

SULFUR IN HISTORY: THE ROLE OF SULFUR IN "BLACK POWDER"

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ABSTRACT

After a short outline of the history of black powder the subject of this article is a discussion of the concerted mechanism of the reactions in exploding gunpowder. Evidently, the first step of the powder reaction is the reduction of potassium nitrate to nitrite by charcoal and/or hydrogen sulfide, which originates from the reaction of sulfur with the minor hydrogen content of charcoal. Sulfur is then inserted into the nitrite to yield potassium thionitrate, KSN_2 . The latter causes a rapid ignition of the charcoal/nitrate mixture through its strongly exothermic decomposition into thiosulfate and dinitrogen oxide, which is totally consumed by its explosive reaction with carbon monoxide to yield nitrogen and carbon dioxide.

1 GUNPOWDER - A CHINESE INVENTION ?

Probably no other event in the history of mankind has influenced the rise and fall of cultures and also the destiny of individuals more than the invention of gun powder and the introduction of firearms. Apparently, gun weapons, i.e., cannons, were first employed in Europe nine years after the beginning of the Hundred Years' War on August 25th, 1346 in the battle of Crecy-en-Ponthieu near Abbeville on the Channel coast. Edward II with 20 000 English soldiers fought this battle against a superiority of 60 000 French soldiers under Philippe VI. The effect of the cannons and the superior strategy of the English must have been devastating: the number of French nobles and commons killed was greater than the number of Englishmen who fought at all.

For 500 years until the last century the efficient explosive of the firearms, "black powder", consisted of a mixture of 75 % saltpetre, 15 % charcoal

powder and 10 % sulfur. Who the technical advisors and the engineers of Edward II were, and where and from whom his cannons were built has not been recorded. In a copy dating from 1393 of a document from 1313 of the city of Ghent there exists a marginal note which states "Item in this year the "Bussen" (i.e. the cannons) were invented in Germany". A powder inventor Berthold Schwarz may not have existed at all. But if this name was not invented later on, then the references must have dealt with one of the first gun manufacturers.

It is certain that the fuel for the cannon balls used by Edward II was invented much earlier, probably in ancient China. Even at the beginning of our chronology, in the Han Dynasty, which lasted from 25 to 250 A.D., the Chinese had already the Shen-nung pents'ao-ching, an encyclopedia of natural sciences. In addition to rock salt, sodium sulfate, cinnabar and other mineral, vegetable and animal substances, saltpetre and sulfur are also mentioned there. Naturally occurring saltpetre, Siao si, was found in the northern provinces of China. The deposits were exploited by the State through convicts under the supervision of "saltpetre people", or private concerns received mining rights. Merchants who wanted to trade in saltpetre required a licence. In connection with the technical application of fire, particularly through metallurgy, the Chinese acquired at an early stage the knowledge of charcoal, Mu tan. This product was already produced in charcoal-kilns. In a similar way also the third component of gunpowder, namely sulfur, Lin huang, could be obtained. Sulfur was, likewise, known in China a long time before the production of the powder and was employed especially for medical purposes, e.g., the cure of ulcers and gall-bladder diseases as well as for the pest control in the cultivation of bamboos.

What idea could have induced a for ever unknown Chinese alchemist to produce mixtures of saltpetre, charcoal and sulfur and ignite them? The matter in question probably dealt with the termination of a long series of tests concerning inflammable materials. It was perhaps also a theoretical aspect which could have stimulated him to do such an experiment. An indication supporting this point can be drawn from the Chinese philosophy and natural science, the Tao. The Chinese philosophy, particularly in the Chin and Han era, was dominated by the ancient antagonistic cosmic principles of Yang and Yin. Yang and Yin signify the first two primordial forces of the universe. Yang is the male constructive power, the brightness. Yin is female, the power of the darkness and coldness. Just as Yang and Yin control the sky, the earth and human beings, in the same way they govern natural substances and are the driving forces for chemical reactions. Thus, saltpetre was assigned to the Yang Principle, coal and sulfur to the Yin Principle. According to Sung Ying-Hsing, the interaction between Yang and Yin was responsible for the explosive power of gunpowder. Even today, the Yang and Yin Principles play a role in the chemistry of China: The cation

