EXPLOSIVES

A SYNOPTIC AND CRITICAL TREATMENT OF THE LITERATURE OF THE SUBJECT AS GATHERED FROM VARIOUS SOURCES

BY

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PREFACE.

THE application of physical chemistry to the problems of explosives is to be desired for several reasons. A glance at well-known works on explosives, such as those of O. Guttmann, L. Gody, and M. Eissler, will show that in considering explosives one is dealing with a topic in which the desired coöperation of practice and science is far from having reached the most advantageous point. On closer inspection it appears that the indefatigable labor of decades in the manufacture and use of explosives has yielded rich experimental material which is still waiting a thorough working over and coördination in accordance with scientific laws. Both scientist and technologist might achieve many interesting results, hitherto entirely overlooked, by a thorough mutual examination of this field of work.

The days of purely empirical progress in the technique of explosives are numbered. The development of our knowledge of explosive processes forces us more and more into the narrow field of an exact chemistry of explosives, or, in other words, a physical-chemical science dealing with the velocities of chemical reactions and chemical equilibria at very high temperatures and pressures. It is to the diligent use of these physical-chemical methods that we owe the lasting worth of the classical experiments of Berthelot and Abel. Of more recent works those of van't Hoff, le Chatelier, and Nernst hold prominent places.

In view of the facts just mentioned it seems a worthy task to gather together the facts recorded in the literature of explosives, arrange them in accordance with the physical-chemical views, and take a survey of the present status of the chemistry of explosives and its most important aims. By this means the subject may be presented for convenient reference and future use. Such a treatment of the subject should be of value primarily for the theoretical scientist who might desire to secure a detailed acquaintance with the practical problems relating to explosives, in order, perhaps, to subject them to a mathematical-chemical treatment such as we have indicated above as desirable.

But there is an advantage also for the technologist who is interested in the scientific treatment of his subject and who does not possess an advanced mathematical knowledge, in so far as such a classification can reveal to him the advantages of the physical-chemical standpoint for the further development of our knowledge of explosive processes. On this account theoretical-mathematical discussions have been completely omitted in the following pages, however much they might, perhaps, have contributed to a clearer conception of the idea and sometimes might even have simplified the subject.

As an essential part of the work in hand it is deemed necessary to give references, in the following enumeration, to the original literature, especially so far as they touch those points, such, for instance, as the catalytic reaction acceleration, which might be of special significance in the technique of explosives. As has been intimated in the title of the book, we have made use of only such experimental facts as are found in the literature within every one's reach. We have refrained from mentioning other material which has become known to us through our personal relations with the technique of explosives. The restraining influence of industrial discretion may be given as an excuse, if we have, by way of precaution, omitted critical remarks where contradiction exists between literature and our own knowledge of the facts.

DR. H. BRUNSWIG.

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EXPLOSIVES

PART I.

CHAPTER I.

GENERAL BEHAVIOR OF EXPLOSIVE SYSTEMS.*

CONDITIONS GOVERNING EXPLOSIVE REACTIONS.

1. Among the many phenomena which may accompany an explosion, such as detonation, flame and the shattering of near-by objects, the most important is a sudden rise of pressure in the immediate region of the explosive. Freezing water, steam at high tension and highly compressed gases, when expanding suddenly, can produce certain phenomena similar to those produced by explosions, but in each of the former cases there occurs, at the moment of transformation, a sudden fall from an original high pressure, while in the case of explosive substances there is a sudden rise in pressure.

2. Explosive reactions, such as are produced by explosive gaseous mixtures or explosives ordinarily

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* Literature: M. Berthelot, Force mat. exp., 1883. E. Sarrau, Theorie des explosifs, 1895. E. Cohen, Studien zur chemischen Dynamik, 1896. J. van't Hoff, Vor. theor. phys. Chem., 1898–1900. P. Duhem, Thermodynamique et Chimie, 1902. J. W. Mellor, Chem. Stat. Dyn., 1904. R. Pictet, Zur mechanischen Theorie des Explosivstoffe, 1902. J. P. Wisser, The Phenomena and Theories of Explosion (without date). V. Jüptner, Expstoff. Verbren, 1906. W. Nernst, Theo. Chem., 8; 1907.

so-called, are always accompanied by a chemical transformation, which, being accelerated by the heat developed and by other causes, proceeds with greater or less velocity. Chemical reactions which do not give rise to increased pressure, because no gaseous decomposition products are set free, exhibit no explosive phenomena. Therefore, thermite, the well-known intimate mixture of a metallic oxide, or other oxygen carrier, with finely divided aluminum, which on being ignited undergoes rapid combustion, but furnishes solid or liquid reaction products only, does not belong to the list of explosives.

3. From the practical as well as the theoretical standpoint facts arise which make it difficult to form an exact conception of an explosive and to fix the conditions which must obtain in order that a given substance may be designated as an explosive. Many phenomena indicate that an explosive is in general to be considered as an unstable system which undergoes spontaneous transformation within an almost infinitely small period of time.* This conception is based essentially upon observations of gaseous mixtures and other homogeneous systems where practically no energy is wasted, but rather where the mere presence of an accelerating, and apparently a nonparticipating agent, is sufficient to cause an explosive transformation.

This conception meets with difficulties so soon as it is applied to a heterogeneous system, where the contact surfaces of the component parts are very small and in certain cases absent. It is true that this difficulty can theoretically be partly overcome by the hypothesis of a mutual reaction of the components in the form of vapor, even in the case of such difficultly volatile com-

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* W. Nernst, Theo. Chem., 672; 1907.

ponents as potassium nitrate or cellulose. Opposed to this view, however, is the fact that systems which at ordinary temperatures are supposed to react extremely slowly often give rise at these temperatures to reactions entirely different from those which take place explosively at higher temperatures, so far at least, as has been determined experimentally.*

Explosives have also been defined as substances whose atomic groups are in unstable equilibrium. According to this conception we might compare them to a cone standing on its apex.† Again it has been conceived that there is a condition of atomic tension‡ which, like a suddenly released spring, can perform work. Such attempts at explanation are applicable only to homogeneous systems. They cannot, without effort, be applied to the technically important types of explosives having as a base heterogeneous mixtures composed, in part, at least, of stable substances.

4. A better comprehension of the meaning of the term "explosive substance" may be had by determining what conditions are necessary to bring about an explosive reaction. Although in practice these conditions have proved to be exceedingly variable yet in the case of every explosion the following conditions, at least, must obtain:

(*a*) The reaction liberates heat and is therefore essentially exothermal.

(*b*) The transformation is one of complete decomposition and hence the explosive system presents extreme sensitiveness.

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* *Vide* sections 23 and 25.

† H. Ost, Lehrbuch der chemischen Technologie, 1907, Abschnitt Explosivestoffe.

‡ A. v. Baeyer, Ber., **18**, 2278; 1885.

(*c*) The decomposition is definitely of such character as to render an explosion so possible that it may be caused by any suitable initial impulse or shock.

The explosive reaction is necessarily connected with these three conditions and in varying degrees which are determined by the nature of the particular explosive system under consideration. Many substances, such as fulminates, nitrogen halides and nitric esters, which in their explosive decomposition develop heat, are also characterized by extreme sensitiveness, and on this account are to be placed in the first class of explosive substances. A second class includes those compounds or mixtures that are also capable of undergoing marked exothermal decomposition, but are less sensitive and therefore demand an especially strong initial impulse to cause them to explode. It is quite easy to understand why substances such as ammonium nitrate, picric acid, potassium chlorate and others have, until quite recently, been considered nonexplosive. Finally, we note that systems possessing an explosive potentiality, but which are capable of several different transformations, frequently seem to prefer that transformation which results in an explosion. This fact might easily suggest the erroneous idea that the direction which a chemical transformation takes generally coincides with that in which the reaction evolves the most heat.*

(*a*) *Exothermal reactions.*

5. A mixture of porous carbon with liquid oxygen is explosive,† while liquid carbon dioxide is not, although both systems, in going over to gaseous carbon dioxide,

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* M. Berthelot, Mech. chim., 1878.

† The explosive "Oxyliquit" is such a mixture.

reach the same final condition with a nearly equal increase of volume. This difference in explosibility is explained by the fact, that in the first case the reaction when once begun is rapidly accelerated by an enormous heat development, while in the second case the reaction is brought almost to a standstill by the absorption of heat. This particular case may be thus generalized: A system which requires outside energy to enable it to undergo a transformation from its initial conditions possesses no explosive properties. If, however, such a system can be so changed that a development of heat is made possible, as, for instance, by the substitution of one component for another, the chief requisite of an explosive is potentially fulfilled. This principle may be better illustrated by an example,* such as the reaction $M_2C_2O_4 = 2\,CO_2 + M_2$ (wherein M represents any metal), which, at normal temperature, takes on an explosive character when it is exothermal.

TABLE 1. RELATION BETWEEN HEAT DEVELOPMENT AND EXPLOSIVE POTENTIALITY.

Reaction.	Heat development (in calories).*	
$ZnC_2O_4 = Zn$ (solid) $+ 2\,CO_2$	−49.1	not explosive.
$PbC_2O_4 = Pb$ (solid) $+ 2\,CO_2$	−16.7	
$CuC_2O_4 = Cu$ (solid) $+ 2CO_2$	+ 5.9	doubtful.
$HgC_2O_4 = Hg$ (liquid) $+ 2\,CO_2$	+17.3	explosive.
$Ag_2C_2O_4 = Ag$ (solid) $+ 2\,CO_2$	+29.5	

* Calculated from 1 kilogram of water at 15° C.

6. Berthelot in particular has pointed out the close connection between explosive reactions and thermochemical relations. In his fundamental work just

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* M. Berthelot, Force mat. exp., 1883, II, 125. English translation by C. N. Hake and W. Macnab, "Explosives and Their Power," 1892.

referred to[*] he not only discusses in full the usual methods and apparatus for the determination of the quantity of heat liberated in explosive reactions, but also describes in detail how the heat of an explosive reaction may be calculated by the application of thermochemical laws. This calculation is based on H. Hess's heat law of constant mass and is universally applicable when both the mass and constitution of the products of the reaction are known.

It is well known that the heat liberated by a change of chemical condition in a system is equal to the excess of the heat of formation of the final products over the heat of formation of the initial products. If we designate by Q the heat liberated, and by Q_1 and Q_2 the heat of formation, from their elements of the bodies, found at the beginning and at the end of the reaction, then we have

$$Q = Q_2 - Q_1.$$

For instance, nitroglycerin when exploded is decomposed according to the equation:

$$4\,C_3H_5(ONO_2)_3 = 12\,CO_2 + 10\,H_2O\ (\text{vapor}) + 6\,N_2 + O_2.$$

Substituting for the nitroglycerin and for the products of its explosion the corresponding heats of formation, which are known for a large number of explosive substances,[†] we have:

$$Q = 428.5 - 98.9 = 329.6.$$

These numbers are to be referred to constant pressure.

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[*] See also M. Berthelot, Traité pratique de calorimétrie chimique, 1905.

[†] M. Berthelot, Thermochemie, 1897. J. Thomsen, Thermochemische Untersuchungen, 1882–86. W. Ostwald, Thermochemie, 1893. H. Landolt, R. Börnstein and W. Meyerhoffer, Physikalisch-chemische Tabellen, 1905. Ann. bureau long., 1904.

If the explosion occurs under constant volume, as is the case in the explosion bomb, then the heat developed is increased by the heat equivalent of the work performed which, under constant pressure, as in the open air, is used up in the expansion of the gases and the compression of the surrounding atmosphere. The two functions just named, i.e., the heat developed under constant volume Q_{tv} and the heat developed under constant pressure Q_{tp}, are related for all gaseous systems, as expressed in the following equation:

$$Q_{tv} = Q_{tp} + 0.54\,(n_1 - n) + 0.002\,(n_1 - n)t,$$

where n and n_1 represent the number of gram molecules of gas shown in the equation before and after the reaction; and t, the temperature of the surrounding air reckoned from 0 degrees up. In seeking the heat of explosion of nitroglycerin for constant volume, such, for instance, as obtains in the explosion bomb, it must be remembered that the volume of the explosive itself, when compared with that of its decomposition products, is so small that it may be neglected for the purpose in hand; hence, n in the preceding equation then becomes zero and

$$n_1 = \tfrac{29}{4} = 7.25.$$

If the explosive process is carried on at ordinary temperature $t = 15°$ C. and

$$\begin{aligned} Q_{tv} &= Q_{tp} + (0.54 \times 7.25) + (0.002 \times 7.25 \times 15) \\ &= 329.6 + 4.1 = 333.7. \end{aligned}$$

This quantity of heat is set free from 227 grams (1 molugram*) of nitroglycerin and therefore 1 kilogram of nitroglycerin produces 1470 calories of heat. The

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* Charles E. Munroe, Molugrams and Molugram-liters, Proc. A. A. A. S., **38**, 176; 1889.

quantity of heat found in the explosions calorimeter is about 100 calories higher than this, due to the fact that the heat of condensation of the water formed by the explosion has been measured with the heat produced by the explosion itself. The values obtained by calculation and those found by actual experiment agree very closely, however, in their final results.

This method for the calculation of the heat of an explosion is as equally applicable to explosives whose heat of formation is negative (endothermic bodies) as to those whose heat of formation is positive (exothermic bodies). In the former case, Q_1, the heat of formation of the initial substance is negative and the equation becomes: $Q = Q_2 + Q_1$. The right-hand side of the equation now consists of positive qualities only. The left-hand side must, therefore, show a corresponding increase, and hence endothermic explosives are in general characterized by a decided exothermal transformation. In fact, the heat developed by the explosion of a number of endothermic substances, such as acetylene, cyanogen, nitrogen sulphide (N_4S_4) and others, is unusually high. The explosive process is, however, not conditioned on an exothermal reaction; it is unimportant in this connection whether a compound is endothermic or exothermic, and in no case can a negative heat of formation be considered an index of an explosive potentiality. From the thermochemical standpoint this is self-evident, for the negative heat of formation of the substance gives the heat developed by a decomposition into its elements, whereas in the case of its explosion other decomposition products only may be formed. That no doubt may exist on this score we append a table of the best-known explosives with their corresponding heats of formation

TABLE 2. HEATS OF FORMATION OF SEVERAL EXPLOSIVES.

