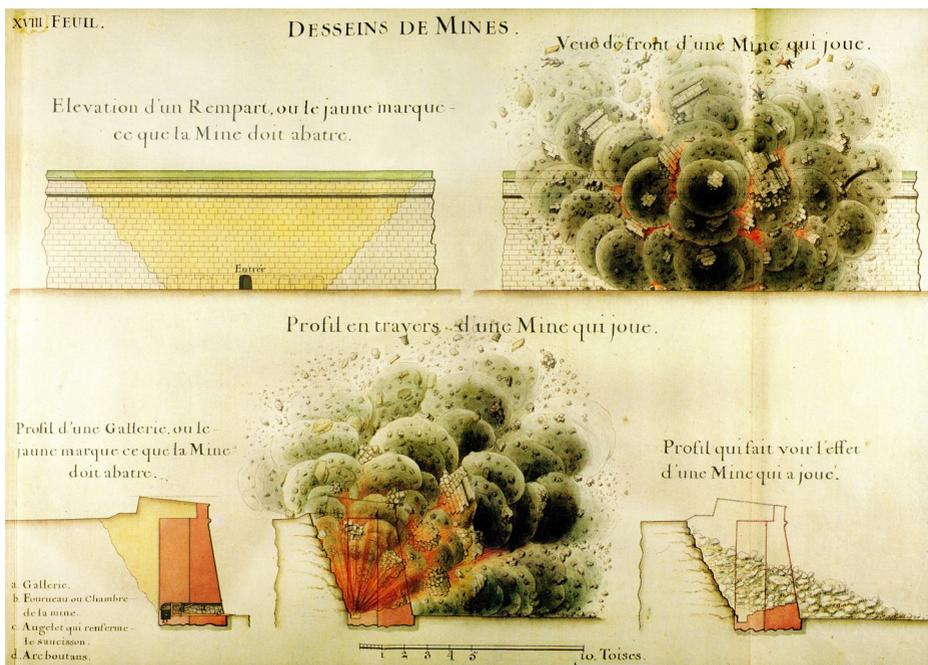


EXPLOSIVES - EB 1911

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The Ordnance Society was formed in June 1986 to promote, encourage and co-ordinate the study of all aspects of the history of ordnance and artillery. It is today, an international society with members from more than 20 countries and all walks of life.

Acknowledgements

I inherited my father's Library with a collection of Encyclopædia Britannica dated 1911. Years, earlier I had read through a number of articles including that on Fortifications and Siegecraft. Although somewhat outdated today, the historical value is still of interest. I had always wanted to make the article in a stand-alone booklet. With the help of Wikisource, I have been able to do that. My thanks go to Charles Blackwood who has cleaned the original plans and diagrams straightening some that needed to be done. Charles has provided most of the photographs from his archive collection to add emphasis to some of the original diagrams. My thanks also go to H.M. Stationery Office, Wikipedia, Wikisource & The Ordnance Society.

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Cover picture: Vauban: Le Triomphe de la Méthode, 1704

EXPLOSIVES

Explosives, a general term for substances which by certain treatment “explode”, *i.e.* decompose or change in a violent manner so as to generate force. From the manner and degree of violence of the decomposition they are classified into “propellants” and “detonators,” but this classification is not capable of sharp delimitation. In some cases, the same substance may be employed for either purpose under altered external conditions; but there are some substances which could not possibly be employed as propellants, and others which can scarcely be induced to explode in the manner known as “detonation.” A propellant may be considered as a substance that on explosion produces such a disturbance that neighbouring substances are thrown to some distance; a detonator or disruptor may produce an extremely violent disturbance within a limited area without projecting substances to any great distance. Time is an important, perhaps the most important, factor in this action. A propellant generally acts by *burning* in a more or less rapid and regular manner, producing from a comparatively small volume a large volume of gases; during this action heat is also developed, which, being expended mostly on the gaseous products, causes a further expansion. The noise accompanying an explosion is due to an air wave and is markedly different in the case of a detonator from a real propellant. Some cases of ordinary combustion can be accelerated into explosions by increasing the area of contact between the combustible and the oxygen supplier, for instance, ordinary gas or dust explosions. Neither temperature nor quantity of heat energy necessarily gives an explosive action.