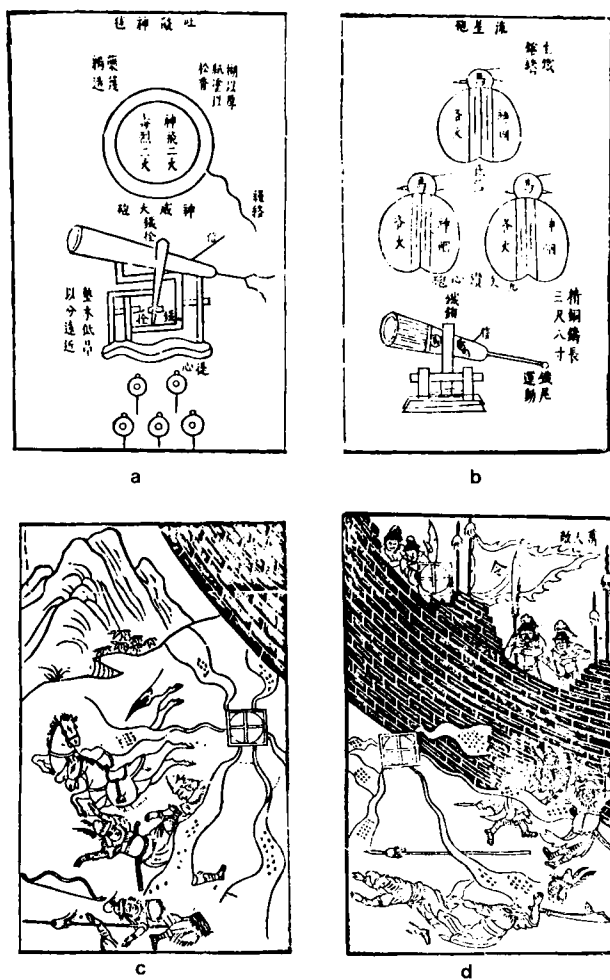


Fig. 1. War machines in Old China.

is called the Yin ion and the anion the Yang ion.

For centuries, the Chinese used black powder for peaceful purposes only: firework displays. Even today, this black powder is the fuel still used for fireworks let off on New Year's Eve. During the Sung Period (960 - 1279) the Chinese succeeded in inventing the "burning arrow" and the rocket. The military use of black powder was recognized comparatively late, namely during the Tang Period in the year 1161 by a war mandarin, Yu-yen-wen. The aim was, at first, only to deter the enemy. A more recent encyclopedia of natural science written

by Lo Tschen-gu around the beginning of the 15th century and bearing the title Tien-kung kai-wu, however, contains also illustrations of war machines. For their cannons, the Chinese used inflammable balls consisting of wool felt, paper and resin (Fig. 1a), bundled arrows (Fig. 1b), stone balls and also grenades producing fog or poisonous gas. Grenades containing explosives were not used but boxes filled with powder were thrown from embankments and were termed Wan shen di (thousand enemy killer) (Fig. 1c, 1d). In an ancient manuscript in the possession of a library in Oxford and dating from the year 1327, an illustration without any further explanation, of a container in the form of a bottle with an arrow placed in its neck has been preserved (Fig. 2). This illustration may indicate that the invention of fire arms came from China to Europe.

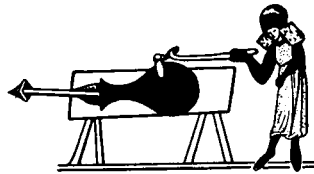


Fig. 2. Powder bottle with arrow.

2 TECHNOLOGY OF BLACK POWDER IN THE EUROPEAN MIDDLE AGES

During the Middle Ages in Europe a technology of gunpowder developed very quickly. Black powder was first manufactured by craftsmen who joined together to form guilds. In their method of production they soon branched off from the dangerous task of pulverising gunpowder in mortars (Fig. 3) and made use of remotely situated old mills. A mill of this kind is supposed to have been put into operation for the first time in 1340 near Augsburg in Germany. Charcoal was available in abundance and sulfur could be relatively easily acquired from southern Italy or Spain. But the "good saltpetre" (potassium nitrate) was imported from India and for this reason it was very expensive. Venice was in the possession of a transportation monopoly. Therefore the possibility of finding lime saltpetre in sheds and gaining it from putrefying urine and blood in pits and then converting this into potassium nitrate by means of a reaction with potash, was a very significant discovery. A further important progress was the granulation of the gun powder which prevented the separation of the components during transport. It should also be mentioned that gunpowder was already in use in the Middle Ages also for peaceful purposes, i.e. for blasting in mining, a method which was much more efficient than the antiquated method of "setting fire".



