion, and has explained the experimental results of Messrs. Noble and Abel. And further, he has been able, with this knowledge, to represent the chemical metamorphosis of the English Service powders by an equation.

5. Noble and Abel assume that the samples of fine-grain and pebble powders used in their numerous experiments were, respectively, of the same composition, and that the samples of R.L.G. powder employed in their earlier experiments, had the composition given under "I," and those used in the later experiments that given under "II" in the table below.

The composition of the same description of powder is, however, not constant.

I requested the late Mr. Wills to analyse pebble and R.L.G. powders from Waltham Abbey, and the results obtained by him, together with those of Noble and Abel, are given in the following table:—

	R.L.G.			Pebble powder.	
	Noble and Abel.		Wills.	Noble and Abel.	Wills.
	I.	II.			
Saltpetre.....	74·95	74·43	75·10	74·67	74·26
Sulphur	10·27	10·09	8·96	10·07	9·51
Charcoal—					
Carbon	10·86	12·40	12·09	12·12	11·58
Hydrogen.....	0·42	0·40	0·54	0·42	0·51
Oxygen.....	1·99	1·27	2·12	1·45	2·55
Ash.....	0·25	0·21	0·20	0·23	0·33
Water.....	1·11	1·05	0·85	0·95	0·76

The samples analysed by Noble and Abel were taken out of the

same barrel, the one from the upper, the other from the lower parts. These two samples showed a difference of no less than 1.54 per cent. of the weight of the powder in the amount of carbon they contain, or the weight of carbon is by one-seventh greater in the second than in the first sample. Mr. Wills found 1.31 per cent. of sulphur less than Noble and Abel in the same description of powder. Such differences in the composition of samples of powder of the same nature, together with the usual errors attaching to complicated and difficult analytical operations, are almost sufficient to explain the variations in the proportions of the products of the combustion of gunpowder, as found by Messrs. Noble and Abel, without requiring a theory like the one proposed by M. Berthelot for that purpose.

6. Noble and Abel analysed the products of explosion by means of Bunsen and Schischkoff's method. The author has proved that by the treatment of the solid powder residue according to this method a portion of the potassic sulphide is converted into potassic hyposulphite, and under certain conditions into potassic sulphate. The quantities of the two salts so produced vary in different experiments. Hence, the fluctuations observed by Noble and Abel in the relative quantities of potassic sulphide, potassic sulphate, and potassic hyposulphite are partly, if not entirely, due to the method of analysis. Potassic hyposulphite is decomposed at temperatures above 225° ; from this fact, as well as from a comparison of the oxygen in the original powder with that of the products of explosion, it follows that the potassic hyposulphite found in powder residues must be regarded as the product of the analytical method.

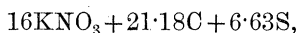
7. It is well known that the higher sulphides of potassium attack metals with great energy at a white heat. Noble and Abel exploded their powders in a hermetically closed steel cylinder at high pressures, and the products remained after explosion from one to two minutes in a fluid condition at a white heat in contact with the iron of the apparatus. These products contain potassic disulphide. The description given by Noble and Abel of their solid powder residues indicates that they contain ferrous sulphide. The absorption of a portion of the sulphur by the iron will increase the amount of potassic carbonate and diminish the quantities of potassic sulphate and disulphide. The quantity of sulphur so uniting with iron depends on pressure, time of cooling, and other conditions, and will vary in different experiments. We have then in the formation of ferrous sulphide another cause of the fluctuation in the quantities of the products of explosion observed by Messrs. Noble and Abel.

8. It follows from the statements given under Nos. 5, 6, and 7, that there is no reason to assume that the chemical metamorphosis of gunpowder cannot be represented by an equation.

9. Noble and Abel calculate the total weight of the solid residue,

which a given weight of powder can produce by its explosion, from the composition of a *portion* of the residue and the composition of the powder. They assume that the portions of powder of the same description used in different experiments, were of the same composition. This is, according to the statements under No. 5, not the case. The calculated quantities of gas and solid residue which a given weight of powder can produce, will, in consequence, be affected by certain errors. These errors compensate each other if the mean of many experiments is taken.