Some metals, *e.g.* aluminium and magnesium, will, in oxidizing, produce a great thermal effect, but unless there be some gaseous products no real explosive action. Explosives may be mechanical mixtures of substances capable of chemical interaction with the production of large volumes of gases, or definite chemical compounds of a peculiar class known as “endothermic,” the decomposition of which is also attended with the evolution of gases in large quantity.

All chemical compounds are either “endothermic” or “exothermic.” In endothermic compounds energy, in some form, has been taken up in the act of formation of the compound. Some of this energy has become potential, or rather the compound formed has been raised to a higher potential. This case occurs when two elements can be united only under some compulsion such as a very high temperature, by the aid of an electric current, or spark, or as a secondary product whilst some other reactions are proceeding. For example, oxygen and nitrogen combine only under the influence of an electric spark, and carbon and calcium in the electric furnace. The formation of chlorates by the action of chlorine on boiling potash is a good instance of a complex compound (potassium chlorate), being formed in small quantity as a secondary product whilst a large quantity of primary and simpler products (potassium chloride and water) is forming. In chlorate formation the greater part of

the reaction represents a running down of energy and formation of exothermic compounds, with only a small yield of an endothermic substance. Another idea of the meaning of endothermic is obtained from acetylene. When 26 parts by weight of this substance are burnt, the heat produced will warm up 310,450 parts of water 1° C. Acetylene consists of 24 parts of carbon and 2 of hydrogen by weight. The 24 parts of carbon will, if in the form of pure charcoal, heat 192,000 parts of water 1°, and the 2 parts of hydrogen will heat 68,000 parts of water 1°, the total heat production being 260,000 heat units. Thus 26 grams of acetylene give an excess of 50,450 units over the amount given by the constituents. This excess of heat energy ^[1] is due to some form of potential energy in the compound which becomes actual heat energy at the moment of dissolution of the chemical union. The manner in which a substance is endothermic is of importance as regards the practical employment of explosives. Some particular endothermic state or form results from the mode of formation and the consequent internal structure of the molecule. Physical structure alone can be the cause of a relative endothermic state, as in the glass bulbs known as Rupert's drops, &c., or even in chilled steel. Rupert's drops fly in pieces on being scratched or cut to a certain depth. The cause is undoubtedly to be ascribed to the molecular state of the glass brought about by chilling from the melted state. The molecules have not had time to separate or arrange themselves in easy positions. In steel when melted the carbide of iron is no doubt diffused equally throughout the liquid. When cooled slowly some carbide separates out more or less, and the steel is soft or annealed. When chilled the carbides are retained in solid solution. The volume of chilled glass or steel differs slightly from that in the annealed state.

Super fused substances are probably in a similar state of physical potential or strain. Many metallic salts, and organic compounds especially, will exhibit this state when completely melted and then allowed to cool in a clean atmosphere. On touching with a little of the same substance in a solid state the liquids will begin to crystallize, at the same time becoming heated almost up to their melting-points. The metal gallium shows this excellently well, keeping liquid for years until touched with the solid metal, when there is a considerable rise of temperature as solidification takes place.

All carbon compounds, excepting carbon dioxide, and many if not all compounds of nitrogen, are endothermic. Most of the explosives in common use contain nitrogen in some form.

Exothermic compounds are in a certain sense the reverse of endothermic; they are relatively inert and react but slowly or not at all, unless energy be expended upon them from outside. Water, carbon dioxide and most of the common minerals belong to this class.

The explosives actually employed at the present time include mixtures, such as gunpowder's and some chlorate compositions, the ingredients of which separately may be non-explosive; compounds used singly, as guncotton, nitro-glycerine (in the form of dynamite), picric acid (as lyddite or melanite), trinitrotoluene, nitro cresols, mercury fulminate, &c. ; combinations of some explosive compounds, such as cordite and the smokeless propellants in general use for military purposes; and, finally, blasting and detonating or igniting compositions, some of which contain inert diluting materials as well as one or more high explosives. Many igniting compositions are examples of the last type, consisting of a high explosive diluted with a neutral substance, and frequently containing in addition a composition which is inflamed by the explosion of the diluted high explosive, the flame in turn igniting the actual propellant.