Fig. 3. Manufacturing of powder in mortars.

3 THE COMPOSITION OF BLACK POWDER AND THE REACTION OF ITS COMPONENTS

The optimum composition of gunpowder has certainly been determined in a completely empirical manner. According to whether they wished to fire more horizontally or more vertically the Chinese employed different mixtures. Charcoal was considered to be only an auxiliary product. The fuses were only impregnated with sulfur and saltpetre. The composition of gunpowders in use in different German and other states during the previous century is almost identical (cf. Table 1 [1]).

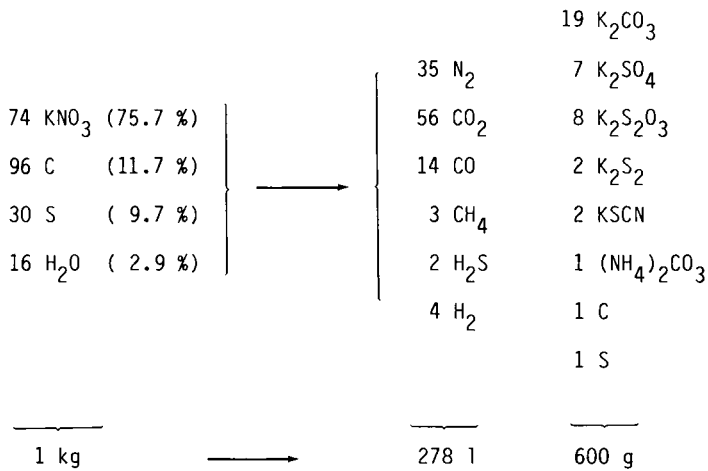
It is remarkable that the 15 % charcoal only contains about 80 % carbon. For the chemist it is more significant to state the composition of gunpowder in moles. 75 g saltpetre, 12 g carbon and 10 g sulfur correspond to 0.74 moles KNO_3 , 1.0 mole C and 0.31 moles S. If we calculate further that 0.74 mole potassium nitrate contains only 1.85 mole active oxygen, then we see easily that the amount of saltpetre despite its high share in the composition of gunpowder, is by no means sufficient to convert carbon and sulfur into their highest oxidation states, since 1 mole C and 0.31 mole S require 3 moles oxygen for the complete oxidation.

Although the composition of gunpowder remains very constant almost independent of the manufacturer, the amount of substances obtained from the reaction products varies within wide limits, in other words, it is not possible to reproduce the course of the powder reaction. Obviously, a branched reaction

TABLE 1
Composition of gunpowder (in weight-%)

	Saltpetre	Carbon	Sulfur
England	75	15	10
Sweden	75	15	10
Russia	75	15	10
Prussia	74	16	10
Saxony	74	16	10
U.S.A.	76	14	10
Austria	75.5	14.5	10

occurs. In a German handbook of chemistry [2] a long chemical equation can be found and is given in columns as follows:



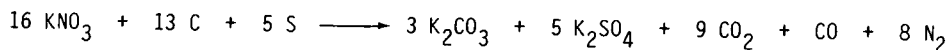
The reaction not only yields gases, mainly nitrogen, carbon dioxide and carbon monoxide. The small quantities of methane, hydrogen and hydrogen sulfide can be explained as products of the pyrolysis of charcoal and of the co-pyrolysis of charcoal, sulfur and water. The predominating portion of the combustion products consists of solids which generate the powder-smoke.