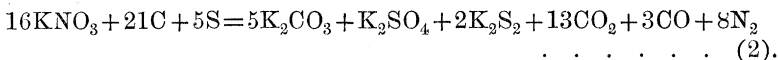
10. Portions of powder taken from different parts of the same barrel show, according to Noble and Abel's analyses, greater differences in their composition than samples of different descriptions manufactured at Waltham Abbey, pebble, rifle fine-grain, rifle large-grain, and fine-grain powder; hence, we are justified in taking the mean of the analyses of these powders, and expressing thereby the composition of the English Service powder. The mean of the analyses of Noble and Abel, and Wills, can be represented by the symbols—



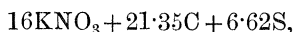
if hydrogen, oxygen, and ash of the charcoal, and the hygroscopic moisture of the powder are neglected.

11. From evidence described in the paper it follows, with a high degree of probability, that during the combustion of gunpowder potassic disulphide, and not monosulphide, as is usually assumed, is formed.

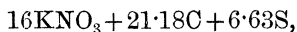
12. If the errors arising from the analytical method are corrected as explained in the paper, if allowance is made for the sulphur which has united with the iron of the apparatus, and, finally, if, for the reasons adduced under No. 9, the mean is taken of the thirty-one analyses published by Noble and Abel, then the explosion of the powders of Waltham Abbey, as conducted by Noble and Abel in a confined space, can be represented very nearly, if not quite accurately, by the following equation:—



1·63 atoms of the sulphur contained in the powder have united partly with hydrogen and formed sulphuretted hydrogen, partly with iron and produced ferrous sulphide. The entire amount of the oxygen contained in the charcoal is eliminated with hydrogen as water, the rest of the hydrogen either remains free or produces methane with carbon and ammonia with nitrogen. The composition of the powder, calculated from the mean composition of the products of explosion of thirty-one experiments, can be represented by the symbols



which are almost identical with



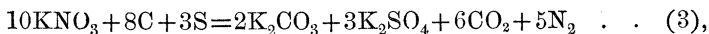
representing the mean composition of the powders found by direct analysis.

13. An increase of pressure during combustion appears to diminish the amount of carbonic oxide, and, in consequence, according to equation 8, to increase the quantities of potassic carbonate, potassic disulphide, and carbonic acid. These fluctuations in the quantities of the products of combustion are, however, *very small*, and may be neglected without serious error.

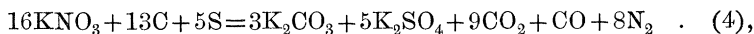
14. Craig had asserted that the nature of the products of explosion of gunpowder depended on the pressure developed during combustion. Karolyi, in order to test this assertion, made experiments with Austrian Service powder, and arrived at the conclusion that pressure had no influence on the quality or quantity of the products furnished by these powders.

The experimental results of Karolyi, and the differences between these results and those obtained by Noble and Abel, have enabled the author to develop a chemical theory of gunpowder competent to explain the observations of Bunsen and Schischkoff, Linck, Karolyi, Noble, and Abel, and other investigators, and which is in harmony with the thermochemical relations of the reacting substances.

According to this theory the combustion of gunpowder takes place in two stages, one succeeding the other. The reactions of the first stage cause the explosion of the powder. *Gunpowders which differ considerably in their composition* are transformed during the first stage according to the equation



but as it is probable that at the same time some carbonic oxide is produced, the following would more correctly represent the reactions:—



The constituents of the powder, and those of the products of combustion are, according to equation 4, nearly in the same ratios as they are according to 3.

During the first stage of the combustion potassic disulphide is not formed.

The oxygen of the potassic carbonate, potassic sulphate, and the carbonic acid, as represented by equation 3, stand to each other in the most simple possible ratios, if these substances are to be produced by the combustion of a mixture of saltpetre, carbon, and sulphur. In other words, equation 3 represents the most simple distribution of the oxygen of the decomposed saltpetre amongst the products of combus-

tion produced during the first stage. And because these products are, according to equation 4, nearly in the same relative proportions as they are according to 3, it follows that the distribution of the oxygen of the saltpetre between potassic sulphate, potassic carbonate, and carbonic acid, as required by equation 4, corresponds nearly to the most simple ratios which can exist under the conditions of the experiments.