No.	Explosive.	Heat of formation of 1 kg. cal.	Literature.
✓1	Acetylene, gaseous.......	−1977	Mixter, Am. J. Sci., (4) **12**, 347; 1901.
2	Hydrogen nitride, solid...	−1565	Berthelot & Matignon, Ann. chim. phys., (6) **27**, 289; 1892.
3	Cyanogen, liquid.........	−1317	Berthelot, Ann. chim. phys., (6) **18**, 127; 1889.
4	Stibine, gaseous..........	− 694	Berthelot and Petit, Ann. chim. phys., (6) **18**, 77; 1889.
5	Sulphur nitride, solid.....	− 693	Berthelot & Vieille, Ann. chim. phys., (5) **27**, 204; 1882.
6	Ammonium hydronitride, solid.	− 317	Berthelot, Thermochimie, 1897, II, 72.
✓7	Diazobenzene nitrate, solid.	− 284	Berthelot & Vieille, Mem. poudr. salp., I, 103; 1882.
✓8	Mercury fulminate, solid..	− 221	Berthelot & Vieille, Mem. poudr. salp., II, 6; 1884.
9	Trinitrobenzene, 1.2.4, solid.	− 43	Berthelot & Matignon, Ann. chim. phys., (6) **27**, 289; 1892.
10	Trinitrobenzene, 1.3.5, solid.	+ 26	Berthelot & Matignon, Compt. rend., **113**, 246; 1891.
11	m-Dinitrobenzene, solid..	+ 40	
✓12	Trinitrotoluene, solid.....	+ 115	
13	Phosphine, gaseous.......	+ 144	Ogier, Ann. chim. phys., (5) **20**, 14; 1880.
✓14	Picric acid, solid.........	+ 204	Sarrau & Vieille, Compt. rend., **93**, 213, 269; 1881.
15	Nitromannite, solid......	+ 357	
✓16	Nitroglycerin, liquid.....	+ 415	Berthelot, Ann. bureau long., 723; 1904.
17	Nitroethane, liquid......	+ 424	Berthelot & Matignon, Ann. chim. phys., (6) **30**, 565; 1893.
18	Potassium picrate, solid...	+ 440	Sarrau & Vieille, Compt. rend., **93**, 203, 269; 1881.
19	Nitromethane, liquid....	+ 472	Berthelot & Matignon, Ann. chim. phys., (6) **30**, 565; 1893.
20	Methyl nitrate, liquid....	+ 518	Berthelot, Ann. bureau long., 723; 1904.
21	Ethyl nitrate, liquid.....	+ 533	
✓22	Nitrocellulose, solid......	+ 559	Sarrau & Vieille, Compt. rend., **93**, 213, 269; 1881.
23	Potassium chlorate, solid.	+ 766	Berthelot, Ann. bureau long., 709; 1904.

calculated on one kilogram of the substance. It appears from this table that among compounds generally recognized as being capable of explosive decomposition are found not only those with negative heats of formation, such as mercury fulminate, diazobenzene nitrate and others, but also a still greater number, such as nitroglycerin, nitrocellulose, nitromannite and the like, with positive heats of formation.

7. In the case of many explosive transformations, two or more courses of reaction are possible. Hence, in any particular case if the composition of the products of the explosion is not known the calculation of the heat of decomposition by the method described cannot be made. As an actually observed example of the great difference in the quantity of heat developed through a difference in the courses of the chemical transformation, we might cite in this connection guncotton, an explosive which has in itself an insufficient quantity of oxygen for complete combustion. It may be seen by calculation that the course of the explosion may be carried out under such varying conditions that the gaseous products, carbon dioxide, carbon monoxide,

TABLE 3. DEPENDENCE OF THE HEAT OF EXPLOSION UPON THE COURSE OF THE REACTION.

Weight of guncotton in grams calculated on a liter exploding chamber.	Equations for the decomposition of guncotton = 4 $(C_{24}H_{29}(NO_2)_{11}O_{20})$.	Calories.
50	$30\,CO_2+71\,CO+41\,H_2+CH_4+35\,H_2O+22\,N_2$	820
150	$35\,CO_2+67\,CO+39\,H_2+3\,CH_4+34\,H_2O+22\,N_2$	825
300	$47\,CO_2+57\,CO+29\,H_2+13\,CH_4+32\,H_2O+22\,N_2$.	900
500	$63\,CO_2+42\,CO+16\,H_2+20\,CH_4+37\,H_2O+22\,N_2$.	1010

hydrogen, methane, and water vapor, appear in varying proportions. A. Noble* has found the heat of explosion of guncotton having a nitrogen content of 13.2 per cent, corresponding to the formula $C_{24}H_{29}(NO_2)_{11}O_{20}$, as shown in Table 3.

8. The heat of an explosion may nearly always be arrived at, in a much simpler manner than by calculation, through the use of the explosion calorimeter, taking always a weight of explosive bearing a known ratio to the inner volume of the vessel in which the

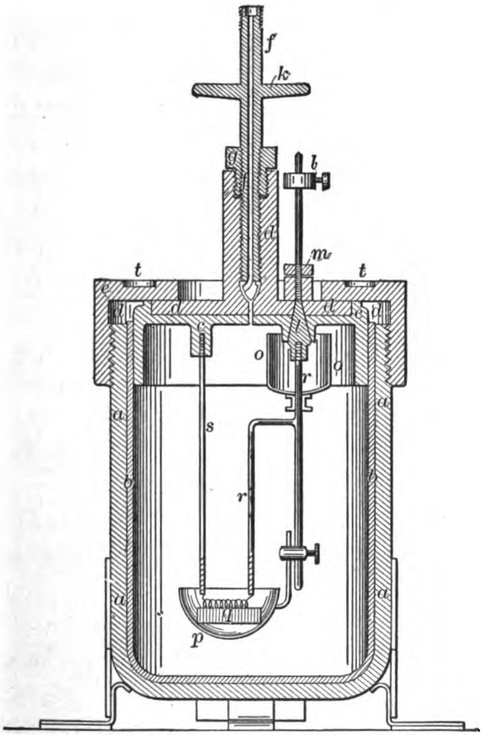

FIG. 1. Calorimetric Bomb.

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* A. Noble, Phil. Trans., A., **205**, 201; 1905.

explosion is to take place. The explosive transformation is carried out in an explosion bomb fitted with an electrical priming device.* This is contained in a water calorimeter whose temperature can be held quite constant with the help of a stirring apparatus and a very sensitive thermometer. The increase in temperature caused by the explosion is observed. This multiplied by the water equivalent of the apparatus gives the quantity of heat set free by the explosion.

9. The energy content of an explosive system, expressed as the "heat of explosion," is a measure of the maximum potentiality for work. The considerable differences in energy contents existing among the technically important explosives may be seen from Table 4. Among explosives having the greatest energy content are nitroglycerin (explosive gelatin, dynamite, nitroglycerin powder), and nitromannite. In the second class are guncotton (guncotton powder), picric acid and several ammonium-nitrate explosives. Finally come black powder, ammonium nitrate itself and — what seems astonishing at first glance — mercury fulminate. Mercury fulminate does not serve directly as an explosive, but as a primer, and for this purpose it is one of the most powerful. While in general practice the comparative worth of an explosive often appears different from that expressed in the energy-content table, a deeper study of the subject shows that these heats of explosion may be regarded as a measure of relative efficiency in the case of those explosives standing near each other, because their technical use is similar.

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* M. Berthelot, Force mat. exp., I, 221; 1883. E. Sarrau and P. Vieille, Mem. poudr. salp., II, 133; 1885. W. Macnab and E. Ristori, Mitt. Art. Geniew, **26**, 93; 1895: **35**, 1131; 1904.

TABLE 4. ENERGY CONTENT OF IMPORTANT EXPLOSIVES.

No.	Name.	Heat of explosion, calories.*	Work in kilograms.	Comparative value.†
1	Explosive gelatin (7 per cent collodion cotton)	1640	700,000	100
2	Nitroglycerin	1580	670,000	96
3	Nitromannite	1520	645,000	92
4	Dynamite (75 per cent nitroglycerin)	1290	550,000	79
5	Nitroglycerin powder (40 per cent nitroglycerin)	1290	550,000	79
6	Guncotton (13 per cent N)	1100	465,000	66
7	Guncotton powder	900	380,000	54
8	Collodion cotton (12 per cent N)	730	310,000	44
9	Ammonium nitrate explosive (ammonium nitrate and 10 per cent nitronaphthalene)	930	385,000	58
10	Picric acid	810	345,000	49
11	Black powder	685	290,000	41
12	Ammonium nitrate	630	265,000	38
13	Mercury fulminate	410	175,000	25

* Calculated on 1 kilogram, explosive, constant volume and liquid water.

† Taking explosive gelatin as 100.

A surprising result is obtained by a comparison of the energy content, expressed in calories, of the explosion of powerful explosive substances with that of the burning of ordinary fuels. Thus 1 kilogram of petroleum in burning to carbon dioxide and water furnishes about 12,000 calories; coal, about 8000 calories; and dry wood, 3500–4000 calories; while dynamite (with 25 per cent kieselguhr) in exploding furnishes only 1300 calories. The energy content of explosives is usually thought to be very great, while really they are technically valuable only because they liberate all their energy in a very short space of time. As a fact, explosives are unproductive and costly sources of energy.

(*b*) *Sensitiveness.*

10. Every system that possesses explosive potentiality has also a characteristic sensitiveness. The degree of sensitiveness that explosive substances and mixtures exhibit varies considerably. In the technical sense, an explosive system is characterized as being the more sensitive the less the energy, of whatever kind it may be, that is required to bring about an explosive reaction.

11. Theoretically, an explosive reaction must be capable of being brought about without loss of energy, if we accept the theory (section 3) that all explosive systems are to be conceived of as being already in a state of slow decomposition, and that a sufficient acceleration of the action, by means of a suitable agent, is all that is necessary to so accelerate the transformation that it takes on an explosive character. Yet, as already pointed out (section 3), the technically important transformations take place principally with heterogeneous substances, and furthermore, they occur at first only on the surfaces of contact of the component parts as, for example, between potassium chlorate and starch. The velocity of the reaction depends entirely upon the size of the surfaces in contact with each other and sinks to zero if these are lacking. The sensitiveness of such heterogeneous mixtures of stable components exists only after the substance has been so prepared that a sufficient number of surfaces of contact have been created, as, for instance, in the case of black powder, by melting the sulphur about the other components.

From the foregoing it might be concluded that sensitiveness of the highest possible degree is to be desired in order to overcome, with a minimum energy, the time- and force-consuming resistance which opposes the explosive decomposition. Yet practical considerations of the admissible sensitiveness of explosives prescribe a limit of readiness of decomposition as well as a low degree of sensitiveness. Extremely sensitive substances, such as the diazo compounds, nitrogen halides and the like, are difficult to manipulate. The danger of an accidental explosion occurring with such substances is so great that no practical use has been found for them, notwithstanding the high explosive force in many of them. On the other hand, a too small degree of sensitiveness, such as may be found in the case of moist or wet explosives, is shown to be detrimental to the utilization of the energy of the explosive, since, in this case, even the strongest initial impulse is not able to bring about the explosion.

12. The great diversity, with regard to sensitiveness, which has been observed among the substances capable of explosion, is to be accounted for partly on chemical and partly on physical grounds.

13. Certain groups of atoms have a special tendency to explosive decomposition, and the hypothesis has been proposed that in such cases, where even a slight initial impulse is sufficient to cause the substance to explode, we are dealing with a specifically loose molecular structure. From the study of the compounds of acetylene, A. v. Baeyer* has come to the conclusion that the high degree of sensitiveness of the acetylides, and especially of the polyacetylides, is due to a considerable inner strain on the carbon bonds. Since the direction of the lines of force between carbon atoms united by multiple bonds is deflected from the straight

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* A. v. Baeyer, Ber., **18**, 2276; 1885.

line, it follows that the strain is proportionately increased. J. H. van't Hoff * explains that the existence of the many explosive substances found among the compounds of carbon is due to the chemical inertness of the carbon bonds, which allow the existence of molecules whose arrangement *in no way conforms* to molecular equilibrium. A slight mechanical impulse is thus often sufficient to overcome the molecular tension and to bring about the transition to a more stable arrangement and union of the atoms. This view, according to which the sensitiveness is due to the strained position of certain carbon bonds, has also been extended to other elements, and, according to J. H. van't Hoff,† the following atomic groups are especially characterized by the more or less ease with which they break down:

$O - O$ in ozone, in peroxides and others; example $C_2H_3O.O - O.C_2H_3O$, acetyl peroxide.
$O - Cl$ in chlorates, perchlorates and others; example $CH_3.O - Cl$, methyl hypochlorite.
$N - Cl$ in NCl_3, nitrogen trichloride.
$N = O$ in inorganic and organic nitrites, in nitro bodies and others; example $C_2H_5.O.N = O$ ethyl nitrite.
$N = N$ in diazo compounds, in hydronitric acid and in others; example $C_6H_5.N = N.O.NO_2$ diazobenzene nitrate.
$N \equiv C$ in the fulminates, in cyanogen C_2N_2 and others.
$C \equiv C$ in acetylene C_2H_2 and in the polyacetylenes.

Where carbon or hydrogen is in contact with an oxygen atom in such strained molecular combinations as exist in the organic nitrates, the decomposition of

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* J. H. van't Hoff, Ansichten uber die organische Chemie, 1881, I, 34; II, 240.