Explosive Mixtures.—The explosive mixture longest known is undoubtedly gunpowder (*q.v.*) in some form—that is, a mixture of charcoal with sulphur and nitre, the last being the oxygen provider. Besides the nitrates of metals and ammonium nitrate, there is a limited number of other substances capable of serving in a sufficiently energetic manner as oxygen providers. A few chlorates, perchlorates, permanganates and chromates almost complete the list. Of these the sodium, potassium and barium chlorates are best known and have been actually tried, in admixture with some combustible substances, as practical explosives. Most other metallic chlorates are barred from practical employment owing to instability, deliquescence or other property.

Of the chlorates those of potassium and sodium are the most stable, and mixtures of either of these salts with sulphur or sulphides, phosphorus, charcoal, sugar, starch, finely-ground cellulose, coal or almost any kind of organic, *i.e.* carbon, compound, in certain proportions, yield an explosive mixture. In many cases these mixtures are not only fired or exploded by heating to a certain temperature, but also by quite moderate friction or percussion. Consequently, there is much danger in manufacture and storage, and however these mixtures have been made up, they are quite out of the question as propellants on account of their great tendency to explode in the manner of a detonator. In addition, they are not smokeless, and leave a considerable residue which in a gun would produce serious fouling.

Mixtures of chlorates with aromatic compounds such as the nitro- or dinitro-benzenes or even naphthalene make very powerful blasting agents. The violent action of a chlorate mixture is due first to the rapid evolution of oxygen, and also to the fact that a chlorate can be detonated when alone. A drop of sulphuric acid will start the combustion of a chlorate mixture. In admixture with sulphur, sulphides and especially phosphorus, chlorates give extremely sensitive compositions, some of which form the basis of friction tube and firing mixtures.

Potassium and sodium perchlorates and permanganates make similar but slightly less sensitive explosive mixtures with the above-mentioned substances. Finely divided metals such as aluminium or magnesium give also with permanganates, chlorates or perchlorates sensitive and powerful explosives. Bichromates, although containing much available oxygen, form but feeble explosive mixtures, but some compounds of chromic acid with diazo compounds and some acetylides are extremely powerful as well as sensitive. Ammonium bichromate is a self-combustible after the type of ammonium nitrate, but scarcely an explosive.

Explosive Compounds.—Nearly all the explosive compounds in actual use either for blasting purposes or as propellants are nitrogen compounds and are obtained more or less directly from nitric acid. Most of the propellants at present employed consist essentially of nitrates of some organic compound, and may be viewed theoretically as nitric acid, the hydrogen of which has been replaced by a carbon complex; such compounds are expressed by $M \cdot O \cdot NO_2$, which indicates that the carbon group is in some manner united by means of oxygen to the nitrogen group. Guncotton and nitro-glycerine are of this class. Another large class of explosives is formed by a more direct attachment of nitrogen to the carbon complex, as represented by $M \cdot NO_2$. A number of explosives of the detonating type are of this class. They contain the same proportions of oxygen and nitrogen as nitrites but are not nitrites. They have been termed nitro-derivatives for distinction. One of the simplest and longest-known members of this group is nitrobenzene, $C_6H_5NO_2$, which is employed to some extent as an explosive, being one ingredient in rack-a-rock and other blasting compositions. The dinitro-benzenes, $C_6H_4(NO_2)_2$, made from it are solids which are somewhat extensively employed as constituents of some sporting powders, and in admixture with ammonium nitrate form a blasting powder of a “flameless” variety which is comparatively safe in dusty or “gassy” coal seams.

Picric acid or trinitrophenol, $C_6H_2 \cdot OH \cdot (NO_2)_3$ is employed as a high explosive for shell, &c. It requires, however, either to be enclosed and heated, or to be started by a powerful detonator to develop its full effect. Its compounds with metals, such as the potassium salt, $C_6H_2 \cdot OK \cdot (NO_2)_3$, are when dry very easily detonated by friction or percussion and *always* on heating, whereas picric acid itself will burn very quietly when set fire to under ordinary conditions. Trinitrotoluene, $C_6H_2 \cdot CH_3 \cdot (NO_2)_3$, is a high explosive resembling picric acid in the manner of its explosion (to which in fact it is a rival) but differs therefrom in not forming salts with metals. The nitromethyls, $C_{10}H_6 \cdot OH \cdot NO_2$, and higher nitration products may be counted in the list. Their salts with metals behave much like the picrate's.