The oxygen of the potassic carbonate stands to the oxygen of the potassic sulphate and of the carbonic acid, according to equation 3, as

$$1 : 2 : 2.$$

If a mixture of saltpetre, carbon, and sulphur shall produce, by its combustion, the greatest possible amount of heat, and if at the same time the products—potassic sulphate, potassic carbonate, and carbonic acid—shall be formed in such proportions that the heat of formation of one shall stand to the heat produced by each of the other two in the most simple ratio possible, then the combustion must take place according to equation 4.

The heat developed by the formation of potassic carbonate stands to that furnished by potassic sulphate and carbonic acid respectively as

$$1 : 2.05,$$

and

$$1 : 1.04.$$

if the powder is transformed according to equation 4.

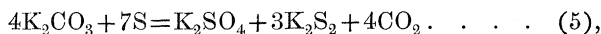
The relations between the quantities of oxygen in the chief products of combustion and those of the heat produced by their formation are, from a theoretical point of view, of the greatest interest.

15. Gunpowder, as a rule, contains more carbon and sulphur than is required by equations 3 and 4.

The carbon left free at the end of the first stage of the combustion now acts on the potassic sulphate, formed during this stage, according to the equation



and the free sulphur upon potassic carbonate according to



and some of the free carbon reduces carbonic acid to oxide.

These reactions constitute the second stage of the combustion of gunpowder; they are endothermic, heat is not evolved but is rendered latent; they are not of an explosive nature, and, in practice, are probably seldom complete. During the second stage of the combustion the temperature of the products of explosion is diminished and the volume of the gas is increased.

16. The quantitative relations between the constituents of gunpowder and the chief products of combustion at the end of the second stage can be expressed by one equation.

If x , y , and z be positive numbers and a represents how many molecules of carbonic oxide are formed by the complete combustion of a weight of powder containing x molecules of saltpetre, y atoms of carbon, and z atoms of sulphur, we have

$$\begin{aligned} x\text{KNO}_3 + y\text{C} + z\text{S} = & \frac{1}{28}[4x + 8y - 16z - 4a](\text{K}_2\text{CO}_3) \\ & + \frac{1}{28}[20x - 16y + 4z + 8a](\text{K}_2\text{SO}_4) \\ & + \frac{1}{28}[-10x + 8y + 12z - 4a](\text{K}_2\text{S}_2) \\ & + \frac{1}{28}[-4x + 20y + 16z - 24a](\text{CO}_2) \\ & + a\text{CO} \\ & + \frac{1}{2}x\text{N}_2. \quad \dots \dots \dots (8), \end{aligned}$$

as the general equation of the complete combustion of gunpowder.

By means of this equation the chief products of combustion—potassic carbonate, potassic sulphate, potassic disulphide, and carbonic acid—can be calculated from that portion of a given weight of powder which transforms itself into these products.

The correctness of the equation is proved by the agreement of the calculated numbers with those observed by Bunsen and Schischkoff, Linck, and Karolyi in their experiments on the explosion of gunpowder, and also with the corrected mean numbers derived from Noble and Abel's investigation.

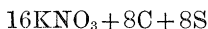
17. The total volume of gas developed by the combustion of a given weight of powder, if calculated according to equation (8), is not affected to more than from one to two per cent. if we put $a=0$, and in doing so we gain a considerable simplification of the equation. If V represents the volume of gas evolved by the combustion of a quantity of powder containing 16 molecules of saltpetre, y atoms of carbon, and z atoms of sulphur, and W the units of heat developed by the same weight of powder, we have, on the assumption that $a=0$,

$$V = \frac{160 + 20y + 16z}{14} \dots \dots \dots (9),$$

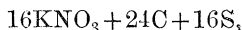
$$W = 1000[1827 \cdot 154 - 16 \cdot 925y - 8 \cdot 788z] \dots \dots (10).$$

The volume of gas becomes *greater*, and the amount of heat *diminishes*, when y and z are increased, and *vice versâ*.

Quantities of saltpetre, carbon, and sulphur represented by the symbols



produce the greatest amount of heat and smallest amount of gas, and such as correspond to—



the largest volume of gas and the smallest quantity of heat, if the mixtures are considered which can transform themselves during combustion according to equation (8), in which a is put $=0$.