† J. H. van't Hoff, Vor. theo. phy. Chem., 1900, III, 95.

the compound takes place with the development of considerable heat. The oxidation products produced by this decomposition (carbon dioxide and water) are among those compounds which in their formation give rise to the greatest development of heat. This may explain the fact that the sensitiveness of the organic nitrates and nitro bodies increases with an increasing number of nitro-groups, as in the case of "nitrated" glycerin where the sensitiveness is greatest in the case of trinitroglycerin and seems very slight in the case of mononitroglycerin,* or that of nitrocellulose where the higher its nitrogen content the more easily will it explode from a blow or from heat.† Mononitrophenol does not detonate with a detonator containing 2 grams of fulminate. Dinitrophenol, however, detonates with a detonator containing 1 gram of the same substance, while trinitrophenol requires a detonator containing but 0.3 gram to bring it to complete detonation.‡ Reasoning from similar relationships, Berthelot comes to the conclusion that, other things being equal, the sensitiveness of explosive substances is the greater the more the heat developed by the explosive reaction is.§

14. In line with the foregoing is the fact that many endothermic compounds, which in general develop more heat than exothermic compounds, are also known to be highly sensitive. The compounds of nitrogen with the halogens (nitrogen chloride, bromide and iodide) are among the most sensitive substances with which we are acquainted. According to Berthelot,‖

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* A. Mikolajzak, Glückauf, **22**, 629; 1904. W. Will, Ber., **41**, 1107; 1908.

† J. M. Eder, Ber., **13**, 169; 1880.

‡ W. Will, Chem. Ind., 131; 1903.

§ M. Berthelot, Force mat. exp., I, 73; 1883.

‖ M. Berthelot, Force mat. exp., I, 390; 1883.

their tendency to decomposition becomes the more marked in proportion as the atomic weight of the halogen becomes greater, and at the same time their endothermic character increases. The mercury compound of hydronitric acid, HgN_6, far exceeds in sensitiveness, under blows or friction, the very sensitive mercury fulminate, $Hg(CNO)_2$; the breaking of a crystal of the former substance always causes an explosion.* This fact is particularly noticeable because mercuric hydronitride and mercury fulminate present a number of characteristics in common; both salts have the same molecular weight, the same density and almost the same heat of decomposition; furthermore, the products of their explosion have the same volume, and, in both cases, are gases that do not undergo dissociation:

$$HgN_6 = 3\,N_2 + Hg.$$

$$Hg(CNO)_2 = N_2 + Hg + 2\,CO.$$

Besides the halogen compounds of nitrogen and the derivatives of hydronitric acid just mentioned, the diazo compounds, as well as the fulminates, and the metallic acetylides are characterized by both a considerable negative heat of formation and a high degree of sensitiveness. On the contrary, those explosives which are exothermic compounds, such as nitroglycerin, nitromannite, nitrocellulose and nitrostarch, possess a considerably lower sensitiveness. Yet highly sensitive substances, such as lead picrates,† are occasionally

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* Th. Curtius, Ber., **24**, 3345 (1891). Th. Curtius and J. Rissom, Prak. Chem., (2) **58**, 261 (1898). M. Berthelot and P. Vieille, Mem. poudr. salp., VIII, 7; 1895. L. Wöhler and O. Matter, Z. ges. Schiess Sprengstoffw., **2**, 181, 203, 233, 265 (1907).

† A. Dupré, Mem. poudr. salp., XI, 94, 1901.

found in this group of substances with positive heat of formation.

15. From the foregoing, sensitiveness and heat of formation appear to be related, yet the laws of this relationship have not been completely explained. This is probably due to the influence which the physical condition of the explosive substance exercises on its sensitiveness, and this is a factor which is very difficult to bring under a common law. Among them might be mentioned physical state,* viscosity, structure, density,† hardness and perhaps also conductivity for heat, sound and the like. In the test for sensitiveness such considerations are often much more important than differences in the atomic structure of the molecule. By successive compressions of an explosive mixture its sensitiveness can be brought to the vanishing point, a fact which has often been noticed in the case of compressed detonators as well as cartridges of explosives; it has been observed by Berthelot and others (section 74) even in the case of highly sensitive chlorate mixtures.

16. The sensitiveness of an explosive mixture apparently bears no relationship to that of its component parts. This applies also to added substances which in themselves are not explosive. It is a well-known fact that hard, sharp-edged admixtures, such as sand, powdered glass and even metallic particles, increase considerably the sensitiveness of an explosive towards shock, blow and friction, and the explosives industry makes frequent use of this principle. It has not yet been indisputably demonstrated that the influence of such hard admixtures upon the sensitiveness under a

* W. Will, Ber. Kon. angew. Chem., II, 425; 1903.

† F. Lenze, the same, p. 401.

blow is due to the concentration of the pressure on the sand or glass points. The sensitiveness is often greater on softer metals than on harder ones. Yet, admixtures lessen the sensitiveness when they have a tendency to soften the explosive, or, when they inclose its smallest particles like an elastic envelope. For this reason, substances such as water, methyl alcohol, acetone, also glycerin, paraffin, vaseline, and even camphor, caoutchouc, and fatty oils have found applications as admixtures in the manufacture of explosives.* It is found, for example, that if cottonseed oil be mixed in varying proportions with finely crystallized picric acid, the addition of more than 3.2 per cent of oil to the picric acid entirely destroys its ability to be detonated by blows or friction, and even by the influence of 2-gram detonators. Other fatty oils, especially castor oil, have a similar effect and each of such admixtures seems to have its own specific influence.† If the protecting envelope, which weakens the effect of the initial impulse upon the explosive, is broken, even partly, the sensitiveness again increases. If, for instance, a mixture of 9 parts picric acid with 1 part nitronaphthalene, be warmed until the latter melts, and then the mixture is allowed to cool and solidify, the mass cannot be caused to explode by the detonation of a 2-gram detonator. If the same mass be now finely powdered, and then compressed to the same density as the previous solid mass, it can be detonated without fail with a 1-gram detonator.

17. The sensitiveness of an explosive increases with elevation of temperature, a fact which is in harmony

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* M. Berthelot, Force mat. exp., II, 317; 1883. See also Dautriche, Compt. rend., 143, 641, 1906: 144, 1030; 1907. E. Désortiaux, Dict.-aire exp., 1893; O. Guttmann, Ind. Exp., 1895; J. P. Cundhill and J. H. Thomson, Dict. Exp., 1895; J. Daniel, Dict. mat. exp., 1902.

† K. Esop, Mitt. Art.-geniew., 30, 644; 1899.

with the general acceleration of exothermal reactions by increase of temperature, though it is not easy to explain every case thereby. According to A. W. Cronquist,[*] nitroglycerin confined between steel plates required under the fall-hammer for detonation:

At 15° C.	0.8 mkg. of energy;
At 30° C.	0.6–0.7 mkg. of energy;

according to experiments of others:[†]

At 16° C.	0.2 mkg. of energy;
At 94° C.	0.1 mkg. of energy;
At 182° C.	slightest blow.

Nitroglycerin explosives (guhr dynamite, explosive gelatin, gelatin dynamite) show similar behavior (Fig. 2).[‡]

18. Information as to the sensitiveness of explosives at various temperatures is recorded for but a very few substances. This is partly due to the difficulty experienced in expressing the degree of sensitiveness in units of any particular form of energy. As a rule, that lowest amount of energy developed by a blow which is just able to bring about a true explosion is the figure sought. But already the nonconformity of the results of different experiments made to determine the sensitiveness of nitroglycerin towards shock demonstrates the imperfection of our methods of testing. Notwithstanding the most careful adjustment of experimental conditions (see further on), the most contradictory results are occasionally obtained because the kinetic energy employed is not evenly distributed over the substance to be tested. Many circumstances which

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[*] A.W. Cronquist, Berg-u. Hüttenmänn. Z., 221; 1894.

[†] L. Gody, Mat. exp., 271; 1896.

[‡] W. Will, Kon. angew. Chem., II, 421; 1903.

are but little understood favor a local concentration of the impulse and cause explosion from an impulse which otherwise is able to produce a similar

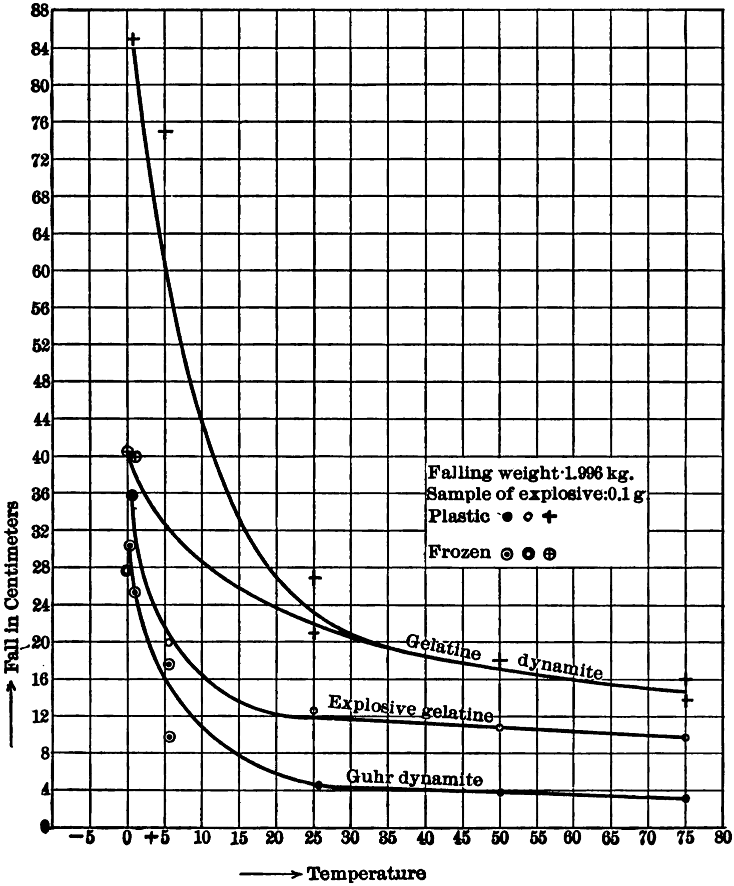

FIG. 2. Relation between Temperature and Sensitiveness.

result only with a much more sensitive substance.* Explosive liquids which adhere to flat surfaces, or are

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* Ph. Hess, Z. angew. Chem., **17**, 545; 1904. W. Will, *loc. cit.*

held by capillary tension, seem especially easy to detonate by a blow. Perhaps this phenomenon explains the heightened sensitiveness of explosives which contain partly frozen nitroglycerin often observed in practice,* although nitroglycerin itself in the solid state is much less sensitive than when in the liquid state.

The ordinary methods for the determination of the sensitiveness of explosive substances must, from the foregoing considerations, be restricted to recognizing qualitative differences. The following are the most important tests usually applied.†

1. *Percussion Test.* One-tenth gram of the substance to be tested is inclosed in thin tin foil and laid on a base of brass, iron or other material. An iron or brass rod of suitable dimensions is set on top of the sample so prepared and is then struck several direct blows with a hammer of known weight.

This kind of test for sensitiveness under a blow can be carried out more precisely by the use of an impact machine. Fig. 3 shows an impact machine, such as has been used for this purpose.‡ The device consists of a vertically sliding weight *a* and an inserted anvil *b*, whose construction is shown in Fig. 4. A small steel cylinder *B*, set in the steel block *A*, has drilled in its upper surface a round hole *E*, 1 millimeter deep and 7 millimeters in diameter. The explosive to be tested is packed into this hole and inclosed within a small piece of tin foil. The plunger *D*, which, while held in place

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* Ph. Hess, Z. angew. Chem., **17**, 545; 1904. W. Will, *loc. cit.*

† W. Will, Chem. Ind., 1903; 131. K. Esop. Mitt. Art. Geniew., **30**, 644; 1899. Mém. poudr. salp., XII, 134; 1903.

‡ L. Lenze, B. Kon. angew. Chem., II, 399; 1903: Z. ges. Schiess Sprengstoffw., **1**, 287; 1906.

by the crosspiece *C*, moves freely in a vertical direction and whose under surface fits exactly into the hole drilled in the steel cylinder *B*, is slightly pressed down on the sample of explosive, covered with tin foil, and the fall-hammer (Fig. 3) is then allowed to fall upon it.

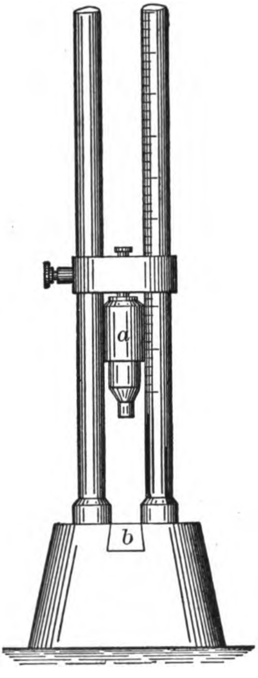

FIG. 3. Impact Machine.

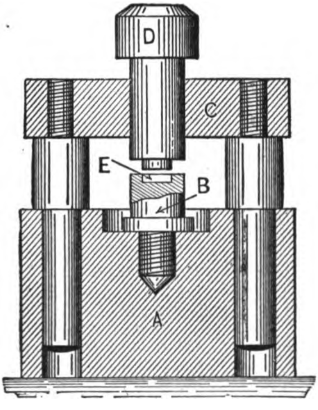

FIG. 4. Construction of Anvil and Plunger.

2. *Friction Test.* One-tenth gram of the substance to be tested is well rubbed in a rough porcelain mortar. If the mortar is warmed or if sharp sand, coarse powdered glass, or other similar substance be added to the explosive, the test is made more sensitive. This test may also be carried out by rubbing the explosive sub-

stance between two wooden blocks covered with emery cloth.

3. *Shooting Test.* The substance to be tested is shot into from a gun at short range under conditions where the thickness of the target, the velocity of the projectile and other factors may be varied.