4 THE ROLE OF SULFUR IN BLACK POWDER

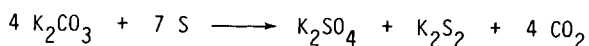
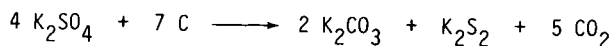
Many famous chemists were occupied with the theory of the chemical reaction which causes the ignition of the powder and the explosive course of the reac-

tions: Albertus Magnus (1193 - 1280), Roger Bacon (1214 - 1294), Claude Louis Berthollet (1748 - 1822), Joseph Louis Proust (1754 - 1826), Jöns Jacob Berzelius (1779 - 1848), Robert Bunsen (1811 - 1899). In the works of Albertus Magnus before 1280 a reference to a mixture of powder resembling that of gunpowder can be found. As an alchemist, Albertus Magnus could not be prosecuted on account of his high rank as a bishop! The English monk Roger Bacon mentioned a mixture of this kind in an "Epistle" in which he defends himself against the reproach of having to do with black magic. The mixture burned quickly and exploded on enclosure. Bacon recommended it as a "children's plaything". But he certainly was not the inventor of gunpowder. The facts provided by the sources are, strangely enough, so closely connected that they suggest the possibility of gunpowder being invented independently in Europe and China. In the year 1857 Robert Bunsen, together with his student L. Schischkoff, a Russian officer, published a treatise "Chemical Theory of Gunpowder" [3]. In Liebig's Annalen, volumes 212 and 213, an article by Debus [1] exists, consisting of 110 pages and dealing with this subject. An oxidation process followed by a reduction process is supposed to take place.

1. Procedure (oxidation):



2. Procedure (reduction):



These equations, however, can scarcely be acknowledged as explanation of the course of the reaction in question. Nowadays, this would mean that the reaction had to be subdivided in bimolecular individual stages. On attempting this, the problem immediately arises that two of the constituents of the powder reaction have no molecular structure. Only the sulfur forms molecules. Charcoal consists mainly of graphite carbon particles, strictly speaking, it consists of two-dimensionally cross-linked macromolecules. Potassium nitrate, as a salt, is a coordination polymer. In the case of modern explosives the oxygen required for the rapid combustion is molecularly dispersed in the material.

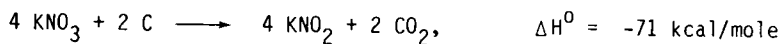
A fact which ought to make a convincing chemical theory of gunpowder intelligible is that here evidently a concerted reaction exists. Saltpetre and charcoal alone, or saltpetre and sulfur alone will not yield gunpowder. The black powder burns off so quickly that the attempt to follow the details seems hopeless. One can merely try to draw conclusions from the results or try to repro-

duce some parts of the experiment separately. Among the solids of the powder smoke there are, quite unexpectedly, some compounds to be found which are reduction products of sulfur: Thiosulfate and polysulfide. Apparently, the question may also be raised: How can a strong oxidizing agent also operate as a reducing agent? The author, during his activities on the lapis lazuli and ultramarine pigments, made a discovery which, quite evidently, concerns this gunpowder problem: It was well known that ultramarine blue can be converted into ultramarine red through oxidizing agents such as chlorine, hydrogen chloride plus oxygen, nitrogen dioxide and also with nitric acid vapours. This procedure is based on the discharge of the sulfur radical ions S_3^- and S_4^- . Surprisingly enough, if ultramarine red is melted with oxidizing agents like potassium nitrate, potassium nitrite and even potassium chlorate, ultramarine blue is formed again [4].

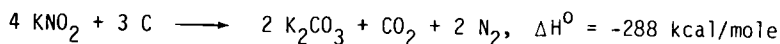
Debus disputed the statement of the earlier workers that the powder smoke included thiosulfate but confirmed the content of polysulfide. He believed that the polysulfide resulted from air oxidation of sulfur. The fact that thiosulfate actually does exist in the powder smoke can be proved by means of a very impressive experiment. When gunpowder, to which some sodium nitrate has been added, is ignited beside a beaker containing a saturated solution of thiosulfate as is obtained by melting $Na_2S_2O_3 \cdot 5H_2O$, the thiosulfate starts to crystallize.

