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TRANSACTIONS.

Some Properties of Explosives.

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COMPARED with other branches of chemistry, the subject of explosives has received less attention than many. This is due to the risks attaching to their investigation, which requires costly safety precautions, and to the somewhat restricted and specialised field of application.

The late war provided a great stimulus to the investigation of explosives. Methods of manufacture of certain substances were brought to a very high degree of perfection, and processes of filling and application were carefully worked out, but much of this work was of necessity directed to the practical side.

A large field of research on fundamental principles, essential to future progress, remains for investigation.

It is proposed in this lecture to describe some steps that have been taken, both before and during the war, to obtain an insight into the principles of explosive phenomena by quantitative measurements of some of the more important properties of explosives, the work for the most part having been carried out at the Research Department, Woolwich.

Before discussing these measurements, it may be well to define what is understood by the term explosive, and this is conveniently done by stating that its function is to exert a sudden intense

pressure on its surroundings when suitably activated. This pressure is developed by the decomposition of the explosive into gas, with concomitant liberation of heat. It follows, therefore, that the fundamental features possessed by an explosive are:

(i) Potential energy in virtue of its chemical constitution, independent of external agencies.

(ii) Formation of gaseous products with simultaneous liberation of energy.

(iii) Rapid decomposition when suitably excited.

The investigation of the first of these involves a study of the thermochemistry of different types of chemical compounds, determination of heats of formation, and heats of explosion. On these properties depend directly the power and sensitiveness of the explosive, and indirectly the chemical stability. Thus the exothermic character of the decomposition of an explosive renders it liable to break down at the ordinary temperature, so that if the whole of the heat were conserved, the temperature of the explosive and rate of decomposition would be gradually raised to a pitch when explosion would spontaneously occur.

The investigation of the second involves the study of the chemical reactions attending all rates of decomposition up to explosion, and the equilibria established among the decomposition products, at different temperatures and pressures.

The investigation of the third involves measurement of the rate of propagation of the explosion wave and all the phenomena in the proximity of the detonating mass of explosive. This rate of propagation in the explosive largely determines the pressure developed, and is the criterion for classification of explosives as either high or low explosives. It has therefore a close connexion with the effects that they produce.

It is the object of this lecture to consider, in the first place, some of the properties of explosives, with special reference to the chemical constitution and the physical properties of the compounds themselves. An attempt will be made to trace a reflection of the molecular arrangement of the compounds in such important properties as the heat of formation, the chemical stability, the sensitiveness, and the violence that explosives exhibit.

A second part will deal with the constants and properties of the amatsols, in view of the importance that they assumed during the war.

PART I.

The Influence of Constitution and Physical Condition.

The principal properties that will be considered, in conjunction with structure, composition, and physical form, are those of:

- (1) Heat of formation.
- (2) Heat of explosion and gases evolved.
- (3) Chemical stability.
- (4) Sensitiveness to shock.
- (5) Rate of detonation.
- (6) Pressure developed.

Special methods for determining most of these properties have been evolved in the Research Department, Woolwich, and it is these that have furnished most of the recently obtained data quoted in the sequel.

In each case a short account of the methods employed will be given before proceeding to the discussion of the properties.

(1) *Heat of Formation*.—The necessity for meeting certain requirements in explosive compounds, such as rapidity of action, stability on storage, and convenience of handling, imposes conditions which lead to a sacrifice of the original energy of combustion of the elements of which the explosive is composed.

In considering the thermal data, it is instructive to compare an explosive with a system containing carbon and hydrogen in the same ratio as they exist in the explosive, together with sufficient oxygen for their complete combustion. Such a system is found

TABLE I.

Heat of Explosion or Combustion of 1 Kilo.

One kilo. of the following system.	Heat in kg. cal. (water gaseous).	
	Explosion.	Combustion.
(1) Glyceryl trinitrate	1478	—
(2) Carbon and hydrogen, in ratio as in glyceryl trinitrate, together with oxygen for complete combustion.....	—	2420
(3) Elements present in glyceryl trinitrate.....	—	1885
(4) Trinitrotoluene.....	924	—
(5) Carbon and hydrogen, in ratio as in trinitrotoluene, together with oxygen for complete combustion.....	—	2278
(6) Trinitrotoluene, together with oxygen for complete combustion.....	—	2009
(7) Elements present in trinitrotoluene, to- gether with oxygen for complete com- bustion	—	2035
(8) Trinitrotoluene, together with ammonium nitrate for complete combustion	1004	—

to evolve considerably more heat for the same weight than the explosive itself, and this is due to the handicap imposed by the heat lost by forming the explosive from its elements, to want of oxygen for total combustion, to dilution with nitrogen, or to a combination of these.

It will be seen from the table [(1) and (2)] that the system of carbon, hydrogen, and oxygen corresponding with glyceryl trinitrate evolves for the same weight 64 per cent. more heat than this powerful explosive can evolve.

Conceiving the steps in its formation from carbon and hydrogen to propane, thence to glycerol, and thence to glyceryl trinitrate, energy is successively locked up in forming them, but chiefly during the process of hydroxylation of propane. The loss due to the heat of formation of glyceryl trinitrate as given by the difference between its heat of explosion (1) and that of the combustion of its elements (3) is 22·8 per cent. of the heat which the substance evolves on explosion.

Trinitrotoluene evolves on detonation a much lower quantity of heat (4) than glyceryl trinitrate (1), and, moreover, the heat evolved is a much smaller proportion of that evolved by the corresponding system of elements (5) than in the case of glyceryl trinitrate. Such a system would evolve 147 per cent. more heat than is produced by the simple explosive, as against 64 per cent. for glyceryl nitrate. In trinitrotoluene, however, we have a substance in which the deficit of oxygen is so great that 1 kilo. would require 0·74 kilo. of additional oxygen for its complete combustion. Trinitrotoluene suffers, therefore, from its uncompensated character as regards the oxygen it carries for the combustion of its elements. The extent to which it suffers from the lost energy involved in its formation from the elements may be gathered from the table, where the heat evolved from combustion of its elements (7) is set down in comparison with the heat experimentally found when trinitrotoluene is burned in oxygen (6). In this case, the heat due to the combustion of the elements, together with their necessary oxygen, is only 1·3 per cent. more than that which is evolved by a system composed of trinitrotoluene and its necessary oxygen. It will be seen, therefore, that the lower total energy associated with trinitrotoluene is due, for the most part, to its want of oxygen, but that when the compensated explosive, glyceryl trinitrate (1), and the compensated system of trinitrotoluene with the oxygen it requires for complete combustion (6), are each of them compared with the heat evolved by the systems made up of their carbon and hydrogen and necessary oxygen, (2) and (5), the loss suffered by trinitrotoluene is much less than that by glyceryl

trinitrate in the proportion of about one to four. This is due to the lower heat of formation from the elements, and especially to the much smaller wastage of energy by methylation as compared with hydroxylation. Thus, whilst the heat of detonation of trinitrotoluene is much less than that of glyceryl trinitrate, it has been formed with much less wastage of energy.

When an explosive mixture is made with an oxygen-bearing salt, such as ammonium nitrate, in proportions for the complete oxidation of all the combustible elements of the system, the heat evolved, whilst greater than that given by trinitrotoluene itself, is still less than half of what the combustible elements in trinitrotoluene would give if they underwent combustion in oxygen. This is, of course, again due to the adverse effect of the high heat of formation of ammonium nitrate.