4. *Behavior with a Mercury Fulminate Detonator.* A capsule of tin foil is filled with the substance to be tested and a fulminate detonator is placed in the middle of the mass and detonated. The degree of sensitiveness of the explosive is judged by the strength of the detonator which will cause it to detonate. Instead of allowing the explosive to lie loose it may be inclosed in a lead cylinder. Under these conditions substances may be detonated which are not detonated when unconfined.

5. *Temperature of Detonation.* One-tenth gram of the substance to be tested is placed in a test tube and subjected to gradually increasing temperature, and it is noted at what temperature ignition, explosion or detonation takes place.

6. *Ignition Test.* Two and one-half grams of the substance to be tested are heated gradually in an iron dish on an oil bath and ignited with a flame. It is noted whether the combustion takes place quietly or is accompanied by explosion or detonation. According to another method of procedure, 1 gram of the substance to be tested is thrown on a red-hot iron plate. In still another method, 3 grams of the substance to be tested are put in a test tube and ignited by means of a powder fuse.

The data obtained with an impact machine* are given in Table 5. The fall-hammer used weighed 2 kilograms,

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* W. Will, Z. ges. Schiess Sprengstoffw., I, 209; 1906.

and was of a somewhat different construction from that described above. In the table, column 1 gives the names of the explosives employed, and column 2 the observed height of fall of the hammer. The reciprocals of the figures in column 2 express the relative degrees of sensitiveness of the explosives. The comments indicate how, by means of such data, it is possible to divide the different technically important explosives into classes expressing the different degrees of safety with which such explosives may be transported.

TABLE 5. EXPLOSIVES ARRANGED ACCORDING TO THEIR SENSITIVENESS UNDER THE FALL HAMMER.

CLASS I. HEIGHT OF FALL UP TO 7 CENTIMETERS.

Name.	Fall in centimeters.
Mercury fulminate	2
Trinitroglycerin (dry)	4
Lead picrate	5
Silver picrate	5
Iron picrate	7
Copper picrate	7
Dinitroglycerin (dry)	7
Guhr dynamite (plastic)	7

Comment: Detonators and explosives of like sensitiveness detonate by ignition. Transportation unsafe.

CLASS II. HEIGHT OF FALL, 7-25 CENTIMETERS.

Name.	Fall in centimeters.
Explosive gelatin (plastic)	12
Explosive gelatin (frozen)	12–15
Gelatin dynamite (plastic)	17
Guhr dynamite (frozen)	20
Explosive gelatin from dinitroglycerin (dry)	25
Guhr dynamite from dinitroglycerin (dry)	25

Comment: Very sensitive towards shock or blow, burn rapidly or explode on ignition. Danger of explosion in transportation.

CLASS III. HEIGHT OF FALL, 26-100 CENTIMETERS.

Name.	Fall in centimeters.
✓ Wurfel pulver (a cubical smokeless powder)	20–30
Trinitrocresol	30
Cheddite, type 60	32
Rottweiler leaf powder (smokeless) No. 1172	32
✓ Smokeless sporting powder	30–45
Leaf powder (smokeless)	30–54
✓ Picric acid*	35–95
Cheddite, type 41	36
Hexanitrodiphenylamine	40
Trinitrobenzene	40–50
✓ Tetranitromethylaniline*	40–65
✓ Trinitrotoluene*	57–90
Zinc picrate	60
✓ Black powder (Hirschmarke) 4	70
✓ Ammonium picrate	80
Sodium picrate	80
✓ Blasting powder	85
✓ Compressed guncotton, with 15 per cent water	85
Trinitrodimethylaniline	95
✓ Compressed collodion cotton, with 15 per cent water	100
✓ Black powder (coarse grain)	100
Roburite I, a	105

* Under different experimental conditions, such as: moist or dried; in powder form or pressed; loose or in tin foil; with or without plunger.

Comment: (*a*) Black powder, slightly sensitive towards shock and blow; easily ignited; burns up rapidly on ignition with fuse. An explosion in transportation not impossible.

(*b*) Chlorate explosives, fairly sensitive to shock and blow; difficultly ignited and not at all with fuse. Explosion in transportation not impossible.

(*c*) Aromatic nitro bodies, sensitive to shock and blow, difficultly ignited and not at all with fuse. Explosion in transportation not impossible.

(*d*) Nitrocellulose with 15 per cent water, slightly sensitive to shock and blow, difficultly ignited and not at all with fuse. Explosion in transportation not impossible.

(*e*) Smokeless powder, fairly sensitive to shock and blow, relatively easily ignited; burns quickly away (puffs off) on ignition with fuse. Explosion in transportation not impossible.

CLASS IV. HEIGHT OF FALL, 100–200 CENTIMETERS.

Name.	Fall in centimeters.
Ammoncarbonite	110
Astralite	110
Donarite	110
Dinitrobenzene	120
Rottweiler saltpeter blasting powder	135
Dinitrophenol	150
Petroklastit	150
Trinitroxylene	170
Trinitronaphthalene	175
Fulmenit	Over 180
Wetterfulminit	" 180
Rottweiler safety powder	" 180
Anagons blasting powder	" 180
Guncotton with over 20 per cent water	" 180
Collodion cotton with over 20 per cent water	" 180

Comment: Nitrocellulose with over 20 per cent of water not sensitive to shock or blow; difficultly ignited and not at all with fuse. Explosion in transportation impossible. Safety powders, little sensitive to shock and blow; difficultly ignited and not at all with fuse. Explosion in transportation impossible. Aromatic nitro bodies little sensitive to shock and blow; difficultly ignited and not at all with fuse. Explosion in transportation impossible.

19. The importance attached to the sensitiveness of explosive substances may be realized from the inspec-

tion of regulations governing their commercial transportation.* This matter is of moment not only in the economic development of the explosive industry, but it is closely connected with the common good. Explosives whose transportation is attended by especially great danger on account of their high sensitiveness are *entirely* forbidden in traffic.

(c) *Initial impulse.*

20. Initial ignition, or, more generally, initial impulse is that impulse which is necessary in order that a sensitive system, capable of exothermal transformation, is caused to explode. Since the resistance which, especially in the case of heterogeneous systems, prevents spontaneous explosive decomposition must first be overcome, the initial impulse performs a very essential, though only preparatory, work.

21. In the case of homogeneous systems, i.e., gaseous mixtures or liquid explosives, this work may be regarded as consisting in a breaking up of single molecules, as in the case of the dissociation of the molecules of water into hydrogen and oxygen, when a moist explosive mixture of chlorine and hydrogen is exposed to the action of a beam of light. In the case of heterogeneous systems it produces first of all physical changes which are essential for the explosion, such as local melting of the sulphur in black powder, whereby the various component parts of the powder are brought so close together that a mutually accelerative momentum, usually a rise of temperature, can cause the explosive reaction to take place. Unless the components of

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* Section B of the German railroad regulations of Oct. 26, 1899. H. Wichelhaus, Z. ges. Schiess Sprengstoffw., 1, 208; 1906. W. Will, do., 1, 209; 1906.

black powder were brought together in this way it would undoubtedly last thousands of years without the least decomposition in the direction of explosion. In many cases the explosive substance is enveloped by a thin film of some inert substance which, as in the case of moist nitrocellulose, must first be removed by vaporization, or in some other way be neutralized before the reaction velocity necessary for decomposition can be attained. But when the mere presence of a substance (nonparticipating so far as the end products are concerned) is sufficient to bring about the explosion, such, for example, as the presence of platinum black in a mixture of hydrogen and oxygen, the work of the initial impulse sinks to zero, and this substance acts simply as an accelerating agent for a reaction which has already commenced to take place.

22. Any kind of energy such as the various forms of mechanical energy (impact, pressure, friction), all kinds of radiating energy (heat, light, electricity, radium emanations,* etc.) and even chemical energy may be used to bring about an explosive decomposition. To make the most effective choice for each particular case from these various forms of energy is one of the most important problems of the chemistry of explosives, both in the field of practice and in the laboratory.

The law of equivalent transformation of energies, as seen in other fields, does not seem to hold when applied to their potential power to cause an explosive reaction, and it is, therefore, not at all a matter of indifference which kind of energy, in any given case, is used to bring about an explosion. In many cases the reaction is

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* W. P. Jorissen and W. E. Ringer, Ber., **39**, 2093; 1906. A mixture of chlorine and hydrogen was made to combine partially by the aid of radium bromide.

brought about by a light blow, but is not effected by the use of an equivalent amount of heat. In other explosive systems, violent mechanical impulses have little or no effect, while the action of a chemically active ray of light, even for a short time, brings about the explosion. Mercury fulminate is more sensitive to shock than silver oxalate. If the two substances are heated side by side, the oxalate will explode before the fulminate.* To what extent the different forms and physical characteristics of the two substances affect these results (section 16) cannot now be judged.

23. Notwithstanding our knowledge of the behavior of sensitive substances toward the various initial impulses, the problem of choosing the most effective method of bringing about the explosive reaction is not yet satisfactorily solved. The character and intensity of an initial impulse influence the course of an explosive reaction to such a large extent that it has been said, and not without justification, that the effectiveness of an explosion depends more upon the initial impulse than upon the explosive itself. F. Abel † thus described an experiment which illustrates the significance of the initial impulse: Two iron cylinders, closed at one end, were charged in the same manner with black powder

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* M. Berthelot, Force mat. exp., I, 71; 1883.

Note. The recent experiments of one of us, Kibler, showed that mercury fulminate puffed off (detonated) at 210° C., while silver oxalate puffed off at 245° C. The sample to be tested was dropped into a thin copper cartridge case about 2 inches in length and ¼–⅕ inch in diameter. This was plugged loosely with a small piece of cotton, passed through a piece of wood, and immersed for exactly 5 seconds in a bath of molten "bismuth metal." If it failed to puff off, the sample was changed, the temperature raised 5 degrees and the trial repeated.

† F. Abel, Phil. Trans., **159**, 67; 1869. E. Sarrau, Mém. poudr. salp., X, **43**, 49; 1899.

and the explosion brought about in one by means of a fuse and in the other by means of a detonator. In the first case the cylinder remained intact, while in the other it was broken in small pieces. The behavior of ammonium nitrate shows that in the case of a simple explosive compound, the course of the reaction may be greatly modified by the intensity of the initial impulse. Of the seven or eight possible ways in which this salt may decompose three are explosive,* as follows:

TABLE 6. DECOMPOSITION OF AMMONIUM NITRATE.

No.	Decomposition equation.	Q* Heat of explosion, calories.	V_0 Gas volume, liters.	$Q \times V_0$.
1	$2NH_4NO_3 = 2N_2 + 4H_2O + O_2$.....	421	976	411,000
2	$2NH_4NO_3 = N_2 + 4H_2O + 2NO$....	140	976	137,000
3	$NH_4NO_3 = N_2O + 2H_2O$.........	151	836	126,000

* Q at constant volume; water as vapor.

The product, $Q \times V_0$, is described by M. Berthelot as a characteristic expressing the maximum work performed by the explosion.† Reaction No. 1, in which all the nitrogen is set free, gives the highest results; it is brought about by sudden heating to a very high temperature under great pressure, and can actually be accomplished only with the aid of a strong detonator. Reaction 2, in which only the nitrogen of the ammonium radical is set free, is the result of an insufficient initial impulse with a weak detonator. By gradual heating without material increase of pressure, as with a free flame, ammonium nitrate decomposes according to reaction 3, in which all the nitrogen remains in combination with oxygen.

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* M. Berthelot, Force mat. exp., II, 183; 1883.

† M. Berthelot, Force mat. exp., I, 66; 1883.

24. Of all the possible initial impulses only those few that combine reliability with safety in manipulation have acquired importance. These may in the end be referred to the following typical methods of initiation:

(*a*) Initiation by means of a spark, heat or flame.
(*b*) Initiation by impact.
(*c*) Initiation by means of a detonator.
(*d*) Initiation by transmission of an impulse (influence).

(*a*) *Initiation by means of a spark, heat or flame.*

25. This kind of initial impulse is based on the theory that chemical reaction is accelerated by rise of temperature. Most reactions are doubled in velocity by a rise of about 10 degrees in temperature.* Lesser accelerations, and also much higher ones (even to sevenfold), are known. Incidentally, it is to be mentioned that the acceleration quotient often changes with the temperature. In the case of explosives this acceleration quotient for equal rises of temperature seems to be considerably more than double, and, in the case of nitrocellulose, reaches fourfold.†

M. Berthelot ‡ has shown that substances, which, by gradual increase of temperature, are not explosive, such as picric acid, trinitronaphthalene, potassium chlorate, etc., can nevertheless be caused to explode if they are suddenly heated to a much higher temperature than is necessary to bring about decomposition (section 3). In order to demonstrate this in the case of potassium chlorate a glass tube of 25 to 30 millimeters diameter,

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* J. van't Hoff, Vor. theo. phys. chem., I, 224; 1898.

† W. Will, Mitt. Zentral. wissen. techn. Unt., **3**, 25; 1902.

‡ M. Berthelot, Ann. Chim. Phys., 6, Series **16**, 23; 1889. Mém. poudr. salp., X, 280; 1899.

closed at one end, is held in a large gas flame in an almost perpendicular position so that the flame covers from about 50 to 60 millimeters and heated till the bottom of the tube is at a red heat. In the meantime, a glass rod, which has been drawn out at the end to the thickness of a stout wire, is dipped several times in molten potassium chlorate. When several decigrams of the salt remain clinging to the rod it is dipped down into the heated tube until about 10 millimeters distant from the bottom, taking care not to touch the sides of the latter. The potassium chlorate melts and falls slowly, drop by drop, onto the bottom of the red-hot tube. Each single drop explodes with a sharp report as soon as it comes in contact with the glass.

The following experiment, devised by A. Dupré,* leads likewise to the same conclusion: A 0.5 millimeter platinum wire which is in connection with a powerful electric current, is bent in the form of a loop in such a way that the two ends do not come into contact with one another. A drop of melted potassium chlorate is laid on this loop, and at first a current is sent through the wire which is sufficient only to melt the mass of potassium chlorate on the rod. Then the full power of the current is suddenly sent through the wire with the result that an explosion of the potassium chlorate almost invariably takes place. The experiment is not successful if traces of potassium chloride from a former experiment are present since this substance induces a rapid, but not explosive decomposition, at a lower temperature.