The opinion has generally been supported that the reaction of sulfur with melting nitrate causes the series of reactions occurring by burning off gunpowder. However, it is possible on top of liquefied saltpetre to generate a layer of likewise liquid dark-brown sulfur without any reaction occurring. Sulfur does not react with potassium nitrate by ignition until it has reached a temperature of $350^\circ C$, i.e. $15^\circ C$ above the melting point of the salt ($335^\circ C$) whereas commercial black powder (Jagdpulver No. 2, Dynamit Nobel AG) ignites explosively even at about $300^\circ C$. Thus, the reaction of nitrate with sulfur will definitely not induce the powder reaction. On heating commercial gunpowder slowly, two points can be clearly observed, firstly, that it fumes long before ignition, and secondly, the perception of the characteristic smell of the powder-smoke which is attributed to the nitrous gases. The fact that a reaction takes place before reaching the melting point of potassium nitrate ($334^\circ C$) is confirmed by a thermogravimetric study (see Fig. 4). When firstly the main part of the sulfur is sublimed in a vacuum at constant temperature within the region of 120 to $130^\circ C$, a reaction of adsorbed nitrate with coal, obviously not affected by the sulfur, takes place. This points to the fact that the special manufacturing processes of gunpowder are essential for the reactivity of the product, because no reaction proceeds at such a low temperature if charcoal and

potassium nitrate are mixed without further measures. The reaction of potassium nitrate and potassium nitrite with charcoal has been analyzed in detail by Shah [5] and has mainly been traced back to the two steps



and



with hyponitrite as an intermediate product.

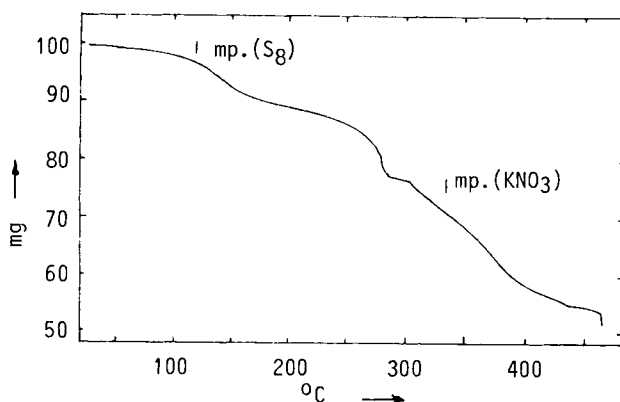
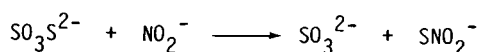


Fig. 4. Loss in weight of 100 mg of a commercial gunpowder on heating with a rate of 2 K/min in a vacuum thermobalance.

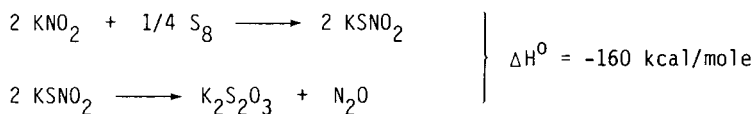
In connection with the black powder reaction the behaviour of the detonating powder compiled by Glauber as early as 1661 and consisting of a mixture of 3 parts of potassium nitrate, 1.5 parts of sulfur and 1 part of potassium carbonate seems to be valid. Angelo Angeli attributed the extremely violent explosion to a reaction of nitrite and thiosulfate which are formed by melting the starting materials [6]. Angeli also reported the explosion of mixtures of nitrites and thiocyanates [7]. Not long ago, a similar explosion - in ignorance of the German literature - occurred in a laboratory in Berkeley [8]. On considering which bimolecular step could cause the reaction of nitrate with thiosulfate or thiocyanate, one comes almost inevitably to the hypothesis that this step is only possible by the transfer of a sulfur atom:





In fact, a mixture of sulfur and potassium nitrite in a tube also explodes - even at 250 °C - and just as violent as the Glauber-mixture [4].

The reaction of sulfur with sodium nitrite proceeds slowly compared with the reaction with potassium nitrite. On top of melted sodium nitrite (melting point 284 °C) floating sulfur promotes the development of dinitrogen monoxide on the lower side. By overheating the melted substances ignition of sulfur is caused and it is oxidized by N₂O to SO₂. After the melted substance has been cooled down and solidified, the presence of thiosulfate in abundance can be proved. M. Schmidt [9] has found that sulfur with sodium nitrite in boiling dimethylformamide reacts to sodium thiosulfate and dinitrogen monoxide. He assumed that the salts of "polysulfane nitric acids" (nitropolysulfides) and sodium thionitrate were formed as intermediates. By reacting sulfur with a solution of bis(triphenylphosphane)immonium nitrite ("PNP:NO₂") in acetone it is possible to obtain a solution which permits crystallization of dark red PNP:S₂NO₂, which can be converted by triphenylphosphane into green PNP:SNO₂ [10]. This supports the hypothesis that, also in the gunpowder reaction, one of the most important steps is the reaction of sulfur with nitrite to give the explosive thionitrate for which the presence of thiosulfate in powder smoke is a convincing proof.