Generally, it can be said, in comparing nitric esters with nitro-compounds, that whilst a large proportion of oxygen can be readily introduced into the molecule of nitric esters by means of the $\text{O}\cdot\text{NO}_2$ -group, they have the disadvantage of a higher heat of formation, as the heat which is lost in the combination of carbon and hydrogen is more in the case of the paraffins than in the case of the aromatic hydrocarbons, and, further, much heat is wasted in hydroxylation.

From the point of view of total heat energy, then, an advantage rests with explosives in which the oxygen is supplied either in the uncombined form, as in the liquid air explosives, or by a compound of which the heat of formation is small. Of this type are explosives in which petrol or nitrobenzene, for example, is used in conjunction with nitrogen peroxide, the heat of formation of which from its elements is low (1.7 kg. cal. per mol.), loss of energy by the formation of a compound between combustible and oxygen-bearing substance being in this case avoided. Thus 1 kilo. of a mixture of nitrogen peroxide and nitrobenzene, arranged for complete combustion, would give 1790 kg. cal. (water gaseous), or 21 per cent. more than glyceryl trinitrate.

Such mixtures, therefore, have the advantages of being readily arranged for complete combustion, and of being constituted so that there is little loss in the formation of their components. They are consequently very powerful, and may also be very violent, but have the practical drawbacks associated with the handling of volatile liquids.

It is now of interest to follow the effect of the introduction of nitro- and other groups. The heats of combustion, from which are deduced the heats of formation, have been the subject of study at the Research Department, Woolwich, and an account of the work

and of the values for the most important nitro-derivatives of benzene, toluene, phenol, and methylaniline is being published in the names of Messrs. Garner and Abernethy.

It has been found that there is no constant difference produced by the introduction of a nitro-group or of successive nitro-groups into the benzene nucleus, but that the internal energy of the molecule, as shown by its heat of formation, varies with the position of the entering nitro-group with reference to other nitro-groups and to other substituting groups. Generally, it is found that the molecule has the greatest strain—lowest heat of formation—in which the nitro-groups are adjacent to one another, and this strain is reflected in the lower chemical stability and the greater sensitiveness to impact of those members of the series possessing the lower heat of formation. The heats of formation of the isomerides of trinitrotoluene range from $+10.2$ kg. cal. per mol. for the 2:4:6- to -2.0 (carbon-diamond) for the 2:3:4-compound, and all these isomerides give off more gas on heating at a given temperature, and explode by the application of a blow of less energy, than the symmetrical substance. As a further example, 1:2:4-trinitrobenzene has been found to be more sensitive and less chemically stable than the symmetrical 1:3:5-isomeride. This will be further alluded to in the portion of this paper which deals with chemical stability.

The comparatively low heat of formation of the compounds in which adjacent nitro-groups occur will be noted in connexion with the well-known difficulty of preparing substances in which there are two nitro-groups in the ortho-position to one another.

The introduction of nitro-groups in the parent substances of the four series mentioned above produces compounds which, at least after three groups have entered, have for the most part still a heat of formation greater than that of the original substance, but from results obtained so far, it appears to require four nitro-groups to bring the heat of formation markedly below that of the parent substance. Thus the heats of formation of benzene, toluene, phenol, and methylaniline, compared with those of their symmetrical trinitro-derivatives, are respectively -10.6 and $+4.9$, -3.8 and $+10.2$, $+33.2$ and $+47.1$, and -7.9 and $+7.1$ kg. cal. per mol. (carbon-diamond). A fourth group (in the side-chain) in the case of trinitrophenylmethylnitroamine brings the heat of formation to -11.4 , which is below that of methylaniline. It will be seen, also, that whilst the introduction of a hydroxyl group is productive of a considerable increase in the heat of formation, oxygen can be added in the form of nitro-groups without any serious

degradation in the energy of the molecule, and this is of importance in explaining the explosive character of nitro-compounds.

In another type of explosives, such as are used as initiators, which require to be of a very sensitive character, a very low or negative heat of formation reflects their great internal strain. Examples of these are mercury fulminate, which absorbs 62.9 kg. cal. per mol. in its formation from its elements (Berthelot), and lead azide, which absorbs 105 kg. cal. per mol. (Martin), and is characterised by the strain resulting from the rings containing three nitrogen atoms.

The work on the heat of formation of the benzenoid substances has been more recently the subject of special study, on account of its bearing on the properties of explosives used on the largest scale, and so has been more fully treated in the foregoing remarks.

The heat of formation of all explosive substances is of fundamental importance in affording data for the study of their chemical characteristics and the evaluation of their explosive properties.

(2) *Heat of Explosion and Gases Evolved*.—The methods of determination of the heat of explosion and of estimating the volume and nature of the gases have hitherto been unsatisfactory so far as high explosives are concerned. For propellants the problem is simpler, as the pressures developed in the apparatus, even when they simulate those occurring in guns, are comparatively small, for example, not exceeding 25 tons per square inch. Methods have been described for high explosives, but in these the proportion of explosive to vacuous space has frequently been too small, thus introducing a condition unrepresentative of practice, or when this is avoided by the more practical method of detonating the explosive in its own volume enclosed in some resisting envelope, gases only, and not calorimetric values, have hitherto been reported (Poppenberg and Stephan, *Zeitsch. ges. Schiess- u. Sprengstoffw.*, 1910, 5, 291).

The difficulties to be overcome with high explosives are very great when it is considered that the pressures developed locally are of the order of 300 tons per square inch. Whilst a final form of the calorimetric bomb for measuring the heat of detonation of high explosives has not yet been reached, it has been found possible in a bomb of moderate capacity to measure the heat developed from the detonation of explosives pressed to a high density in containers representative of practical conditions. The difficulties of designing a bomb which withstands the blow without leakage have been overcome, and the gaseous products of detonation can be measured and analysed. The explosive, compressed to any

desired density, is retained in a stout envelope, usually of steel, and complete detonation is secured by applying to it an intense impulse from a fulminate or lead azide detonator, retained, as has been found necessary, in steel of considerable thickness. The detonator is fired electrically by an insulated connexion passing through the obturated plug of the bomb. The bomb is immersed in a calorimeter of the type described for the propellant bomb (Robertson, *Proc. Roy. Soc.*, 1907, [A], **79**, 320), and the gases collected in the gas holder described in that paper, water, ammonia, and hydrocyanic acid being also estimated.

Some of the values that have been obtained for the heat evolved by the detonation of simple explosives in this bomb are given in the following table, and the values for guncotton and for glyceryl trinitrate are added for comparison.

TABLE II.

Heat and Gases on Detonation.

Explosive detonated at density = 1.3.	Calories per gram (water gaseous).	Total gases, c.c. per gram.
<i>m</i> -Dinitrobenzene	820	727
Trinitrobenzene.....	940	820
Trinitrotoluene	924	728
Trinitrophenol	914	744
Trinitrophenylmethylnitroamine..	1090	794
Guncotton (Nitrogen, 13 per cent.)	982	875
Glyceryl trinitrate	1478	713 (Berthelot)

The comparatively high heat value for dinitrobenzene is of interest when it is remembered that this is not far from the value of the heat energy contained in some military propellants, but it was left to this war to demonstrate that a compound with only two nitro-groups in the benzene ring, and requiring an addition of 95 per cent. of its own weight of oxygen for its complete combustion, could be used without admixture as a high explosive for shell. Its other constants, which reflect its properties and possibilities, will be referred to below.