To an explosive spontaneous decomposition of potassium chlorate by sudden overheating is due the powerful explosion which took place on the 12th of May,

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* A. Dupré, J. Soc. Chem. Ind., **21**, 217; 1902.

1899, in the Kurtz works at St. Helens.* The potassium chlorate was contained in casks of 254 kilograms' contents each, and the magazine contained altogether not less than 156,000 kilograms. The explosion began from a fire which had caught on the wood of a crystallizing box saturated with potassium chlorate. The flames reached the magazine with great rapidity. Soon the wood of the casks caught fire and heavy white fumes arose. The workmen who had fled at the outbreak of the fire stopped a short distance away and watched the conflagration with interest without having an idea of the danger which hovered over all the spectators. It could be seen how the fire from the east row of casks, feeding on the streams of molten chlorate which flowed from them, was carried to the row of casks on the west side. Suddenly, about 10 minutes after the outbreak of the fire, an explosion took place which shook the entire surrounding country and was felt within a radius of several miles. The destruction caused by the explosion was unusually great and the loss was estimated to be at least $250,000.

(*b*) *Initiation by impact.*

26. This kind of initial impulse may be referred to that just discussed if we suppose that the kinetic energy of the blow is, in whole or in part, transformed into heat on the spot struck. In accordance with this theory is the experience that the kinetic energy, which is necessary to cause the explosion, is less the higher the temperature of the explosive (section 17).

M. Berthelot has sought to prove that mechanical shock does not, as a rule, cause the explosion directly but indirectly through the heat produced. Previous to

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* Ann. Rept. H. M. I. Exp. for 1900.

this* chemists were inclined to the opinion, on the strength of experiments with very sensitive explosives such as silver fulminate, nitrogen iodide, nitrogen chloride and the like, that violent agitations of the particles of the substance could directly bring about chemical reaction. M. Berthelot's† experiments, however, prove that a reaction, even one that is already begun, is not accelerated when the substance in reaction is placed on a tuning fork or in a glass tube vibrating over 7000 times per second. As a fact nitrogen iodide did explode at from 100 to 200 vibrations, but only because the vibrations produced a rise of temperature sufficient for more rapid decomposition.

The phenomena of the transmission of an explosion from one explosive cartridge to another separated from it (section 28) proves, however, that very violent vibrations, as such, can bring about an explosive reaction.

(c) *Initiation by detonators.*

27. Priming by means of detonators is often regarded as a kind of combination of the methods just discussed, which takes place under very high pressure.‡ In fact, the reaction products of an explosive substance detonated by a detonator, even in a vacuum, do not differ from those obtained under a high pressure by means of sparks or blows. Perhaps we have here to do, however, with a particular form of decomposition by transmission (influence), with the difference that in the case of the detonating mercury fulminate, instead of having to do with the transmission of the

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* F. Abel, Phil. Trans., **159**, 67; 1869.

† M. Berthelot, Force mat. exp., I, 125; 1883.

‡ C. E. Bichel, Glückauf, **41**, 1194; 1905. L. Wöhler and O. Matter, Z. ges. Schiess Sprengstoffw., **2**, 181; 1907.

explosive decomposition from one cartridge to another of the same kind, the impulse of a relatively small quantity is transmitted to a large quantity of an explosive of a different kind.

We have A. Nobel* to thank for the knowledge that the explosive force of an explosive compound and of mixtures capable of detonation can be disengaged by means of mercury fulminate, and it was he who introduced the detonators of this substance still used to-day. He was the first to show that this detonator can bring about an explosion where simple ignition fails. The number of systems having explosive potentiality has been greatly increased by this discovery, especially since the observation of H. Sprengel† that every compound capable of internal combustion and every mixture of oxidizing and combustible components can in this manner, under the influence of a detonator, actually be brought to decompose.

(*d*) *Initiation by transmission* (*influence*).

28. We must not suppose that explosions by transmission of energy (influence) are caused by a direct transmission of heat; nor can they be brought about by a propulsion of particles from the decomposing explosive upon the explosive that is brought to explosion. The influence remains the same, though somewhat reduced in intensity, if films of glass, metal or water ‡ be interposed between the two explosives, in which case a specific influence upon the intensity of

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* Eng. Pat. No. 1813, of July 20, 1864.

† H. Sprengel, Dingler's Pol. J., **212**, 323; 1874.

‡ George F. Barker *in re* U. S. Blasting Oil Co. *vs*. George M. Mowbray *et al*, Circuit Court of U. S.; 1870.

the transmitted energy seems to be communicated to these mediums (section 137).

A fact not yet explained is that the chemical and physical characteristics of the *primer* is of significance with regard to the question whether the phenomenon of detonation is occasioned by transmission, and by what quantities of explosives. Thus 6.5 grams of the extremely sensitive nitrogen iodide is not sufficient to bring guncotton to explosion, while 0.3 gram of mercury fulminate fully suffices. In experiments with nitrogen chloride at least 3.25 grams must be used to bring about the explosion of guncotton. The quantity of nitrogen chloride necessary is thus seen to be far more than the quantity of mercury fulminate. This seems very surprising, since 3.25 grams of nitrogen chloride, both in respect to the amount of energy set free and the velocity of its decomposition, is far superior to 0.3 gram of mercury fulminate. L. Wöhler* explains this peculiar feature in reference to the transmission of an explosion, leaving out of the question the chemical and physical characteristics of the primer, in the necessity to produce a very high pressure locally. This the 0.3 gram of mercury fulminate is able to do, while the 6.5 grams of nitrogen iodide are not.

In order to test this theory, L. Wöhler and O. Matter† have compared a number of highly sensitive explosives, such as silver hydronitride, diazobenzene nitrate and trimercuraldehyde perchlorate, in respect to their detonating power (section 178). Although sulphur nitride and also diazobenzene nitrate possess a greater potential energy than mercury fulminate, even 0.5 gram

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* L. Wöhler, Z. ges. Schiess Sprengstoffw., **3**, 74; 1908.

† L. Wöhler and O. Matter, Z. ges. Schiess Sprengstoffw., **2**, 181, 203, 244, 265; 1907.

of these substances is not able to detonate picric acid, when only 0.25 gram of mercury fulminate is sufficient.* On the other hand, 0.0237 gram of silver nitride, which in potential energy is considerably below mercury fulminate, is sufficient to detonate the acid — a quantity only one-twelfth as great as the mercury fulminate necessary. No definite relationship between the minimum quantity of a detonator and the chemical nature of the substance to be detonated could be observed. The picric acid was most easily detonated by the silver nitride AgN_3; then followed trinitrobenzene, trinitrotoluene and trinitrocresol, trinitroresorcinol (0.08 gram), trinitrobenzoic acid (0.1 gram) and, finally, trinitroxylene (0.25 gram). For other detonators, especially mercury fulminate, the succession of the above-named substances is different. The author comes to the conclusion that the result of these experiments disproves the hypothesis of F. Abel, in regard to the nature of detonation by transmission. F. Abel† believed that the origin of such differences in ability to transmit an explosive transformation to a neighboring explosive substance could be explained on the hypothesis that there exists a synchronism of "molecular vibrations" between the priming substance and the explosive, similar to that existing between a stringed musical instrument where a vibrating string can cause another string tuned to the same key to vibrate with it. Victor Meyer,‡ on the other hand, has pointed out that if a real synchronism of molecular vibrations were the cause of this phenomenon then each explosive substance must show such perfect

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* See also M. Berthelot and P. Vieille, Mém. poudr. salp., I, 108; 1882–83.

† F. Abel, Phil. Trans., **159**, 512; 1869. See R. Threlfall, Phil. Mag., (5) **21**, 175; 1886.

‡ V. Meyer, Ann., **264**, 127; 1891.

synchronism with itself that it would furnish the best detonator for itself. But this is far from being the case. At present the conception of M. Berthelot* seems the most plausible. According to this theory the "explosion waves" are to be regarded as the fundamental cause of the transmission of explosive impulses, and these waves have the power of propagating themselves and causing explosions through intervening mediums such as water.

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* M. Berthelot, Force mat. exp., I, 118; 1883.

CHAPTER II.

VELOCITY OF EXPLOSIVE REACTIONS.

29. According to the initial impulse employed and the circumstances under which an explosive system is brought to explosion, certain phenomena accompany the decomposition which are usually described as rapid combustion, as explosion, as explosion of the second order or as detonation. The character of an explosive reaction is determined primarily by the greater or less velocity with which it takes place. If suitable methods for bringing about the explosion are at our disposal and can be regulated *ad libitum*, then we have the surest means of adapting an explosive to its various technical uses. The utilization of the energy of guncotton furnishes an instructive as well as historically interesting example. When detonated with the help of a detonator, a row of guncotton cartridges, placed one after the other, 1 meter in length, requires only about 0.0002 second for complete detonation. The velocity under these conditions reaches to from 5000 to 6000 meters per second.* On the other hand, if the same guncotton be exploded by means of a stream of fire from a percussion cap, as when utilized for ballistic purposes, or by means of a cord of twisted guncotton, as was attempted by v. Lenk,† then it decomposes with considerably less velocity. If this takes place in a closed or confined space the velocity can reach as high

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* F. Abel, Dingler's Pol. J., **213**, 428; 1874.

† S. J. v. Romocke, Geschichte der Explosivstoffe, II, 196; 1896.

as several hundred meters per second. In fact, the effect upon guns of such guncotton charges, fired by the method of v. Lenk, is more or less destructive on account of the explosion velocity. P. Vieille (section 67) first succeeded in lowering the velocity of decomposition in firearms to about 10 meters per second by colloidizing the guncotton, and in this way its explosion rate was so modified that its use for ballistic purposes was made possible.*

30. When we consider that two stages of the reaction — a decomposition through the initial impulse and a propagation of the explosive transformation — must take place in every true explosion, it is seen that the velocity of the explosive reaction is to be viewed from two points of view. In the first stage of the explosion the initiating impulse, whether a spark, blow or otherwise, brings about an explosive reaction in a limited portion of the explosive system, which may be an explosive mixture of oxygen and hydrogen, or guncotton, etc. From this moment the explosive system itself, acting from the portion already detonated outwards, takes the part of the initial impulse and brings about, in the second stage, the propagation of the explosive reaction. In every explosion, therefore, we have to deal with the *concatenation* of two decomposition processes, each of which has a different cause and which, therefore, so far as velocity is concerned, need not necessarily be equal nor even belong to the same order of magnitude, although they have a certain dependent relation to each other. The following example will aid in explaining this condition of affairs. According to the experiments of H. Dixon,† the pres-

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* P. Vieille, Mém. poudr. salp., VI, 256; 1893.

† H. Dixon, Phil. Trans., **175**, 617; 1884.

ence of a small quantity of water vapor in a mixture of carbon monoxide and oxygen accelerates their combination to carbon dioxide, since an absolutely dry mixture of these gases will not combine at all under the influence of an electric spark, while the combination takes place the more rapidly, within certain limits, the more water vapor there is present.

The velocity of the reaction, $2\,CO + O_2 = 2\,CO_2$, which in the absence of water is equal to zero, becomes greater and greater in proportion as the latter increases in quantity and influence. In the same proportion with which the velocity of the first stage of the reaction increases, the velocity of the reaction once begun, i.e., the second stage, also increases. When, for instance, in two experiments, the mixture of gases above mentioned was dried over phosphorus pentoxide and sulphuric acid, respectively, and in three further experiments mixed with water vapor corresponding to the pressures 9.2 millimeters, 41.8 millimeters and 148.8 millimeters, respectively, the velocities of the propagation of the explosion in the five cases were, respectively, 36, 119, 175, 244, 317 meters per second. The explosive character of this reaction is, according to these experiments, dependent not only upon a certain velocity of propagation. but also upon the velocity of the reaction itself.

31. That the propagation of the energy proceeding from the initial impulse and acting upon the explosive system to a degree sufficient to cause the explosive reaction cannot, however, take place instantaneously but requires an appreciable time, may be seen from the fact that it is a matter of ignition by means of heat, i.e., by sparks or flame. The explosive system must be heated at some point to such a degree that the

heat released by the reaction thus started, referred to the time unit, exceeds the unavoidable loss of heat by conduction or radiation. Otherwise the explosive reaction would not take place. Therefore the more intense the initial heat impulse is, the more rapidly, as a rule, the system reaches the temperature necessary for the explosive transformation. This temperature is designated as the ignition temperature.

The following conception of van't Hoff* helps to a clearer understanding of this dependence of the ignition temperature upon the intensity of the initial impulse. Imagine a point *O* (Fig. 5) in a room filled with atmospheric air at 0° C. brought to the temperature *T* by a small electric spark. Because of the local heating a transfer of heat takes place which progresses from

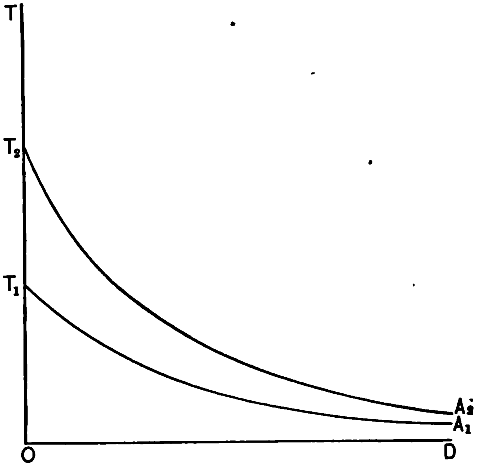

FIG. 5. Temperature Effect in Air.

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* J. H. van't Hoff, Dynam. chim., 121; 1884. E. Cohen, Chem. Dyn., 140; 1896. See also P. Duhem, Thermodynamique et chimie, 463; 1902.

point to point with a gradually falling temperature which continually approaches the original temperature, 0 degrees. This action can be represented by the curve T_1A_1, where the temperatures are represented on the ordinate axis OT and the intervals of the progressive movement of heat on the abscissa OD.