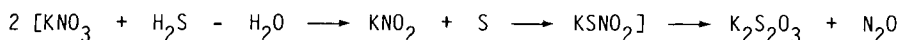


The reaction of gaseous S₈ to which the reaction enthalpy refers is a very strongly exothermic one. It is therefore not surprising that the reaction of potassium nitrite with sulfur proceeds explosively and it can be assumed that potassium thionitrate is a highly endothermic compound, in other words, an explosive.

During the reaction of sodium or potassium nitrite with sulfur in dimethylformamide, dimethylsulfoxide or hexamethylphosphoric acid triamide, and also the reaction with PNP nitrite or with potassium nitrite chelated by crown 18C6 in acetone it is possible to observe the formation of dark blue radical ions S₃⁻ in the initial phase of the reaction, and it can also be proved analytically that the reactions, apart from thiosulfate and sulfide, yield also sulfate to a considerable extent [10]. A direct relation between the nitrite - sulfur reaction and the reactions resulting from the ignition of the gun powder is obvious. On the whole, the reaction of sulfur with nitrite is a complicated radical reaction. Apparently, the concerted activity of sulfur with charcoal

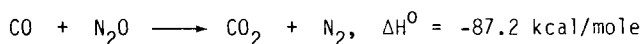
when reacting with saltpetre is caused by, firstly, the reduction of nitrate to nitrite by charcoal and, secondly, the reaction of sulfur with nitrite to give explosive thionitrate.

K.A. Hofmann [11] pointed to the possibility that the gunpowder reaction could be initiated through the ignition of hydrogen sulfide by solid potassium nitrate at 285-290 °C. This would explain the concerted reaction of the three components of gunpowder also. Actually it can be easily demonstrated that charcoal reacts with sulfur at 150-180 °C to yield hydrogen sulfide. It is noteworthy that the reaction of solid potassium nitrate and hydrogen sulfide at elevated temperatures produces sulfate, thiosulfate, dinitrogen oxide and ammonia [12]. $K_2S_2O_3$ and N_2O point to thionitrate as intermediate. The overall reaction

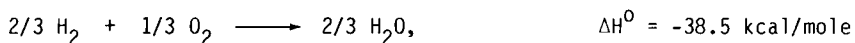
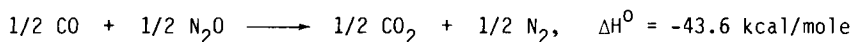


produces 66.45 kcal/mole, heat enough to start the powder explosion.

Finally, an inquiry must be made concerning the whereabouts of the dinitrogen monoxide which, along with the thiosulfate, must be formed by the decomposition of thionitrate. The answer to this question is given by the fact that the gaseous products of the powder reaction contain also carbon monoxide in excess in the presence of which N_2O is not stable. CO and N_2O , after ignition, react together explosively [13]:



We realize now also the significance of water in gunpowder: It is well known that the oxidation of carbon monoxide is catalyzed by water via OH radicals. The explosion of black powder can thus be attributed both to an exploding solid $KSN O_2$ and an exploding gas mixture N_2O and CO. It is worth noting that, relating to equal gas volumes, more energy is supplied by the reaction of dinitrogen monoxide with carbon monoxide than by the oxy-hydrogen gas reaction:



Dinitrogen monoxide can be regarded as the ozone of the chemistry of nitrogen (see Table 2).

TABLE 2
Thermodynamical data

	ΔH^0 [kcal/mole]	ΔS^0 [cal/K·mole]
$O_3 \longrightarrow O_2 + O$	25.16	30.94
$N_2O \longrightarrow N_2 + O$	39.67	31.64
$NO_2 \longrightarrow NO + O$	72.67	31.34
$CO_2 \longrightarrow CO + O$	126.79	34.70

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