The values obtained for trinitrotoluene and for picric acid differ from those reported by Poppenberg, who gives 641 and 793 calories per gram respectively. The new results have been obtained, as has been said, by detonating the explosives enclosed in a steel envelope at a density of loading in the envelope of 1.3, and they agree with results calculated from gas analyses from larger quantities, also confined in steel envelopes and detonated in a large, exhausted vessel.

The heat values obtained for trinitrotoluene and picric acid are

interesting in that the difference in heat energy given by the two explosives is small, although trinitrotoluene requires 74 per cent. of its own weight of oxygen for its complete combustion, whilst picric acid requires only 45 per cent. This considerable disadvantage in the case of trinitrotoluene is, however, counter-balanced by the lower heat of formation of 2:4:6-trinitrotoluene (10.2 kg. cal.) (carbon-diamond) as compared with trinitrophenol (47.1 kg. cal. per mol.), or a difference of about 160 gram-cal. per gram in favour of trinitrotoluene. This difference is due to the energy lost by hydroxylation as compared with methylation of the benzene, as is shown by the molecular heats of formation (carbon-diamond), -10.6 kg. cal. for benzene, -3.8 kg. cal. for toluene, and +33.2 kg. cal. for phenol.

The sometimes alleged inferiority of trinitrotoluene to picric acid as an explosive therefore receives little support when total energies of the respective substances are considered. There is, however, a somewhat higher quantity of gas from unit weight of picric acid, as might be expected from its higher oxygen content.

It will be observed that trinitrophenylmethylnitroamine has a much higher heat of detonation than trinitrotoluene or trinitrophenol, and this is in accordance with all the properties of this substance, which is used as an energetic intermediary between the detonator and a main explosive.

It will also be seen that the total heat energy of all these explosives falls considerably short of that of glyceryl trinitrate, in spite of the high heat of formation of that substance, this being due to the difficulty in getting a stable nitro-compound containing enough oxygen in the form of nitro-groups to oxidise the combustible elements of the molecule.

The technique of the calorimetry of high explosives is being further developed in the direction of using charges of considerably greater magnitude, so that corrections due to the presence of initial detonant will be correspondingly reduced, and less sensitive explosives detonated with certainty.

(3) *Chemical Stability*.—The chemical stability of explosive compounds can be determined by the rate at which they undergo decomposition, an elevated temperature being required to bring this to a measurable degree for most of the explosives used in practice. In one of the methods considered, the explosive is caused to decompose either in a stream of inert gas, where the products are determined volumetrically (Will, *Zeitsch. angew. Chem.*, 1901, **14**, 743), or spectroscopically (Robertson and Napper, T., 1907, **91**, 764; Robertson, T., 1909, **95**, 1241). In another, the decomposition is followed by observing the rise in pressure of

the gases given off in a vacuum, as in the method devised by Farmer (T., 1920, 117, 1432), which is applied to most of the more stable nitro-compounds. In this case, the explosive is contained in a tube connected with a mercury manometer, the tube and its contents being kept at a constant temperature in a specially fitted bath.

Explosives appear to be continuously decomposing at a rate which is a function of the temperature, but that rate is slow at ordinary temperatures in the case of explosives capable of practical employment. Thus trinitrotoluene at 140° gives off gas extremely slowly. The cellulose nitrates are less stable than trinitrotoluene, and glyceryl trinitrate still less stable. At a temperature as low as 55°, the evolution of nitrogen peroxide from 5 grams of glyceryl trinitrate can be observed in a 2-metre tube by means of the spectroscope.

This intrinsic decomposition proceeds even when the explosive is dry; but hydrolysis may be superadded in the presence of moisture, and both of these types of reaction are accelerated by the products of decomposition. Thus nitrogen peroxide, a product of the degradation of cellulose nitrates and of glyceryl trinitrate, rapidly accelerates the intrinsic decomposition of these esters, possibly on account of its strongly oxidising properties, whilst the acceleration of their hydrolysis is due to its acid-forming properties.

It has been shown (*loc. cit.*) that retention of nitrogen peroxide in the presence of cellulose nitrate undergoing regulated decomposition induces an acceleration. Thus it was shown that the higher the concentration of nitrogen peroxide existing in the gases in contact with the heated cellulose nitrate, the greater was the amount by which the rate of decomposition exceeded the minimum rate characteristic of the completely purified explosive when it is caused to decompose with simultaneous removal of its volatile products. Even a nitro-compound like picric acid, which is very much more stable, has been found to undergo an accelerated decomposition in the presence of nitrogen peroxide, although, of course, at a temperature much above that required for this effect with cellulose nitrates.

The slow decomposition which occurs during warm storage for the most part results in the formation of less simple products than those developed on detonation, and the rate of their evolution is influenced by the chemical constitution and composition of the explosive, as well as by the following factors:

(a) The quantity of heat evolved by the decomposition of the

explosive; this has a positive value, but less than the heat evolved on detonation.

(b) The temperature of storage; the rate of decomposition is about doubled for a rise of 5° .

(c) The conductivity of the explosive for heat and its specific heat, especially where large masses are involved, since these properties determine the extent to which heat is retained in the central portions of the mass; explosives, like organic materials in general, are bad conductors of heat, the conductivity of many having been found to be about the same as that of porcelain.

(d) The action of the products of decomposition on the unchanged material; this includes such acceleration as that caused by nitrogen peroxide, mentioned above.

(e) The physical condition of the explosive; this influences the retention or diffusion, and possible elimination, of disturbing impurities.

(f) The presence of foreign substances; these may either exert a powerful accelerative influence, or, on the contrary, may reduce the rate of decomposition by combining with products which would otherwise accelerate.

Most explosive substances can be induced to undergo a regulated decomposition if care be taken steadily to withdraw, by suitable means, the heat evolved by the exothermic reaction and those gaseous products which act as catalysts in accelerating decomposition, for example, by leading a stream of gas through the system or by conducting the operation in a vacuum, or by permitting the environment to absorb the heat.

The temperature-coefficients of such decompositions lie between 1.7 and 2.3 for 5° . This is greater than for many other types of chemical reactions, for which the rate is approximately doubled for a rise of 10° . It is important that this temperature-coefficient should be known throughout a range extending from the storage temperature, on the one hand, to a higher one at which the rate of decomposition can be measured in a reasonably short space of time. Examples of temperature-coefficients which provide this link between warm storage temperatures and a much higher temperature are included, among others, in table III (p. 12).

These temperature-coefficients have been determined by various methods of experiment.

The decomposition over the longest range quoted is for glyceryl trinitrate, the method used being that described previously (Robertson, T., 1909, **95**, 1241). When that paper was written, 90° was the lowest temperature at which decomposition had been

TABLE III.

Temperature-coefficients.