(8.) The product of (9) and (10) divided by 2×1000 ,

$$\frac{V \times W}{2000} = 10440.88 - 12.09y^2 + 1208.39y - 15.95yz + 993.867z - 5.022z^2 \\ = E \quad \dots \quad (11),$$

will assume different values for powders of different composition. The energy of a mixture of saltpetre, carbon, and sulphur will be, *cæteris paribus*, proportional to the volume of gas, and also to the amount of heat produced during its combustion. Hence, the product of the two, E , may be used, according to the proposal of M. Berthelot, as a measure of the relative energies of powders of different composition.

(9.) If in equation (8) x is put $=16$, and $a=0$, we obtain :

$$16(\text{KNO}_3) + y\text{C} + z\text{S} = \frac{1}{2.8}[64 + 8y - 16z](\text{K}_2\text{CO}_3) \\ + \frac{1}{2.8}[320 - 16y + 4z](\text{K}_2\text{SO}_4) \\ + \frac{1}{2.8}[-160 + 8y + 12z](\text{K}_2\text{S}_2) \\ + \frac{1}{2.8}[-64 + 20y + 16z](\text{CO}_2) \\ + 8\text{N}_2 \quad \dots \quad (13),$$

and from this, if the coefficients of the potassic carbonate, potassic sulphate, and potassic disulphide are put $=0$, the equations :

$$64 + 8y - 16z = 0 \quad \dots \quad (14),$$

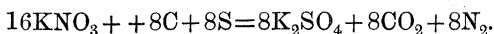
$$320 - 16y + 4z = 0 \quad \dots \quad (15),$$

$$-160 + 8y + 12z = 0 \quad \dots \quad (16).$$

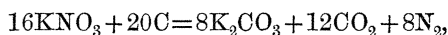
These equations represent in a plane three sides of a triangle. The co-ordinates of points within this triangle represent quantities of carbon and sulphur, which can, with 16 molecules of saltpetre transform themselves according to equation (13), whereas the co-ordinates of points outside this triangle indicate mixtures which cannot do so, such mixtures containing either too much or too little of carbon or sulphur.

The co-ordinates of points on the sides of the triangle represent mixtures which will burn with the production of two, and those of the points of intersection of two sides with formation of only one potassium salt.

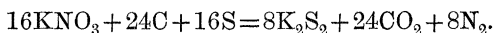
The two sides represented by equations (14) and (16) intersect in point $y=8$, and $z=8$. These values introduced into (13) give :



In the same manner we obtain for the point of intersection corresponding to equations (15) and (16):



and finally, the sides whose equations are (14) and (15), intersect in point $y=24$ and $z=16$, hence

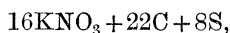


The geometrical construction of the co-efficients of equation (13) possesses the great advantage of indicating by the co-ordinates of the points of a triangle the composition of the infinite number of mixtures of saltpetre, carbon, and sulphur which can transform themselves during combustion according to equation (13), and enables us to deduce *geometrically*, as is shown in the paper, the qualitative nature and the quantitative relations of the products of combustion, as well as the volume of gas and the amount of heat developed by each mixture.

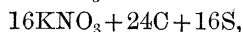
(20.) It is proved in the paper that the composition of a powder which can transform itself during combustion according to equation (13), and for which E in equation (11) shall be a maximum, is indicated by the co-ordinates of the point of intersection of the sides of the triangle represented by the equations (14) and (15).

If, therefore, such quantities of powders of different composition are compared, which contain 16 molecules of saltpetre, the one composed of $16\text{KNO}_3 + 24\text{C} + 16\text{S}$ will possess the greatest energy.

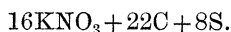
(21.) If E is calculated for *equal weights* of two powders of different composition, the difference of the values of E is found to be *very small*, if the powders contain from 21 to 24 atoms of carbon, and from 8 to 16 atoms of sulphur for every 16 molecules of saltpetre. Equal weights of the two mixtures



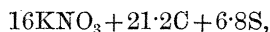
and



give for E [equation (11)] the values 16.84 and 16.95 respectively. If, therefore, a mixture of saltpetre, carbon, and sulphur is required, which shall possess the greatest or nearly the greatest amount of energy, and at the same time contain the smallest amount of carbon and sulphur compatible with this condition, theory would point to the mixture



The gunpowders of most nations fluctuate about



which numbers are very near those required by theory.