All these nitro compounds can be reduced by the action of nascent hydrogen to substances called amines (*q.v.*), which are not always explosive in themselves, but in some cases can form nitrates of a self-combustible nature. Amino acetic acid, for

instance, will form a nitrate which burns rapidly but quietly, and might be employed as an explosive. By the action of nitrous acid at low temperatures on aromatic amines, *e.g.* aniline, $C_6H_5NH_2$, diazo compounds are produced. These are all highly explosive, and when in a dry state are for the most part also extremely sensitive to friction, percussion or heat. As many of these diazo compounds contain no oxygen their explosive nature must be ascribed to the peculiar state of union of the nitrogen. This state is attempted to be shown by the formulae such as, for instance, $C_6H_5 \cdot N : N \cdot X$, which maybe some compound of diazo benzene. Probably the most vigorous high explosive at present known is the substance called hydrazo acid or azoimide (*q.v.*). It forms salts with metals such as AgN_3 , which explode in a peculiar manner. The ammonium compound, NH_4N_3 , may become a practical explosive of great value.

Mercuric fulminate, $HgC_2N_2O_2$, is one of the most useful high explosives known. It is formed by the action of a solution of mercurous nitrate, containing some nitrous acid, on alcohol. It is a white crystalline substance almost insoluble in cold water and requiring 130 times its weight of boiling water for solution. It may be heated to $180^\circ C.$ before exploding, and the explosion so brought about is much milder than that produced by percussion. It forms the principal ingredient in cap compositions, in many fuses and in detonators. In many of these compositions the fulminate is diluted by mixture with certain quantities of inert powders so that its sensitiveness to friction or percussion is just so much lowered, or slowed down, that it will fire another mixture capable of burning with a hot flame. For detonating dynamite, guncotton, &c., it is generally employed without admixture of a diluent.

Smokeless Propellants.—Gunpowder's and all other explosive mixtures or compounds containing metallic salts must form smoke on combustion. The solids produced by the resolution of the compounds are in an extremely finely divided state, and on being ejected into the atmosphere become more or less attached to water vapour, which is so precipitated, and consequently adds to the smoke. The simplest examples of propellants of the smokeless class are compressed gases. Compressed air was the propellant for the Zalinski dynamite gun. Liquefied carbon dioxide has also been proposed and used to a slight extent with the same idea. It is scarcely practical, however, because when a quantity of a gas liquefied by pressure passes back again into the gaseous state, there is a great absorption of heat, and any remaining liquid, and the containing vessel, are considerably cooled. Steam guns were tried in the American Civil War in 1864; but a steam gun is not smokeless, for the steam escaping from the long tube or gun immediately condenses on expansion, forming white mist or smoke.

At the earliest stage of the development of guncotton the advantage of its smokeless combustion was fully appreciated. That it did not at once take its position

as *the* smokeless propellant, was simply due to its physical state—a fibrous porous mass—which burnt too quickly or even detonated under the pressure required in firearms of any kind. In the early eighties of the 19th century it was found that several substances would partly dissolve or at least gelatinize guncotton, and the moment when guncotton proper was obtained as a colloid or jelly was the real start in the matter of smokeless propellants.

Guncotton is converted into a gelatinous form by several substances, such as esters, *e.g.* ethyl acetate or benzoate, acetone and other ketones, and many benzene compounds, most of which are volatile liquids. On contact with the guncotton a jelly is formed which stiffens as the evaporation of the gelatinizing agent proceeds, and finally hardens when the evaporation is complete. Whilst in a stiff pasty state it may be cut, moulded or pressed into any desired shape without any danger of ignition. In fact, guncotton in the colloid state may be hammered on an anvil, and, as a rule, only the portion struck will detonate or fire. Guncotton alone makes a very hard and somewhat brittle mass after treatment with the gelatinizing agent and complete drying, and small quantities of camphor, Vaseline, castor oil and other substances are incorporated with the gelatinous guncotton to moderate this hard and brittle state.