	Temp.-coeff. for 5°.	Limits of experiment.
Mercury fulminate	1.7	50—80°
Glyceryl trinitrate.....	2.2	60—135°
Guncotton	1.9	125—150°
Tetryl	1.95	100—115°
Picric acid	2.3	140—180°
2 : 4 : 6-Trinitrotoluene	1.85	140—180°
2 : 4 : 5-Trinitrotoluene	1.8	120—140°
do.	1.8	140—180°

observed. Since then, in conjunction with W. S. Simpson, quantitative results have been obtained by the same spectroscopic method down to 60°. Certain refinements were introduced, such as distribution of the glyceryl trinitrate, present necessarily in larger quantities, over silica wool, and the use of a quartz observation tube lengthened to 2 metres. The over-all temperature-coefficient obtained between 60° and 135° was found to be 2.2 for 5°, and was fairly constant throughout this range.

Whilst there is thus no very great difference in the rate of increase in the velocity of decomposition with rise in temperature among explosives of widely different types, their resistance at the same temperature varies enormously.

Examples are given in table IV (p. 13) of the rates of decomposition of a number of explosives. An attempt has been made to institute a comparison among these rates by quoting the volume of gas evolved from 1 kilo. of the explosive per hour (after forty hours' heating) at 140°, either experimentally determined, or deduced from the results obtained at the nearest temperature at which the experiment was carried out.

The figures quoted are the rates of gas evolution at an early stage in the decomposition, before the usual marked acceleration caused by the products of decomposition sets in. This acceleration differs greatly in different explosives, and this has to be taken into consideration when questions involving safety are concerned.

Considering, in the first place, the gas evolved from those aromatic nitro-compounds given in the table, it is not until a trinitro-derivative is reached that a measurable gas evolution is obtained. Of these, the most stable is 1:3:5-trinitrobenzene, which gives off only a trace of gas when heated for many hours even at the high temperature of 180°, or nearly 60° above its melting point.

TABLE IV.

Stability of Explosives.

Rates of gas evolution in c.c. per hour after forty hours from 1 kilo. of explosive.

Explosive.	80°.	120°.	140°.	160°.	180°.
<i>m</i> -Dinitrobenzene	—	—	0*	—	—
2 : 4-Dinitroaniline	—	—	0*	—	—
1 : 3 : 5-Trinitrobenzene	—	—	0*	—	0.05
2 : 4 : 6-Trinitromesitylene	—	—	0.003	—	8.4
2 : 4 : 6-Trinitro- <i>m</i> -xylene	—	—	0.5	8.0	—
2 : 4 : 6-Trinitrophenol	—	—	0.6	—	—
2 : 4 : 6-Trinitroaniline	—	—	4	—	—
1 : 2 : 4-Trinitrobenzene	—	—	8	—	—
2 : 4 : 6-Trinitrotoluene	—	—	9	—	—
2 : 4 : 6-Trinitro- <i>m</i> -cresol	—	—	10	—	—
2 : 3 : 4-Trinitrotoluene	—	—	13	—	—
2 : 3 : 5-Trinitrotoluene	—	1.5	[24]	—	—
2 : 4 : 5-Trinitrotoluene	—	—	32	—	—
2 : 4 : 6-Trinitroanisole	—	—	32	—	—
2 : 4 : 6-Trinitrophenylmethyl- nitroamine	—	8	[128]	—	—
2 : 3 : 4 : 6-Tetranitroaniline ...	—	18	[288]	—	—
3 : 4 : 5-Trinitrotoluene	—	22	[352]	—	—
2 : 4 : 6-Trinitro-3-hydroxy- phenylmethylnitroamine	—	23	[370]	—	—
Cellulose nitrate (N ₂ =13%) ...	—	{ at 135° 2500 }	[5000]	—	—
Glyceryl trinitrate.....	—	{ at 115° 1660 }	[86,000]	—	—
Lead azide	—	—	—	—	40
Mercury fulminate	2.5	—	—	—	—

* Not measurable at 140°.

The influence of the successive introduction into the ring of nitro-groups is shown in the series dinitroaniline, trinitroaniline, and tetranitroaniline, where the fourth group induces a great increase in the gas evolution. In the case of some compounds, the introduction into the ring of a fourth nitro-group leads to an even more marked instability.

Examination of the products of decomposition of trinitrotoluene shows that they are very complex, but they contain a substance resembling the transformation product of uncertain constitution and lower stability, that is associated with the action of alkalis and of light. It is of interest in this connexion that the resistance to decomposition by heating of the mono-, di-, and tri-methyl derivatives of trinitrobenzene runs in line with that of their resistance to the formation of this transformation product by alkalis and by light.

Hydroxylation, as shown in the simpler series of trinitrobenzene and trinitrophenol, and of trinitrotoluene and trinitrocresol,

increases the gas evolution only to a slight extent. It has a more marked influence, however, in trinitrophenylmethylnitroamine, due, apparently, to an acceleration of hydrolysis, a feature which will be treated of later.

Examples are given of the arrangement of nitro-groups in the benzene ring. It will be seen that 1:2:4-trinitrobenzene is less stable than the 1:3:5-compound, and in the case of the isomerides of trinitrotoluene, the 2:4:6-compound is the most stable of all.

On reviewing the order of stability of the compounds in the table generally, it is of interest to note that their decreasing resistance runs in line with the ease with which they can be hydrolysed. Thus, in the case of the two last-mentioned series, the mobile character of one of the nitro-groups in the unsymmetrical trinitro-derivatives is well known. Again, when trinitrophenylmethylnitroamine is hydrolysed, methylamine and picric acid are among the products, and picric acid is found to accelerate the decomposition of the substance (Farmer, T., 1920, **117**, 1603). Picric acid is also found among its products of decomposition in the stability test, and it is no doubt due to the acid properties conferred on trinitrohydroxyphenylmethylnitroamine by the hydroxyl group that that substance possesses a lower stability than trinitrophenylmethylnitroamine.

Trinitroanisole, which partakes of the character of an ester, and is readily hydrolysed, is found to undergo a more rapid decomposition than picric acid.

Of the others, which are the more stable, as shown by their low gas evolution, indifference to hydrolysis is a characteristic feature.

It would thus appear from these indications of lower stability, in conjunction with greater hydrolysability, that the water produced by interaction of the oxygen of the nitro-groups and hydrogen in the side-chains or in the ring, may be a condition for greater chemical action, as shown by the volume of gas evolved.

Compared with the nitro-compounds in the table, the resistance to heat of the nitric esters, cellulose nitrate, and glyceryl trinitrate is of a much lower order.

This is thought to be due, perhaps, less to inherent instability in these nitric esters than to their ready hydrolysis by traces of water formed during the decomposition and the vigorous interaction of the products of hydrolysis.

In addition to considering the effect of the chemical nature of these substances as regards their rate of decomposition, however, it is necessary to take into account their physical condition, since their stability is greatly influenced by the state of aggregation.

Thus the decomposition of trinitrophenylmethylnitroamine was measured a few degrees below its melting point (129.1°) by the method of observing the rate of disengagement of nitrogen in a stream of inert gas, and the values obtained were extrapolated to 135° , a few degrees over its melting point. The disengagement at 135° , when it was actually liquid, was also determined by the same method, when it was found that the rate of decomposition of the liquid substance was fourteen times that which the solid would have had at the same temperature.

When the same explosive was brought into the liquid condition by adding an inert nitro-compound, it was found that it gave off in a vacuum about fifty times as much gas at the same temperature as it did when in the solid condition (Farmer, T., 1920, 117, 1603).