Suppose now the air to be replaced by a homogeneous explosive system, such as a mixture of hydrogen and oxygen, and an electric spark of such low intensity be sent through this that it cannot bring about either ignition or explosion,* but can initiate a chemical reaction. The local increase of temperature caused by the electric spark will here, as in the preceding case, be disseminated, but with the difference that the decrease of temperature will be less, especially in the immediate vicinity of the spark, because the chemical reaction between the components of the mixture is itself a source of heat. This reaction can be illustrated by the curve T_1A_1 (Fig. 6).

As soon as the electric spark possesses a greater intensity entirely different results are obtained in the case of a mixture having explosive potentiality. It is true that in air only a higher local temperature increase obtains, and the fall of temperature as it is disseminated to the neighboring particles of air is greater, corresponding to the curve T_2A_2 (Fig. 5). But in an explosive mixture as the temperature of the electric spark is increased the chemical reaction between the two gases becomes stronger, and the fall of temperature is so influenced that it becomes smaller the more rapidly the chemical reaction occurs. It is not difficult

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* According to F. Emich (Naturw. Rundschau, **12**, 575; 1897) this condition is brought about by electric sparks less than 0.22 millimeter in length.

to imagine a case where the temperature decrease becomes $T = O$, i.e., the disseminating heat waves regain the original temperature. This possibility is graphically expressed by the curve T_2A_2 (Fig. 6). If, now, the temperature of the electric spark be still more increased it will cause such a vigorous development of heat by the chemical reaction between the gases that the temperature of the disseminating heat waves neither decreases nor remains constant, but constantly increases as expressed by the curve T_3A_3. It is easily seen that a heat dissemination decreasing in temperature cannot bring about an explosion in the explosive system, but that a heat dissemination increasing in temperature can easily do so. The temperature T_2, which is produced by the dissemination of a constant temperature, forms, from this point of view, a kind of limit and corresponds to what is characterized as ignition temperature.

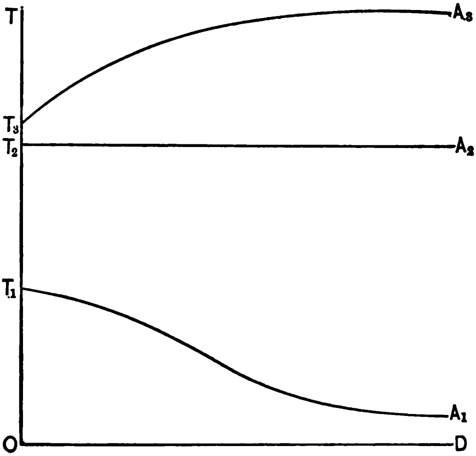

Fig. 6. Temperature Effect in Explosive Mixtures of Gases.

The above exposition can give no intimation as to the size of the factor OT_2, or, in other words, how high the ignition temperature is for any given system, and what time is necessary to obtain this temperature, because it gives neither the intensity of the electric spark or other source of heat nor the nature of the explosive system. This ignition temperature must undoubtedly be determined in connection with a large number of other factors, such as the thermal conductivity and the readiness with which the gaseous mixture diffuses, as well as the dependence of the velocity of reaction upon the heat of reaction and the temperature coefficient, influence of pressure and other local conditions. The ignition temperature, therefore, affords little clue to a knowledge of explosive reactions and it can by no means be taken as that temperature at which a reaction between the component parts of a homogeneous explosive mixture first begins.

With regard to the other initial impulses the same thing is true, as, for instance, in the case of the explosion of a mixture of chlorine and hydrogen by means of light. The union of chlorine and hydrogen occurs explosively in a strong light, but only gradually in diffused light because, as we suppose, the heat developed by the reaction is conducted away before the mixture becomes heated to its ignition temperature. What makes the reaction brought about by ignition by means of a detonator so valuable for the utilization of explosives is the enormously high velocity with which the reaction is brought about and propagated.

32. The explosive reaction brought about by a detonator owes its peculiar character to the circumstance that it proceeds nearly adiabatically; that is, the amount of heat carried off in unit of time by radiation or conduction is vanishingly small compared to that developed

in the same time by the chemical reaction. We have here to do with conditions which, on account of their great complexity, have so far prevented closer investigation, both of an experimental and theoretical nature. All our knowledge of the velocity of chemical reactions has been obtained by experiments carried on at a constant temperature and does not refer to the changed conditions under which a continuous acceleration of the initial velocity, resulting from self-heating, changes the nature of the reaction. In order to examine this fundamental problem of the chemistry of explosives more closely, G. Bredig and F. Epstein* have considered a simple case, in which the system undergoing chemical transformation was in the same condition in all its parts at the same time. The problem to be solved by their experiment was this: If an exothermal reaction takes place in a jacket impervious to heat, such, for instance, as a Weinhold-Dewar flask, in such a manner that the system is heated by the entire amount of heat generated by the reaction; if further the heat of reaction; the velocity constant of the reaction; the concentration of the components taking part in the reaction; and several other easily determined factors of the homogeneous explosive system in question be known, in what length of time will a certain temperature and, with this, a certain change of chemical condition be reached? Even this comparatively simple statement of the problem led to a complicated mathematical solution, the results of which, however, were confirmed satisfactorily by experiments.

The exothermal reaction $2\,H_2O_2 = 2\,H_2O + O_2$ was

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* G. Bredig and F. Epstein, Z. anorg. Chem., **42**, 341; 1904. See also P. Duhem, Mecan. chim., I, 268; 1897. M. Petrowitch, Compt. rend., **124**, 1344; 1897.

carried as nearly adiabatically as possible in the following manner: A solution of hydrogen peroxide was mixed with potassium iodide as the catalyzing agent in a Weinhold-Dewar flask at a determined moment and the heat generated by the system in a certain time was determined quantitatively with a very sensitive thermometer.

33. All factors which at any time influence the velocity of chemical reactions have also significance in determining the velocity of the two parts of the reaction here considered. The most important of these are: (*a*) Temperature of the explosive system; (*b*) pressure under which it takes place; (*c*) catalyzing agents and similar substances.

1. Initial Velocity of Reaction in Explosive Processes.

34. The velocities which obtain in explosive reactions are very great and therefore difficult to measure. While the velocity of *propagation* of such phenomena can, in many cases, be ascertained we have no exact information in regard to the velocity with which such explosions are initiated under very rapidly increasing temperatures and pressures. The information relative to this which has thus far been obtained is confined almost entirely to processes initiated at comparatively low temperatures and pressures with correspondingly small velocities. To what extent this knowledge may be used in judging the velocity in an explosive reaction is uncertain. The experiments with ammonium nitrate above described (section 23) show that a different kind of decomposition may take place under varying conditions.

(*a*) *Influence of temperature.*

35. All older investigations in regard to the influence of temperature on explosive reactions, especially the velocity of the reaction in explosive gaseous mixtures, are confined to determining as accurately as possible the temperature at which the reaction takes place when accompanied by detonation or by flame. E. Mallard and H. le Chatelier* used for this purpose highly heated porcelain tubes which could be used interchangeably as explosion chambers and as thermometers. A tube could be connected by means of a three-way cock with an air pump, an air container or the gaseous mixture to be investigated. In order to determine the temperature in the tube in each experiment it was evacuated and filled with a measured quantity of air; from this data the temperature in question could be calculated. The tube was then again evacuated and filled with the gaseous mixture to be investigated and observations were made to ascertain

TABLE 7. DETONATION TEMPERATURES OF EXPLOSIVE GASEOUS MIXTURES.

Mixture.	Detonation temperature, ° C.
$2H_2+O_2$	550–570
H_2+2O_2	530
$10H_2+O_2+4N_2$	530–570
$5H_2+2O_2+8N_2$	550
$2H_2+O_2+3CO_2$	560–590
$5CO+O_2$	630–650
$2CO+O_2$	650
$CO+2O_2$	650–660
$5CO+2O_2+8N_2$	650–660
$2CO+O_2+3CO_2$	700–715

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* E. Mallard and H. le Chatelier, Ann. mines, (8), **4**, 274; 1883.

whether the explosion took place at the temperature in question or not. This could be determined both by the sound and by the change in volume which most gaseous mixtures undergo after chemical union takes place. A noticeable result of these experiments was that neither the temperature nor the velocity of the reaction were essentially altered by the presence of other gases which took no part in the reaction.

36. The experiments above described do not take into consideration the possibility that the reaction velocities or detonation temperatures may depend not only on the temperature of the inclosure, but also, perhaps, upon other accelerating influences, such as the catalytic influence exercised by the walls of the heated porcelain tube. To meet this objection, K. G. Falk* repeated these experiments under conditions which should indicate the influence of temperature freed as far as possible from such other influences. If a combustible gaseous mixture be compressed, its temperature rises according to well-known gas laws. By this means the reaction velocity is increased and, from the moment at which the heat developed exceeds that lost by radiation, the chief condition for a reaction accompanied by an explosion is fulfilled. Assuming that the compression takes place very rapidly and as near adiabatically as possible, the temperature which obtains in the gaseous mixture can be calculated from the amount of pressure applied and the measurement of the compression necessary for the explosion to take place furnishes a temperature constant that is characteristic for the reaction in question. In a number of experiments

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* K. G. Falk, Journ. Amer. Chem., **28**, 1517; 1906. Ann. Phys., (4), **24**, 450; 1907. See also L. Bradshaw, Z. phys. Chem., **61**, 376; 1907.

the gas was contained in steel cylinders of various dimensions fitted with air-tight pistons. The temperature T and pressure p at the moment of explosion were calculated from the well-known law for adiabatic compression,

$$\frac{T}{T'} = \left(\frac{p}{p'}\right)\frac{k-1}{k},$$

in which T' and p' represent the initial temperature and pressure, $k = \frac{Cp}{Cv}$, the ratio of the specific heats under constant pressure and under constant volume. The following figures were obtained for the pressures necessary for explosion, and the temperatures of explosion were calculated from them in the case of mixtures of hydrogen and oxygen.

TABLE 8. EXPLOSION TEMPERATURE FOR GASEOUS MIXTURES.

Mixture.	Explosion pressure, atmosphere.	Explosion temperature, ° C.
$4H_2+O_2$	48.2	620
$2H_2+O_2$	36.9	546
H_2+O_2	31.8	523
H_2+2O_2	33.5	535
H_2+4O_2	39.8	576

These figures correspond very closely with those obtained by E. Mallard and H. le Chatelier (section 35).

From the variations in the temperature of explosion due to the addition of indifferent gases it was attempted to draw conclusions in regard to the relations of the velocities of reaction to the velocity coefficients calculated on a 10° C. rise of temperature. In this way there was obtained for the reaction between hydrogen and oxygen a temperature coefficient of 1.31 at temperatures around 530° C. and 1.13 around 630° C. These were nearly the same as the calculated temperature coefficients found for the reaction between carbon monoxide and oxygen (section 41).

37. The fact that the mixture $H_2 + O_2$ (but not $2 H_2 + O_2$, as might be expected) is most easily detonated is explained by K. G. Falk, on the assumption that hydrogen peroxide is first formed.* Leaving out of consideration the primary and often little understood causes of such anomalies, we may state as a general rule governing unequal initial velocities of explosive reactions, that those gaseous mixtures detonate most easily which present the greatest initial velocity, while a lesser initial velocity necessitates a much stronger adiabatic compression; i.e., the substance has apparently a much higher temperature of detonation. Such a sluggishness of detonation is especially characteristic of a mixture of methane and air. According to the experiments of E. Mallard and H. le Chatelier,† such a mixture requires about 10 seconds to ignite when conducted through a porcelain tube at a temperature of from 650° to 660° C., a temperature at which mixtures of hydrogen and carbon monoxide with air ignite immediately. This time becomes correspondingly shorter with rising temperature, but the ignition of methane is not immediate under 1000° C. Ethane conducts itself similarly to methane in respect to its sluggishness of reaction, though it is not so pronounced. If a conclusion can properly be drawn from this gradation in the case of the first two members of this homologous series, this sluggishness of reaction decreases as the

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* See also W. A. Bone, J. Drugman, G. W. Andrew, J. Soc. Chem. Ind., 526, 1209; 1906. W. A. Bone, Chem. News, **97**, 196, 212; 1908.

† E. Mallard and H. le Chatelier, Ann. mines, (8), **4**, 293; 1883.

number of carbon atoms in the molecule increases.* From this conclusion it follows that a mixture of methane and air cannot properly be substituted for a mixture of benzene and air, a fact which deserves to be taken into consideration in the tests of safety explosives for mines (section 161).

38. Among the solid explosive systems for which the probability exists that the reaction products are the same in the case of its gradual transformation, so far as this can be carried out, as in the case of its explosion, are nitrogen chloride, nitrogen sulphide and silver oxalate. The first two decompose into nitrogen and chlorine, and nitrogen and sulphur respectively, and the last into silver and carbon dioxide. As a rule, however, the reaction products from an explosive substance when it undergoes a slow decomposition are not the same as when it undergoes explosion (section 23).

39. J. H. van't Hoff † has succeeded in carrying out a gradual decomposition of nitrogen chloride into its elements under the influence of a constant high temperature and has measured the velocity of the reaction. The compound was decomposed in the dark under water and the nitrogen set free measured at equal intervals. The constant for the reaction velocity corresponded satisfactorily with that obtained by means of the mathematical expression.

$$k = \frac{1}{\text{time}} \log \frac{\text{original quantity}}{\text{quantity remaining undecomposed}}.$$

40. C. Hoitsema ‡ has sought to obtain the velocity

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* F. Richardt, Z. anorg. Chem., **38**, 90; 1904. See also E. Hauser, Chem. Z., 1004; 1907. C. Engler and E. Weissberg, Kritische Studien uber die Vorgänge der Autoxydation, 81; 1904.

† J. H. van't Hoff, Dynam. chim., 32; 1884.