All the smokeless powders, of which gelatinized guncotton's or nitrated celluloses are the base, are moulded into some conveniently shaped grain, *e.g.* tubes, cords, rods, disks or tablets, so that the rate of burning may be controlled as desired. The Vielle powder, invented in 1887 and adopted in France for a magazine rifle, consisted of gelatinized guncotton with a little picric acid. Later a mixture of two varieties of guncotton gelatinized together was used. In addition to guncotton's other explosive or non-explosive substances are contained in some of these powders. Guncotton alone in the colloid state burns very slowly if in moderate-sized pieces, and when subdivided or made into thin rods or strips it is still very mild as an explosive, partly from a chemical reason, *viz.* there is not sufficient oxygen in it to burn the carbon to dioxide. Many mixtures are consequently in use, and many more have been proposed, which contain some metallic salt capable of supplying oxygen, such as barium or ammonium nitrate, &c., the idea being to accelerate the rate of burning of the guncotton and if possible avoid the production of smoke.

The discovery by A. Nobel that nitro-glycerine could be incorporated with collodion cotton to form blasting gelatine led more or less directly to the invention of ballistite, which differs from blasting gelatine only in the relative amounts of collodion, or soluble nitrated cotton, and nitro-glycerine. Ballistite was adopted by the Italian government in 1890 as a military powder. Very many substances and mixtures have been proposed for smokeless powder, but the two substances, guncotton and nitro-glycerine, have for the most part kept the field against all other combinations, and

for several reasons. Nitro-glycerine contains a slight excess of oxygen over that necessary to convert the whole of the carbon into carbon dioxide; it burns in a more energetic manner than guncotton; the two can be incorporated together in any proportion whilst the guncotton is in the gelatinous state; also all the liquids which gelatinize guncotton dissolve nitro-glycerine, and, as these gelatinizing liquids evaporate, the nitro-glycerine is left entangled in the guncotton jelly, and then shares more or less its colloidal character. In burning the nitro-glycerine is protected from detonation by the gelatinous state of the guncotton, but still adds to the rate of burning and produces a higher temperature.

Desirable Qualities.—Smokelessness is one only of the desirable properties of a propellant. All the present so-called smokeless powders produce a little fume or haze, mainly due to the condensation of the steam which forms one of the combustion products. There is often also a little vapour from the substances, such as oils, mineral jelly, Vaseline or other hydrocarbon added for lubrication or to render the finished material pliable, &c. The gases produced should neither be very poisonous nor exert a corrosive action on metals, &c. The powder itself should have good keeping qualities, that is, not be liable to chemical changes within ordinary ranges of temperature or in different climates when stored for a few years. In these powders slight chemical changes are generally followed by noticeable ballistic changes. All the smokeless powders of the present day produce some oxide of nitrogen, traces of which hang about the gun after firing and change rapidly into nitrous and nitric acids. Nitrous acid is particularly objectionable in connexion with metals, as it acts as a carrier of oxygen. The fouling from modern smokeless powders is a slight deposit of acid grease, and the remedy consists in washing out the bore of the piece with an alkaline liquid. The castor oil, mineral jelly or camphor, and similar substances added to smokeless powders are supposed to act as lubricants to some extent. They are not as effective in this respect as mineral salts, and the rifling of both small-arms and ordnance using smokeless powders is severely gripped by the metal of the projectile. The alkaline fouling produced by the black and brown powders acted as a preventive of rusting to some extent, as well as a lubricant in the bore.

Danger in Manufacture.—In the case of the old gunpowder's, the most dangerous manufacturing operation was incorporation. With the modern colloid propellants, the most dangerous operations are the chemical processes in the preparation of nitro-glycerine, the drying of guncotton, &c. After once the gelatinizing solvent has been added, all the mechanical operations can be conducted, practically, with perfect safety. This statement appears to be correct for all kinds of nitrated cellulose powders, whether mixed with nitro-glycerine or other substances. Should they become ignited, which is possible by a rise of temperature (to say 180°) or contact with a flame, the mixture burns quickly, but does not detonate.

As a rule, naval and military smokeless powders are shaped into flakes, cubes, cords or cylinders, with or without longitudinal perforations. All the modifications in shape and size are intended to regulate the rate of burning. Sporting powders are often coloured for trade distinction. Some powders are black leaded by glazing with pure graphite, as is done with black powders. One object of this glazing is to prevent the grains or pieces becoming joined by pressure; for rods or pieces of some smokeless powders might possibly unite under considerable pressure, producing larger pieces and thus altering the rate of burning. Most smokeless powders are fairly insensitive to shock. All these gelatinized powders are a little less easily ignited than black powders. A slightly different cap composition is required for small-arm cartridges, and cannon cartridges generally require a small primer or starter of powdered black gunpowder.