In the preceding table, the figures of gas evolution are referred to the liquid condition, for the sake of obtaining strict comparisons. To those compounds the melting points of which lay above the temperature of experiment, sufficient of an inert nitro-compound was added to render them liquid during the period of heating.

The increase in the rate of decomposition of an explosive in the liquid as compared with that in the solid state is doubtless connected with the greater mobility of the molecules in the liquid condition.

There are reasons for supposing that the decomposition of solid explosives takes place at the surface of the particles. Thus, Hinshelwood and Bowen (*Phil. Mag.*, 1920, [vi], 40, 569) have shown that the rate of gas evolution from solids which give off gas is conditioned by the amount of surface exposed. In working with mercury fulminate, W. L. Turner has shown that the degradation of fulminate on heating, although it does not give rise to a change in the external form of the crystals, can be followed by means of the difference in optical properties between unchanged fulminate and the products of decomposition. After fulminate has been heated until a considerable quantity of gas has been set free, the crystals present the appearance of a central, unchanged nucleus surrounded by decomposition products.

(4) *Sensitiveness to Shock*.—All explosives are more or less readily brought to detonation by a mechanical shock. The investigation of the degree of sensitiveness exhibited is important, as the sensitiveness largely determines the applications to which explosives can be put, and also the character of the precautions necessary to ensure safe manufacture and handling.

The explosive is tested for sensitiveness to two distinct types of

blow: direct impact and friction. The measurement of sensitiveness to direct impact admits of greater quantification, and I propose to deal only with it on this occasion.

The determination of sensitiveness to a blow is generally carried out in a drop-weight machine. The experiments are fraught with many difficulties, and few of the published data can be regarded as trustworthy.

The difficulties are chiefly due to the complex effect which the blow has on the explosive, to the great labour and expense in maintaining the striking surfaces constant throughout the work, and to the interpretation of the results obtained, which has for the most part depended on qualitative personal views.

These difficulties have to a great extent been overcome by the use of a falling weight instrument worked out by Dr. Rotter, of the Research Department, Woolwich. By this method, it is possible to reproduce accurately the disposition of the explosive, whilst the surfaces between which it is struck are carefully standardised by comparing the behaviour of the explosive under investigation with that of a standard explosive. The results of the blow are evaluated, not by personal observations of sound, flash, or by the imperfect guide of assessing the quantity of scattered residues, but by a quantitative measurement of the gas produced at the different heights of fall when the blow delivered has sufficient energy to cause decomposition of the explosive and gas to be evolved.

The results are given in comparison with a standard explosive according to the type under investigation, the usual standards being picric acid, gunpowder, and mercury fulminate. The sensitiveness is expressed in ratios, known as "figures of insensitiveness," which express the relative energies of the blows required to produce explosions of equal degrees of completeness throughout the scale from incipient to complete detonation. A table is appended giving some typical results. Picric acid is taken as 100, and the lower numbers refer to explosives of greater sensitiveness.

The range of sensitiveness is very great. At the one end lie the haloids of nitrogen, which can scarcely be handled without exploding, whilst at the other end are the aromatic nitro-hydrocarbons, which are brought to detonation only by a very heavy blow.

The sensitiveness of explosives to mechanical shock is undoubtedly closely related to their chemical constitution, but the relationships are frequently masked by differences in physical

character, which greatly modify the pressure developed by a blow of given intensity.

Theoretically, all explosives are decomposing very slowly, with evolution of heat, at the ordinary temperature. The energy which must be supplied to raise the rate of decomposition to explosion is a measure of the sensitiveness. It follows that all explosives increase in sensitiveness with rise in temperature. The quantity of heat liberated by the explosive on decomposition plays an important part in raising the rate of reaction to that of explosion, and it is found that, in similarly constituted substances, the higher the heat of explosion the less is the quantity of energy that need be added.

A good example of this is glyceryl trinitrate, which exhibits great sensitiveness when struck between two hard substances, but it is also exemplified in all the series of nitro-compounds into which nitro-groups are successively introduced. Further, in nitro-compounds containing the same number of nitro-groups, but differing in heat of formation, in consequence of the different arrangement of the nitro-groups, it is found that those are the more sensitive which have the lowest heat of formation, that is, presuming a similar metamorphosis to take place on explosion.

The following general observations can be made as to the relation of chemical constitution to sensitiveness.

Aromatic nitro-compounds with one or two nitro-groups in the ring are very insensitive. The effect of introducing more nitro-groups is successively to increase the sensitiveness. This is illustrated by the series of nitroanilines shown in table V (p. 18).

In all cases, increasing sensitiveness is associated with either some peculiarity of constitutional arrangement in the explosive or with higher heat of explosion due to the importation of more oxygen into it, so as to render the substance more nearly balanced for complete combustion. The influence of the position of nitro-groups in the case of isomerides of a substance like trinitrotoluene, for example, is, of course, of a much smaller order than that associated with the highly strained structure of compounds like fulminate and lead azide, as shown by their strongly endothermic character.

(5) *Rate of Detonation*.—The rates of detonation have, for the most part, been determined by the Dautriche method, a column of the explosive under standardised conditions of confinement being contained in a steel tube of 1·2 inches internal diameter and 0·1 inch wall, and detonated by a terminal charge of 50 grams of trinitrophenylmethylnitroamine.

TABLE V.

Sensitiveness of Explosives.

Figures of Insensitiveness (Picric Acid = 100).

	Figure of insensitiveness to impact.
<i>Initial detonants :</i>	
Mercury fulminate	10
Lead azide	20
<i>Nitric esters :</i>	
Glyceryl trinitrate	13
Nitrocellulose	23
<i>Nitro-compounds :</i>	
<i>p</i> -Nitroaniline	over 120
2 : 4-Dinitroaniline	over 120
2 : 4 : 6-Trinitroaniline	111
2 : 3 : 4 : 6-Tetranitroaniline	86
1 : 3 : 5-Trinitrobenzene	107
2 : 4 : 6-Trinitrotoluene	115
2 : 4 : 6-Trinitro- <i>m</i> -xylene	over 120
1 : 3 : 5-Trinitrobenzene	106
2 : 4 : 6-Trinitrophenol	100
2 : 4 : 6-Trinitrotoluene	115
2 : 4 : 6-Trinitro- <i>m</i> -cresol	101
2 : 4 : 6-Trinitrophenylmethylnitroamine	70
2 : 4 : 6-Trinitro-3-hydroxyphenylmethylnitroamine ...	56
2 : 4 : 6-Trinitrotoluene	115
2 : 3 : 4 ,,	92
2 : 4 : 5 ,,	102
3 : 4 : 5 ,,	102
2 : 3 : 5 ,,	108
2 : 3 : 6 ,,	111

The method of Dautriche is well known, and need be only shortly described. The detonation wave, passing along the column of explosive confined in its steel tube, causes detonators fixed to the ends of a loop of the detonating lead-covered fuse to start a wave of detonation in the fuse. These detonators are separated by a known distance in the explosive, and the meeting point of the two approaching waves is displaced from the real centre of the loop by an amount from which, knowing the rate of detonation of the fuse and the distance apart of its initiating detonators, the rate of detonation can be calculated. The meeting point of the waves is recorded as a sharp, transverse line marked on a lead plate, on which the fuse is laid. The lead-covered detonating fuse for this work was standardised in 3-metre lengths by the Mettagang apparatus, in order to obtain its rate of detonation.