‡ C. Hoitsema, Z. phys. Chem., **21**, 137; 1896.

constant *k* at various temperatures, and he succeeded in determining the influence of temperature and rapidity of decomposition for silver oxalate and nitrogen sulphide. He used for this purpose a small flask of about 3 cubic centimeters' capacity provided with a side tube, while a funnel-shaped neck was melted onto a capillary tube, which, being bent at right angles to, and at some distance from, the flask, led to a three-way cock. By means of this cock the flask could be put in connection with an open mercury manometer or with a mercury air pump. The barometer tube, capillary tube and flask were first measured accurately up to a mark made on the side tube. After the explosive substance was placed in the flask the side tube was melted to-

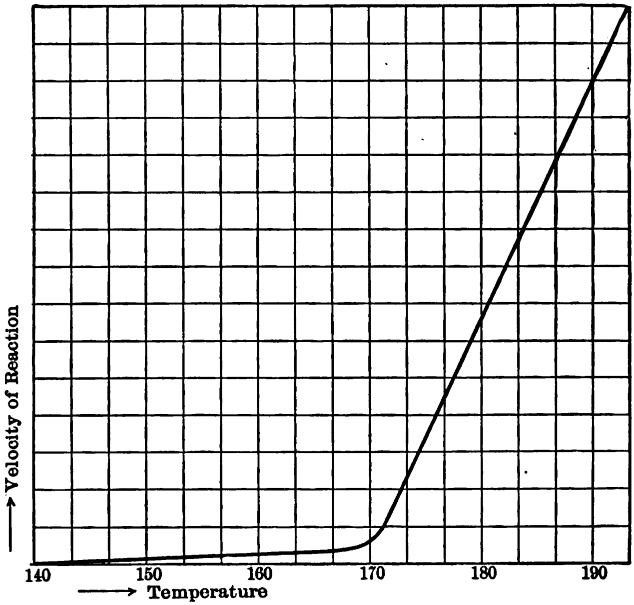

FIG. 7. Relation between the Temperature and the Decomposition Velocity of Explosives.

gether at this mark. The apparatus was weighed before and after charging, then evacuated, after which the flask was immersed in a warm glycerin bath provided with a stirrer to keep it at a constant temperature. The decomposition under these conditions does not take place under constant pressure, since this rises as the gases are formed, yet this circumstance does not seem to have materially influenced the result. Fig. 7 presents a graphic representation of the course of the reaction at various temperatures.

At about 170 degrees the curve undergoes a remarkable change of direction. This is due to the abovementioned characteristic of explosives; namely, the extremely rapid rise in the velocity of decomposition with a rise in temperature (section 25). At certain fairly well defined temperatures, which, though different for different explosives, do not differ very widely, the substance explodes and such explosion temperatures are regarded in practice as a handy test for the various explosives.*

It is generally agreed to regard that temperature at which explosion occurs when an explosive is tested according to the following method of procedure as the *explosion point* of that explosive.† One-tenth of a gram of the substance to be tested is put in a loosely corked test tube and immersed in an oil bath previously brought to a temperature of exactly 100° C. By means of an

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* L. Leygue and P. Champion, Compt. rend., **73**, 1478; 1871. Ph. Hess, Dingler's Pol. J., **218**, 227; 1875. C. E. Munroe, Z. angew. Chem., **3**, 272; 1890. W. Walke, Dingler's Pol. J., **282**, 63; 1891. W. O. Snelling and G. C. Storm, Tech. Paper 12, U. S. Bureau of Mines, 1912.

† The explosion temperature depends of course very much upon the conditions of experiment, and these must be held strictly identical in comparative determinations.

up-and-down stirrer the temperature of the oil bath is held constant. The oil is then gradually and regularly heated, so that the temperature rises 5° C. per minute; this heating is continued until explosion takes place and the temperature is then noted. The explosion points shown in Table 9 were obtained in this manner.

TABLE 9. EXPLOSION POINTS OF VARIOUS EXPLOSIVES.

No.	Explosive.	Explosion points, ° C.
✓1	Guncotton (13 per cent N)	183–186
✓2	Collodion cotton (12 per cent N)...	186–190
✓3	Guncotton powder, gelatinized, fine grain......................	173–176
✓4	Guncotton powder, gelatinized, coarse grain....................	168–172
✓5	Nitroglycerin.....................	160–220
6	Explosive gelatin (7 per cent collodion cotton)..................	180–200
7	Nitroglycerin powder (40 per cent nitroglycerin)..................	170–180
8	Dynamite (75 per cent nitroglycerin).......................	180–200
✓9	Picric acid........................	No explosion up to 225.
10	Nitromannite.....................	160–170
11	Nitrostarch.......................	170–175
✓12	Mercury fulminate................	160–165
✓13	Black powder.....................	No explosion up to 225.
✓14	Ammonium nitrate powder (Roburite I).........................	No explosion up to 225.

These figures are perhaps unexpectedly high for substances of an explosive character and especially that for nitroglycerin* which is little in accord with the sensitiveness of this substance. In fact the result in the case of nitroglycerin is obscured by its fluidity in consequence of which a new surface is constantly being presented to the heated walls of the test tube.

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* W. O. Snelling and C. G. Storm by a very precise method obtain 218°. The Behavior of Nitroglycerin when Heated, Tech. Paper 12, U. S. Bureau of Mines, 1912.

It is also to be mentioned that only carefully prepared, stable explosives show such high explosion points. Badly washed guncotton, for instance, can explode at 120° C. and even lower temperatures. We have, therefore, in the determination of the explosion point, a means by which to ascertain and supervise the condition of an explosive.

41. The decomposition of nitrocellulose under ordinary temperature and pressure, which has been investigated by W. Will * in his study of the stability of nitrocellulose, differs from its explosive decomposition, in that, among other things, besides gaseous and liquid decomposition products, a solid nitrogen-containing residue is formed. In view of this fact there is some doubt as to the range of application of the laws discovered covering the velocity of decomposition in the case of nitrocellulose under different conditions. W. Will heated 2.5 grams nitrocellulose, dried at 40° C., to 135° C. and conducted the volatile, nitrogen-containing decomposition products, as they were formed, in a stream of carbon dioxide, over red-hot copper. The nitrogen oxides formed were thus completely decomposed, the nitrogen collected over caustic soda and the volume read off at stated intervals of one-quarter of an hour. Before each experiment was made, the impurities in the carbon dioxide, such as nitrogen from the air, ammonia and the like, were determined and afterward subtracted from the volume of nitrogen read. The corrected gas volume was calculated to milligrams of nitrogen.

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* W. Will, Z. angew. Chem., 743, 774; 1901. Mitt. Zentral. wissen. techn. Unter. Neubabelsberg, 1900, Vol. 2; 1902, Vol. 3. See also Bergmann & Junk, Z. angew. Chem., 982, 1018; 1904. P. Obermüller, Mitth. Berl. Bezirksver. Deutscher Chemiker, 1904, Vol. 2. See also C. Hall and W. O. Snelling, Nickelodeon, 3, 47, 67; 1910.

As may be seen from the curves (section 208, Fig. 43), in the case of a gradual decomposition of nitrocellulose, we are dealing with a reaction which undergoes a continuous acceleration due to the reaction products formed during the decomposition, especially the nitrogen oxides.* Only in the case of stable nitrocelluloses, and even then only in the beginning of their decomposition, does the relationship approximately hold true that the nitrogen given off in equal intervals of time is proportional to the still undecomposed nitrocellulose. Actually when stable nitrocelluloses were employed the quantities of nitrogen given off in equal times during a rather long experiment were equal, and this quantity was characteristic of the degree of nitration. This velocity of decomposition is also constant for various temperatures, so that by using the general equation which expresses the relation between t and velocity k of a reaction,†

$$\log k = a + bt,$$

where a and b are constant, the increase in velocity may be calculated for any given temperature interval. It was found that the velocity of decomposition is doubled for each 5° C., quadrupled for each 10° C., etc., showing an exceedingly rapid increase in velocity with the temperature. This is characteristic of all exothermal reactions, and hence for explosive reactions (section 25).

42. The course of the reaction by gradual decomposition of nitrocellulose was also studied by A. Mittasch,‡

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* R. Robertson and S. Napper, J. Chem. Soc., **91**, 764; 1907. Z. ges. Schiess Sprengstoffw., **2**, 393; 1907.

† J. van't Hoff, Vorl. theor. phys. Chem., I, 224; 1898.

‡ A. Mittasch, Z. angew. Chem., 929; 1903. O. W. Willcox, the same, 1407; 1908. See also A. Saposchnikoff and W. Yagellowitsch, J. russ. phys. Chem. Ges., **37**, 822.

but the liberated gases and vapors were not carried away. Under these conditions an essential complication of relations was observed. Special observations in regard to the accelerating influence of temperature were not undertaken.

(*b*) *Influence of pressure.*

43. Both general experience in practice and experimental investigations, among others those by M. Berthelot and P. Vieille,* on compressed acetylene, confirm the opinion that increase of pressure exerts an accelerating influence on the initial velocity of explosive reactions. Therefore when a series of observations seems to confirm the exact opposite of this, namely, that an acceleration of reaction takes place under decreased pressure, it becomes apparent that the results have not been influenced by pressure alone. This becomes more probable in the light of the investigations of E. Mitscherlich,† on mixtures of hydrogen and oxygen. It is now known that under certain conditions the reactions between hydrogen and oxygen are very complicated ones, and not only temperature and pressure, but, among other things, the influence of contact, especially with the walls of the container, are to be taken into account in considering them.

44. E. Mitscherlich sought to ascertain whether the pressure which obtains in the gaseous system $2 H_2 + O_2$ influences its detonation temperature, that is, the temperature at which the reaction is accompanied by an explosion. Experiments were conducted under both depressed and elevated pressures, but no important

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* M. Berthelot and P. Vieille, Compt. rend., **123**, 523; 1896.

† See also J. Helier, Compt. rend., **122**, 566; 1896.

results were obtained with the latter. In order to obtain the gas under lowered pressure a mercury air pump was connected with the end of the glass container by means of a T-shaped tube. To avoid injury to the more delicate parts of the apparatus by the explosion, the leg which was connected with the explosion vessel was provided with a plug of asbestos. The other leg of the T-shaped tube was connected with a glass tube, over 760 millimeters in length, which dipped into mercury and on which the rarefaction produced by the air pump could be read. An explosion was immediately recognizable by oscillations in the manometer tube as well as by the light emitted, and when this occurred the temperature was immediately read. The explosive gaseous mixture was contained either in narrow cylindrical glass tubes or in tubes having bulb-shaped enlargements of various diameters. Under these various experimental conditions it was found that the explosion points were dependent upon the size of these enlargements to such an extent that under a given pressure the explosion occurred in the smaller bulbs at a higher temperature than in the larger ones. Considering the relationship between detonation temperature and pressure it appeared that within the limits of 760 millimeters and 300 millimeters the detonation temperature fell proportionately with the decrease in pressure. With increasing pressures, but constant temperatures, the velocity of the reaction

$$2\,H_2 + O_2 = 2\,H_2O$$

was proportionately decreased, and a corresponding rise of temperature was necessary before the explosion could take place.

TABLE 10. INFLUENCE OF PRESSURE ON THE EXPLOSION POINTS OF $2\,H_2 + O_2$.

Diameter of the bulb, millimeters.	375 millimeters' pressure.	750 millimeters' pressure.
	Explosion points, ° C.	
14.6	545	620
10.6	580	650
4.7	595	665

45. In connection with these observations of Mitscherlich regarding the acceleration of reactions under lowered pressures, it is to be mentioned that a fall in the temperature necessary for ignition with decreasing pressure has been noticed in the case of mixtures of several hydrogen compounds, such as those of phosphorus,* silicon,† and antimony‡ with oxygen, and this to such an extent that explosion has been known to occur on suddenly decreasing the pressure on the gases. In all these cases, such as that of a mixture of hydrogen phosphide and oxygen, it could probably be shown that although rarefaction brought about the explosion, yet this should not be taken as proof that the rarefaction itself was the sole cause of the acceleration of reaction velocity.§

In spite of the utmost care to obtain constant experimental conditions, especially as regards pressure and temperature, the velocity of the reaction

$$2\,PH_3 + 3\,O_2 = HPO_2 + H_3PO_3 + H_2O$$

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* Houton de Labillardiere, Ann. chim. phys., **6**, 304; 1817. See also J. van't Hoff, Dynam. chim., 60; 1884.

† C. Friedel and A. Ladenburg, Ann. chim. phys., **23**, 430; 1871.

‡ A. Stock and O. Guttmann, Ber., **37**, 889; 1904.

§ H. J. van de Stadt, Z. phys. Chem., **12**, 322; 1893. W. P. Jorissen, Z. phys. Chem., **21**, 304; 1896. See also T. E. Thorpe and J. W. Rodger, J. Chem. Soc., **55**, 306; 1889.

was extremely fluctuating. It was especially noticeable that a very pronounced acceleration of the reaction did not precede the explosion in all cases, but that, on the contrary, a very rapid reaction velocity without explosion, as well as low velocity with explosion, may occur. A more careful investigation of the mechanism of the reaction shows that in all probability catalyzing agents play a part in the transformation. For example, moisture was at least one of the factors, for even traces of it checked the reaction under great rarefaction.

46. In the above-named cases we were dealing with reactions under pressures not exceeding one atmosphere. So far as the relation in question has been investigated for higher pressures it seems established that increased pressure has a tendency to accelerate rather than to retard the explosive transformation. Gaseous acetylene, for instance, cannot be brought to explosion by simply heating under ordinary pressure but can be if the pressure be increased two- or threefold.* That such apparently subordinate conditions for the bringing about of explosive reactions can be of technical significance is illustrated in the case of acetylene. When acetylene first began to be used for illuminating purposes attempts were made to compress it in storage tanks without realizing the danger that was attached to the compressed gas. The frequent accidents, by explosion, led finally to an investigation of the matter.