It is desired that a propellant shall produce the maximum velocity with the minimum pressure. The pressure should start gently so that the inertia of the projectile is overcome without any undue local strain on the breech near the powder chamber, and more especially that as more and more space is given to the gases by the movement of the projectile up the gun to the muzzle, gas should be produced with sufficient rapidity to keep the pressure nearly uniform or slightly increasing along the bore. The leading idea for improvements in relation to propellants is to obtain the greatest possible pressure regularly developed, and at the same time the lowest temperatures. (W. R. E. H.)

Law.—In 1860 an act was passed in England “to amend the law concerning the making, keeping and carriage of gunpowder and compositions of an explosive nature, and concerning the manufacture and use of fireworks” (23 & 24 Vict. c. 139), whereby previous acts on the same subject were repealed, and minute and stringent regulations introduced. Amending acts were passed in 1861 and 1862. In 1875 was passed the Explosives Act (38 & 39 Vict. c. 17), which repealed the former acts, and dealt with the whole subject in a more comprehensive manner. This act, containing 122 sections, and applying to Scotland and Ireland, as well as to England, constitutes, with various orders in council and home office orders, a complete code. The act of 1875 was based on the report of a committee of the House of Commons, public opinion having been greatly excited on the subject by a terrible explosion on the Regent’s Canal in 1874. Explosives are thus defined: (1) Gunpowder, nitro-glycerine, dynamite, guncotton, blasting powders, fulminate of mercury or of other metals, coloured fires, and every other substance, whether similar to those above-mentioned or not, used or manufactured with a view to produce a practical effect by explosion or a pyrotechnic effect, and including (2) fog-signals, fireworks, fuses, rockets, percussion caps, detonators, cartridges, ammunition of all descriptions, and every adaptation or preparation of an explosive as above defined. Part 1. deals with

gunpowder, providing that it shall be manufactured only at factories lawfully existing or licensed under the act; that it shall be kept (except for private use) only in existing or new magazines or stores, or in registered premises, licensed under the act. Private persons may keep gunpowder for their own use to the amount of thirty pounds. The act also prescribes rules for the proper keeping of gunpowder on registered premises. Part 2. deals with nitro-glycerine and other explosives; part 3. with inspection, accidents, search, &c.; part 4. contains various supplementary provisions. By order in council the term "explosive" may be extended to any substance which appears to be specially dangerous to life or property by reason of its explosive properties, or to any process liable to explosion in the manufacture thereof, and the provisions of the act then extend to such substance just as if it were included in the term "explosive" in the act. The act lays down minute and stringent regulations for the sale of gunpowder, restricting the sale thereof in public thoroughfares or places, or to any child apparently under the age of thirteen; requiring the sale of gunpowder to be in closed packages labelled; it also lays down general rules for conveyance, &c. The act also gives power by order in council to define, from time to time, the composition, quality and character of any explosive, and to classify explosives, and such orders in council are frequently made including new substances; those in force will be found in the *Statutory Rules and Orders*, tit. "explosive substance." The Merchant Shipping Act 1894 imposes restrictions on the carriage of dangerous goods in a British or foreign vessel, "dangerous goods" meaning aqua Fortis, vitriol, naphtha, benzine, gunpowder, lucifer matches, nitro-glycerine, petroleum and any explosive within the meaning of the Explosives Act 1875. The act is administered by the home office, and an annual report is published containing the proceedings of the inspectors of explosives and an account of the working of the act. Each annual report gives a list of explosives at the time authorized for manufacture or importation, and appendices containing information as to accidents, experiments, &c.

Practically every European country has legislated on the lines of the English act of 1875, Austria taking the lead, in 1877, with an explosives ordinance almost identical with the English act. The United States and the various English colonies also have explosives acts regulating the manufacture, storage and importation of explosives.

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↑ Not necessarily heat energy entirely. A number of substances—acetylides and some nitrogen compounds, such as nitrogen chloride—decompose with extreme violence, but *little heat* is produced.