The results given by some of the explosives mentioned in other connexions in this paper are as follows.

TABLE VI.
Rates of Detonation.

Explosive.	Density of loading.	Metres per second.
Trinitrophenylmethylnitroamine	1.63	7520
Guncotton (dry)	1.2	7300
Trinitrophenol	1.63	7250
Trinitrotoluene	1.57	6950
Trinitroxylenes	1.51	6600
<i>m</i> -Dinitrobenzene	1.56	6100
Mercury fulminate	loose	3000

The rate of detonation of an explosive is one of the chief characteristics which serve as an indication of its violence or shattering effect. Whilst the calorific value of an explosive gives the total possible energy which an explosive can exert, the rate of detonation is the rate at which the energy is evolved, and is of great importance as regards the effect produced. The effect of rate of detonation is well marked in the result of the pressure-bar tests, next to be described, a high rate giving a large value for the instantaneous maximum pressure, whilst at a similar density of loading with a lower rate, a lower pressure is obtained, although sometimes with a higher total blow.

The quantity of heat energy available seems to be related to the rate of its expenditure. Thus it will be seen from the table that the rate of detonation runs in line with the heat of explosion as given in an earlier section, and therefore, like this property, is to a large extent dependent on molecular structure.

(6) *Pressure Developed*.—For determining the degree of violence developed by an explosive, the methods hitherto in use have been inadequate. This has been due to insufficient weight being attached to the need for obtaining quantitative measurements, which have a definite physical meaning. Moreover, the importance of maintaining uniform and controlled conditions of such factors as density of loading and degree of confinement of the charge, have not always been sufficiently realised.

An advance in the direction of obtaining quantitative measurements of the pressures developed by explosives over a small measurable interval of time, which is a measure of the violence they exhibit, has been made possible by the application of the method of determining the pressure of a blow put forward by the late Prof. Bertram Hopkinson (*Phil. Trans.*, 1914, [A], **213**, 437). By this method, valuable results have been obtained, which

have thrown light on the properties of explosives and enabled choice to be made among them for specific purposes, such as to initiate detonation in other explosives, and it has proved to be of theoretical importance in obtaining insight into the properties of detonation waves. It has also been fruitful in the investigation of the design of mechanisms, such as detonators, fuses, and gaines,* since it affords definite and immediate information on the essential feature of such components, namely, the violence of the blow that they deliver. As the method developed, its usefulness as a check on supply was appreciated, and instruments were designed for control of the quality of such stores as have been mentioned.

The application of Hopkinson's principle to this wider field of research, and the design of a variety of instruments for the purposes mentioned above, were carried out at the Research Department, Woolwich, by Mr. H. Quinney, formerly Hopkinson's assistant, and a number of other physicists.

The principle on which the determination of the pressure is based depends on the fact that when a charge is fired against the end of a cylindrical steel bar ballistically suspended, a wave of compression travels along the bar and is reflected at the far end as a wave of tension. To investigate the properties of the wave, a short length of the end of the bar farthest from the delivered blow is cut off and the faces surfaced, the short piece (known as the time-piece) being caused to adhere closely to the bar, usually by a film of vaseline. The compression wave travels unchanged through the joint into the time-piece, but the film is unable to transmit a tension. Hence when the amplitude of the reflected tension wave reaching the joint becomes greater than that of the oncoming compression wave, the time-piece is projected off the end of the shaft with a momentum which depends on the pressure exerted by the explosive and the time taken by the wave to traverse the length of the time-piece. This momentum is measured by catching the time-piece in a ballistic pendulum, and the velocity of the propagation of the wave through steel being known, the mean pressure exerted during an extremely small time interval can be calculated. The principle thus essentially depends on the experimental separation of this momentum into its two factors of pressure and time. By the use in succession of time-pieces of different lengths, it is possible to make an approximation to the maximum pressure developed, and to get values for the mean pressure over various time intervals, and the time taken for the

* A term which has become common in connexion with explosive mechanisms, as signifying a tube containing an intermediary detonating explosive or system (Fr. *gaine*, a sheath).

pressure wave to reach its maximum amplitude and fall to nothing. The time interval over which the mean maximum pressure is normally measured is a two-hundred thousandth of a second, and the pressures developed in these experiments reach a magnitude of hundreds of tons per square inch. To protect the end of the bar against the application of such stresses, which no terrestrial substance would withstand, a standardised pellet of material, which is scattered on the explosion, is interposed between the explosive and the end of the bar. This has the effect of degrading the blow to a known extent. Values for pressure, quoted later, are thus

TABLE VII.

Results on Pressure Bar.

Explosive.	Thick- ness of steel enve- lope.	Density of loading.	Pres- sure in tons per sq. inch in 0.5 $\times 10^{-5}$ second.*	Density of loading.	Pres- sure.	Density of loading.	Pres- sure.
Tetryl	None (paper).	—	14.2	1.45	—	1.55	—
	$\frac{1}{16}$ "	1.3	31.7	1.45	34.5	1.55	35.1
	$\frac{1}{4}$ "	1.2	51.2	1.45	55.9	1.55	57.8
	$\frac{1}{2}$ "	1.2	62.3	1.45	—	—	—
T.N.T.	None (paper).	1.2	13.2	—	—	—	—
	$\frac{1}{16}$ "	1.2	—	—	—	1.55 (cast).	31.1
	$\frac{1}{4}$ "	1.2	46.1	—	—	1.55 (cast).	55.0
	$\frac{1}{2}$ "	1.2	56.2	—	—	—	—
Trinitro- phenol	None (paper).	1.2	11.8	—	—	—	—
	$\frac{1}{4}$ "	1.2	43.3	—	—	1.6 (cast).	54
	$\frac{1}{2}$ "	1.2	50.2	—	—	—	—
Trinitro- <i>m</i> - xylene ...	$\frac{1}{4}$ "	1.2	41.5	1.45	43.7	—	—
<i>m</i> -Dinitro- benzene...	$\frac{1}{4}$ "	1.2	32.9	—	—	—	—
2 : 4-Dinitro- toluene ...	$\frac{1}{4}$ "	1.2	31.1	—	—	—	—
Dinitronaph- thalene (crude) ...	$\frac{1}{4}$ "	1.2	14.1	—	—	—	—
Nitro- benzene... (liquid)	$\frac{1}{4}$ "	1.18	4.0	—	—	—	—
Nitro- benzene... (solid)	$\frac{1}{4}$ "	1.2	3.8	—	—	—	—
Benzene..... (solid)	$\frac{1}{4}$ "	1.0	3.8	—	—	—	—

* With constant pellet interposed.

always to be taken as an approximately known fraction of the actual pressure.

By addition of the momentum of the time-piece to that of the bar, which is readily measured by taking the amplitude of its first swing, a value for the total blow delivered to the end of the bar can be expressed in units of momentum without reference to the duration of the blow.

A large amount of work has been done by this method, but it is possible only to refer to a few of the results.

Some examples may be given of the differences brought out among explosives as regards their comparative violence, and the values (table VII, p. 21) at the same time exhibit some other features. The initiating system in all cases was an intense one, and was constant throughout.

Some description may be given of the character of the information that has been obtained in the investigations with the pressure bar.

In carrying out these experiments, it was found necessary to pay the greatest attention to maintaining as constant as possible the density of loading and the thickness of the containing envelope before it was possible to make any deductions.

In all the cases quoted, higher pressures occur at the higher densities of loading, but this result is obtained with the more heavily compressed explosives only when the initiating impulse is sufficiently intense to overcome their insensitiveness to detonation.

From the values given in the table, the important exaltation of effect due to the confinement of the explosive is very clear.

In the case of simple explosives, the measured pressures developed appear to be dependent on the rate of detonation, the heat of explosion, the volume of gas produced, and the density of loading, but further data under standard conditions are required before the effects due to each of these can be ascertained.

By retaining a constant system of initiating impulse, it is possible by this method to determine the sensitiveness of explosives in responding to a detonative blow. Explosives at high densities of loading respond with more difficulty, and especially when lightly confined.

In the case of mixtures, intimacy of contact of the components, obtained, for example, by prolonged incorporation of the ingredients, has also been proved to increase the pressures developed, and to counteract the fall in pressure that occurs with less well-incorporated mixtures when they are heavily compressed and initiated with only a moderate impulse.

Comparing, next, some of the different types of explosives given

in the table as to the pressures they develop, by taking the values obtained in an envelope of $\frac{1}{4}$ -inch steel wall, it is seen that the violence of the blow delivered in the same short interval of time ($1/200,000$ th of a second) is greater with tetryl than with picric acid or trinitrotoluene, and this is in line with all the constants of these substances that have so far been considered. It also affords an explanation of the use to which this explosive is put as an energetic intermediary between detonator and less sensitive explosive. There is little to choose between the results given by picric acid and trinitrotoluene, and this also is in agreement with their respective energy contents, and in fair agreement with observations of the fragmentation of steel containers, which, however, on the whole favour picric acid, with its slight advantage in rate of detonation and higher volume of gas.

The entry of another methyl group to form trinitroxylene brings down the violence, but it is still of a high order, and considerably surpasses that of *m*-dinitrobenzene, which contains nearly as much oxygen for its combustion.

Dinitronaphthalene, with its low heat of formation, gives a distinct explosive value, but the application of the intense impulse to which all these explosives were subjected did not cause any disruption of either nitrobenzene or benzene, the effect obtained being only that which was communicated from the initiating system. It does not appear, therefore, as might have been expected from their low heat of formation, that such a blow is capable of breaking up their structure. Dinitronaphthalene, although, from the point of view of oxygen available for its combustion, is little better than a mononitro-derivative of benzene, still appears to have a definite explosive property.

Just as a certain tardiness has been observed for certain explosives in attaining their proper rate of detonation, especially under an inadequate initiation, so also this has been found, especially in the case of liquid explosives, when they are detonated on the pressure-bar. This and many other applications cannot be described within the limits of this paper, but enough has perhaps been said to indicate the importance of the application, and for the purpose of further research the usefulness, of the principle enunciated by the late Prof. Bertram Hopkinson.

Under the headings of the various properties considered, some attempts have been made at correlation with the chemical structure of the explosive compounds. It does not seem possible, however, in our present state of knowledge to connect up all of these properties, which sometimes act in opposite directions.

Certain broad generalisations, of course, appear, chiefly with regard to the inherent energy of the substance influencing such properties as sensitiveness and violence, but chemical stability is more intimately connected with certain aspects of molecular arrangement. There is obviously overlapping in regard to these features of the influence of total energy and special constitutional arrangement, as has been shown in the case of sensitiveness. As will be seen, there is a wide field for work on all these aspects, as also into all the immediate phenomena of detonation.

PART II.

Explosive Properties of the Amatols.

The importance which the amatols ultimately assumed as the only filling for land service shell, for aerial bombs, and other munitions may warrant some sketch of the explosive properties of these mixtures.

Both the pourable mixture, 40/60 amatol (that is, 40 parts by weight of ammonium nitrate and 60 parts of trinitrotoluene), and the 80/20 mixture, were put forward by the Research Department, Woolwich, in March of 1915, as a result of trials which included investigations into their capacity as detonating fillings for shell, their rates of detonation, and their insensitiveness to shock.

The shortage of trinitrotoluene, which was met by the adoption of these mixtures, and especially of 80/20, in which the ingredients are present in nearly the correct proportions for complete combustion, called urgently for their adoption and manufacture on the largest scale, until, finally, the enormous output of 4000 tons a week was reached.

These explosives were of a type which had hitherto not been used for shell-filling in this country, and much had to be learned as to their chemical and explosive properties. These will now be shortly described, following the same order as in the preceding account.

Heat of Formation, Heat of Detonation, and Gases.—In the case of the balanced explosive 80/20 amatol (more nearly 79/21 for complete combustion), since the heats of formation of the constituents and of the products (CO_2 and H_2O) are known, the heat of detonation can be calculated. This heat of detonation has, however, also been determined in the calorimetric bomb for high explosives described above, and is found to be for 80/20 1004 calories per gram (water gaseous), whilst the value calculated from the heats of formation of trinitrotoluene, of ammonium

nitrate, and of the products carbon dioxide and water formed on detonation, is 1019. The agreement is thus fairly good, and is a useful confirmation of the values for the heat of formation of trinitrotoluene and the heat of detonation of the amatol. It is, of course, much more difficult to calculate the calorimetric value of mixtures, such as 40/60 amatol, which are not compensated for combustion, on account of the complexity of the products formed on detonation. The experimental value found for the detonation of 40/60 amatol is 920 cal. per gram (water gaseous).

A fairly good agreement is obtained in the case of 80/20 amatol between the experimental value for total gases evolved from 1 gram of the detonated explosive, 907 c.c., and 894 c.c., the calculated value. Amatol 40/60 gives off 892 c.c. of total gas per gram.

It will be seen that the addition of ammonium nitrate, with its high heat of formation, has no effect on the heat value of trinitrotoluene in 40/60 amatol, although the quantity of gas is increased, but with the theoretical proportion of the components for total combustion, an increase of more than 10 per cent. in total energy is obtained, and, at the same time, the largest volume of gas. The following table gives the experimentally found heat values and gases of these two amatols in comparison with those of trinitrotoluene.

TABLE VIII.

Amatols—Heat and Gases Produced.

	Calories per gram (water gaseous).	Total gases, c.c. per gram.
Trinitrotoluene	924	728
40/60 Amatol.....	920	892
80/20 Amatol.....	1004	907

Stability.—Whilst chemical stability is a necessity in the case of simple explosives which have to withstand a high temperature during either their preparation or their service life, so also with mixtures no less drastic a demand is made on the ingredients, but, in addition, it is necessary that there should be no chemical action between them.

Pure ammonium nitrate and pure trinitrotoluene have little action on one another, even at 120°, but interaction has to be guarded against when certain impurities are present in either of the technically manufactured products, as the concomitants of such interaction are evolution of heat, which may be dangerous, and the generation of gas, which is objectionable in several ways.

The increased mobility associated with the liquid state has been shown in the foregoing to induce a greater rate of decomposition in

simple explosives like tetryl; a similar acceleration occurs in the case of ammonium nitrate if its melting point is depressed by sodium nitrate, for example, so as to form a eutectic, liquid at the temperature of the experiment, when it is found that the rate of evolution of gas is markedly increased in contact with T.N.T. as compared with the evolution from the mixture of that substance and solid, pure ammonium nitrate.

The following gas evolutions show this:

	C.c. from 10 grams of explosive (50/50) in 40 hours.		
	At 100°.	At 110°.	At 120°.
Crude T.N.T. and NH_4NO_3 (pure)	1.2 c.c.	3.7 c.c.	6 c.c.
Crude T.N.T. and NH_4NO_3 containing 8% NaNO_3	1.2 c.c.	2.7 c.c.	18 c.c.

It will be seen that it is only when the temperature attains that of the melting point of the eutectic of ammonium nitrate and sodium nitrate, about 120°, that an increased reaction, as shown by the greater gas evolution, supervenes.

The above values are for crude trinitrotoluene, that is, trinitrotoluene containing, as has been shown from thermal analysis of the crude product, a little dinitrotoluene, due to incomplete trinitration, and about 4 per cent. of the isomeric trinitrotoluenes, mainly the 2:3:4 (1.5 per cent.) and 2:4:5 (2.5 per cent.). The reactivity with pure 2:4:6-trinitrotoluene is much less, being for the mixture of the pure ingredients represented by only 2 c.c. of gas under the above conditions at 120°, trinitrotoluene alone giving only about 0.05 c.c.

The gas evolution from the mixture of the pure ingredients of 80/20 amatol is 0.5 c.c. under the same conditions.

As these explosives were now used for the first time in quantity for filling munitions of different kinds, and came into contact with a great variety of metals and materials, their compatibility with these was the subject of much study, partly by climatic trials and by experimental work, including the application of the vacuum stability method throughout a range of temperatures. It is not, however, possible to pursue this part of the subject further than the example already given.

Although the isomerides of trinitrotoluene cause a somewhat greater gas evolution with pure ammonium nitrate than the symmetrical compound, the effect of certain impurities in the ammonium nitrate is very much greater. The violence with which pyridine reacts with the more highly nitrated aromatic compounds in which there are two nitro-groups ortho to one another had

been the subject of investigation in the Research Department, and it was accordingly of interest when ammonium nitrate containing pyridine was shown to give rise to tumultuous evolution of gas, even in the cold, with the isomerides of trinitrotoluene, but not with the symmetrical compound. The effect of this interaction can be strikingly shown by the frothing over which occurs when amatol 40/60 containing a small quantity of pyridine or ammonium thiocyanate, for this has a similar effect, is melted in a narrow-necked vessel.

Insensitiveness to Impact.—When this characteristic of the amatols is determined by the method described above, it is found that they are insensitive substances, and they are also found to be insensitive to friction. The influence of heat on the amatols has been investigated as to its effect on their sensitiveness, comparison being made with picric acid, and taken as 100 at 15°.

TABLE IX.

Figures of Insensitiveness of Amatols.

	At 15°.	At 50°.	At 80°.
Amatol 80/20.....	111—120	108	120
Amatol 40/60.....	111	—	107
Picric acid	100	—	75

The amatols are thus by themselves fairly insensitive mixtures, and heating does not raise their sensitiveness, but this may be appreciably increased by the presence of gritty matter and of certain salts.

Rate of Detonation.—This was determined by the Mettegang and Dautriche methods already mentioned. The values for the amatols and trinitrotoluene were found to be as follows.

TABLE X.

Rates of Detonation of Amatols.

	Metres per second.
Trinitrotoluene (cast) at density 1.57.....	6950
Amatol 40/60 (cast) at density 1.55	6470
Amatol 80/20 at density 1.3	4620
" " 1.5	5080
" " 1.5	5200

} in steel tube of 0.1 in.
thickness of wall.

5200 in tube 0.24 in. thick.

Two points of interest appear from this table: addition of ammonium nitrate up to 40 per cent. has comparatively little effect in reducing the rate of detonation much below that of trinitrotoluene, and the rate of detonation of 80/20 amatol is still of the high order of 5000 metres per second, and is little raised

beyond this value when the thickness of the steel wall of the container is increased.

Pressure developed.—In the mixtures of trinitrotoluene with ammonium nitrate, the inorganic salt has been sometimes described as a diluent of the high explosive. So far as the explosive properties of the mixtures are concerned, this is an erroneous view. Thus it has been shown that the total heat energy of the fully compensated 80/20 mixture, as determined experimentally, is the same as the value calculated on the assumption of chemical interaction between the ingredients. Again, the substitution of 40 per cent. of ammonium nitrate reduces the rate of detonation of trinitrotoluene only to a slight extent, and even when 80 per cent. of the salt is present, the rate of detonation is still of a high order. Ammonium nitrate, however, is much more than a convenient source of oxygen, for it can be shown by the quantitative method of the pressure-bar that it can by itself break up explosively with a certain degree of violence.

The following table gives the pressures developed under the same conditions of confinement when ammonium nitrate alone and incorporated with 5, 10, 15, and 20 per cent. of trinitrotoluene, all at density of loading of 1.3, are detonated by the help of the same initiating system. Amatol 40/60 and trinitrotoluene, both in the cast condition, are included for comparison.

TABLE XI.

Pressures Developed by Ammonium Nitrate and Amats.

Ammonium Nitrate.	Trinitrotoluene.	Tons per sq. inch in 0.5×10^{-5} sec.
100	0	12.5
99.5	0.5	15.2
99	1	18.3
98	2	20.0
95	5	25.2
90	10	30.5
80	20	38.1
40 (at density 1.55)	60	53.9
0 (at density 1.55)	100	55.0

A correction of 3 tons has to be deducted for the effect of this initiating impulse, but after this allowance has been made, it will be seen that ammonium nitrate has developed a considerable proportion of the pressure associated with the performance of 80/20 amatol, although it will be observed that small proportions of trinitrotoluene have the effect of activating the ammonium nitrate to a much greater extent than the quantity added would apparently warrant, an indication in itself of the explosive nature

of the ammonium nitrate. It is thus clear that in amatol the ammonium nitrate contributes, not only oxygen to supply the deficit of trinitrotoluene in this respect, but it also behaves in the mixture as the explosive which it is.

Amatol 40/60, which was always used in the cast form, and so had usually a higher density, gives higher pressures than amatol 80/20. Its violence, approaching that of trinitrotoluene as thus measured, is in line with its rate of detonation, which, as has been shown, is little below that of trinitrotoluene, in spite of the 40 per cent. of ammonium nitrate present in the mixture.

Having now described some of the properties and constants of the amatols, it is not necessary to go further into the performance of this explosive, of which the type 80/20 was used in such enormous quantities during the war. It is sufficient to say that it met the demands of the fighting forces and received their commendation.

Before concluding this address, I should like to take the opportunity of referring to the work of my colleagues, past and present, on the scientific staff of the Research Department, Woolwich.

They have devoted themselves with enthusiasm to the study of the chemical and physical problems involved, and to the pursuit of methods of obtaining quantitative knowledge where only qualitative information existed before, and their results have had the three-fold value of advancing scientific knowledge generally, of making it capable of application to matters of national importance, and of indicating directions for further work.