M. Berthelot and P. Vieille,† who carried out this work, sought to discover the limiting pressure above which the velocity of the reaction is so great that

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* M. Berthelot and P. Vieille, Compt. rend., **124,** 1000; 1897.

† Ibid.

acetylene decomposes explosively. They used both a glowing platinum rod and fulminating mercury with which to initiate the reaction. In order to determine at the same time the cooling influence of the walls of the containing vessels, experiments were made with vessels of from 4 to 25 liters' capacity, whose diameters almost equaled their heights, and also with metal tubes having a diameter of 22 millimeters and a length of 3 meters. In the experiments with acetylene, contained in the vessels first described, no definite pressure, below which no explosion occurred and above which an explosion was certain, could be found, but the transition was found to be a gradual one. In the experiments in which metal tubes were used the pressures used were apparently too low, since in no case did an explosive decomposition of the acetylene occur.

(*c*) *Catalytic influences.*

47. As is well known a mixture of equal volumes of chlorine and hydrogen when acted upon by chemically active rays of light unites explosively to form hydrochloric acid gas. R. Bunsen and H. Roscoe,* who investigated this reaction, noticed among other things that even slight traces of air lowered the sensitiveness of this mixture to light in a marked degree. They had

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* R. Bunsen and H. Roscoe, Ann. Phys. Chem., **100,** 43, 481; 1857: **101,** 255; 1857: **108,** 193; 1859. See also E. Pringsheim, Weid. Ann., **32,** 384; 1887. R. Luther and E. Goldberg, Z. phys. Chem., **42,** 257; 1903. H. Dixon, J. Soc. Chem. Ind., **25,** 145; 1906. O. H. Burgess and D. L. Chapman, Proc. Chem. Soc., **22,** 37; 1906. G. Dyson and A. Harden, J. Chem. Soc., **83,** 201; 1903. J. W. Mellor, J. Chem. Soc., **79,** 225; 1901: **81,** 1288; 1902. R. Luther, Z. phys. Chem., **30,** 628; 1899. H. Sirk., Z. phys. Chem., **61,** 545; 1908. M. Pier, the same, **62,** 385 (1908). D. Amato, Chem. Zentral, 899; 1885. W. P. Jorissen and W. E. Ringer (Influence of Radium), Ber., **39,** 2093; 1906. M Wildermann, Z. phys. Chem., **42,** 257; 1903.

previously suspected the existence of this phenomenon from the retardation of the reaction

$$Cl_2 + H_2 = 2\,HCl$$

in the presence of gases taking no part in the reaction. A similar observation was made by H. Dixon,* who proved that moist carbon monoxide and oxygen explode easier than dry (section 30). It is the presence of moisture that exerts a specific influence which, in the present case, shows itself in an acceleration of the velocity of the reaction between carbon monoxide and oxygen.

48. The facts in regard to such reactions may be generally expressed in the statement that sometimes even slight traces of a foreign substance are able to very essentially change the velocity of a reaction, whether it be to raise or to lower it. A. F. Girvan † has attempted to determine quantitatively the smallest quantity of water which must be present in order that an explosion of carbon monoxide and oxygen can be brought about by an electric spark, and he has found that at ordinary temperatures an ignition of the mixture can still take place if 1 molugram of water to 24,000 molugrams of gas be present. It may be mentioned incidentally that A. F. Girvan obtained this proportion by cooling the moistened gaseous mixture to such low temperature that the water was almost entirely thrown out by freezing. The quantity of water vapor remaining after cooling to −51° C., corresponding to a vapor tension of only 0.03 millimeter, was still sufficient to give the gaseous mixture explosive potentiality at the room temperature.

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* H. Dixon, Phil. Trans., **175**, 640; 1884. See also H. B. Baker, Phil. Trans., **179**, 581; 1888. Proc. Chem. Soc., **18**, 40; 1902.

† A. F. Girvan, Proc. Chem. Soc., **19**, 236; 1903.

49. We are indebted to the experiments of J. van't Hoff,[*] and later of Victor Meyer and his pupils, on the velocity of the reaction of explosive gaseous mixtures, for our knowledge of the unexpectedly great significance of catalytic influences in the initiation of explosive reactions. E. Mallard and H. le Chatelier[†] had assumed about 550 degrees as the ignition temperature for a mixture of hydrogen and oxygen. When V. Meyer and A. Munch[‡] sought to determine this temperature more accurately and with this in view worked with special care, such, for instance, as setting the explosion vessel in the bulb of an air thermometer, in order to be sure of a constant temperature, it appeared, as had already been ascertained by J. van't Hoff, that the material and surface condition of the walls of the containing vessel exerted, under certain conditions, a much greater influence than the temperature upon the velocity of the transformation

$$2\,H_2 + O_2 = 2\,H_2O.$$

In the case of two similar glass bulbs, heated to the same temperature at the same time and under the same conditions, one could transform but 10 per cent of the gaseous mixture into water, while the other transformed 100 per cent; when the walls of the vessel were silvered the combination of the gases took place at temperatures less than 200 degrees, while in glass bulbs, under apparently identical conditions, combination was first observed at about 450 degrees.

50. It was also found by M. Bodenstein,[§] inci-

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[*] J. van't Hoff, Dynam. Chim., 58; 1884.

[†] E. Mallard and H. le Chatelier, Ann. mines, (8), **4**, 274; 1883.

[‡] V. Meyer and A. Munch, Ber., **26**, 2421; 1893. See also A. Krause and V. Meyer, Ann., **264**, 85; 1891. P. Askenasy and V. Meyer, Ann., **269**, 49; 1892. F. Freyer and V. Meyer, Ber., **25**, 622; 1892.

[§] M. Bodenstein, Z. phys. Chem., **29**, 681; 1899: **46**, 725; 1904.

dental to his investigations into the relationship between temperature and velocity of the explosive gas reaction, that the velocity constant is influenced to a considerable extent by the vessel used. By comparison of differently shaped porcelain tubes it appeared certain that the velocity constant k (section 39) changes according to the shape of the tube and roughly in proportion to the ratio of the surface of the porcelain walls to the volume of the vessel used. This circumstance points to the fact that the reaction takes place practically entirely on the walls of the containing vessel, and that, therefore, the porcelain exerts a strong catalytic influence upon the combination of the two gases, hydrogen and oxygen.*

By changing the temperature or the pressure the velocity of the reaction could be varied, but this variation was independent of the catalytic action of the walls of the containing vessel. Up to about 600 degrees the formation of water occurred principally on the walls and only to a negligible extent in the body of the gas. If the mixture was put into active motion the transformation became more rapid because the particles of gas were brought more rapidly into contact with the catalyzing agent. A. W. Rowe† came to exactly the same conclusion in a similar investigation into the velocity of the reaction of explosive gases. The influence of the catalyzing agent became more marked with lower temperatures. The chemical influence increased with rising temperature in accordance with the principle that the temperature coefficient of a chemical reaction is considerably greater than

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* See also P. L. Dulong and P. Thénard, Ann. Phys. Chem., **24**, 380; 1823.

† A. W. Rowe, Z. phys. Chem., **59**, 41; 1907.

the coefficient of the mutual diffusion of gases or vapors. The purely chemical reaction of the explosive gas occurred with a velocity of the third order, according to the equation

$$2\,H_2 + O_2 = 2\,H_2O.$$

51. Catalytic influences appear to play an important part also in the case of the ignition or explosion of fire damp. According to E. Mallard and H. le Chatelier* the reaction

$$CH_4 + 2\,O_2 \rightleftarrows CO_2 + 2\,H_2O$$

begins, at about 450 degrees, to be more or less active, according to the physical and chemical characteristics of the body with which the gaseous mixture comes in contact. The reaction can be accelerated by a number of substances (see below), especially palladium sponge, to such a degree that it becomes noticeable at a temperature as low as 200 degrees.

In the investigation by the Prussian Mines Commission† a thorough test was made of the ignition of mixtures of fire damp and air by means of glowing wires for the purpose of making recommendations regarding the construction of safety lamps. It was shown in these experiments that glowing wires of copper, iron, silver, platinum, etc., exerted a specific influence upon the velocity of the reaction between methane and oxygen. The time necessary for the ignition of the explosive mixture depended not alone upon the temperature of the heated wire, nor upon its conductivity for heat, but to a greater degree upon its catalytic

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* H. le Chatelier, Grisou, S. 47.

† A. Hasslacher, H. ber. Kom., 74; 1887. See also H. Couriot and J. Meunier, Compt. rend., **126,** 750; 1898. Ph. Hess, Mitt. Art. Geniew, **29,** 495; 1898. Hamilton Hutchins, Proc. U. S. Naval Institute, **14,** 419; 1888.

power.* Under similar experimental conditions an iron rod ignited the mixture with greater difficulty than a copper one, and this again with greater difficulty than a platinum one. Further, coal dust,† infusorial earth,‡ magnesia,§ barium oxide‖ and similar porous substances that can be heated to incandescence exert also a catalytic effect in accelerating the ignition of explosive fire-damp mixtures, and, in this way, reinforce the influence of a local high temperature. It was found, on the other hand, that easily fusible but difficultly volatile substances, which are able to form a coating over the catalyzing agent, arrest its accelerating effect on the reaction. To such circumstances may be ascribed the efficiency of common salt and other alkali salts as components of several safety explosives ¶ for use in mines (section 165).

VELOCITY OF PROPAGATION OF EXPLOSIVE REACTIONS.

52. So long as the significance of the relation of the initial impulse to the initial velocity of explosive reactions was not known and sparks or flame were the only primers used for explosives, investigations into the propagation of explosive transformations, especially within the body of a homogeneous explosive system, gave moderate and sometimes unexpectedly small velocities. G. Piobert ** found the velocity of

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* P. J. Kirkby, Phil. Mag., (6), **10**, 467; 1905. E. Hauser, Chem. Ztg., 1004; 1907.

† Glückauf, 1373; 1904. See also F. Haber, Thermodyn. Gasreak., 295; 1905.

‡ M. Bodenstein and F. Ohmer, Z. phys. Chem., **53**, 166; 1905.

§ M. Berthelot, Force mat. exp., II, 171; 1883.

‖ M. Berthelot, Compt. rend., **125**, 271; 1897.

¶ F. Heise, Spreng. Zund. Spreng., 114; 1904.

** G. Piobert, Traité d'arte, 1839.

combustion of a prism of black powder in the open air to be only from 10 to 13 millimeters per second, and that the velocity of propagation of the combustion from grain to grain through the mediation of air did not exceed 3.5 meters per second.

53. R. Bunsen,* who investigated more closely the velocity of the propagation of combustion processes in explosive gaseous mixtures, found for mixtures of hydrogen and oxygen 34 meters, and for mixtures of carbon monoxide and oxygen only 1 meter per second, and, since other investigators have obtained similar results with analogous methods of priming, but under other experimental conditions, these figures are accepted as characteristic constants of the system in question. Bunsen's experiments were carried out as follows: The explosive gaseous mixture was forced through a fine opening with a velocity just sufficient to prevent the flame from striking back when the gas was ignited. The velocity with which the combustion is propagated in the gaseous mixture is, under these conditions, equal to the velocity of effusion of the stream of gas. If, for instance, the volume of gas (in centimeters) forced through the opening in one second be represented by V, and the area of the opening (in square centimeters) be F, then the velocity of the propagation of combustion, v, is expressed by the formula

$$v = \frac{V}{F}.$$

54. E. Mallard,† and later W. Michelson,‡ experi-

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* R. Bunsen, Gas. Method., 316, 331; 1877.

† E. Mallard, Ann. mines, (7), **7**, 355; 1875.

‡ W. Michelson, Ann. Phys. Chem., N. F., **37**, 1; 1889. See also H. Mache, Ann. Physik., (4), **24**, 527; 1907. A. Gouy, Ann. chim. phys., (5), **18**, 27; 1879.

mented with the same methods and obtained data which, although not completely checking with Bunsen's results, were of the same order of magnitude. The burning gas, mentioned in the experiments described above, is distinctly distinguishable from the unburned gas by a cone-shaped boundary within the flame.

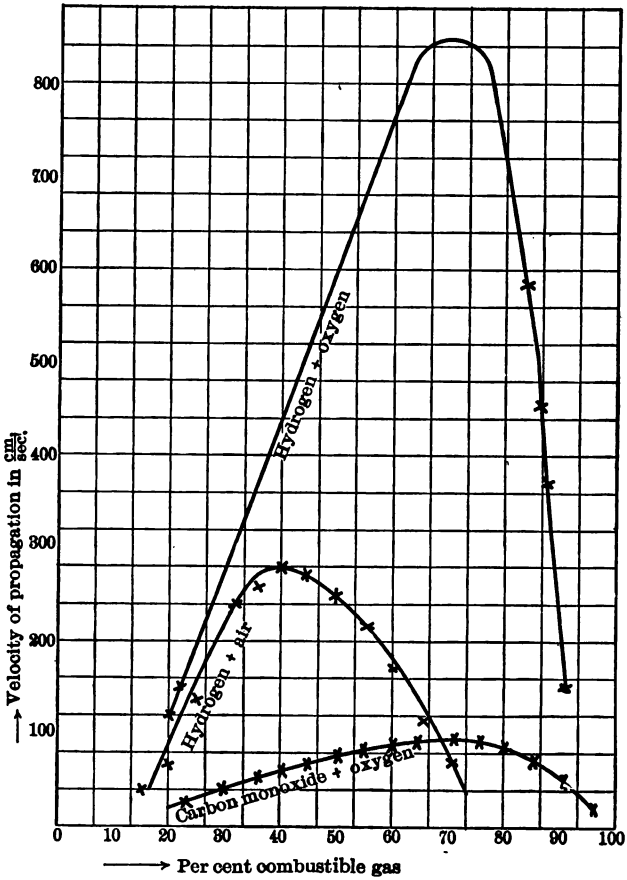

FIG. 8.

Michelson photographed the flame and was able to deduce the capacity of the cone-shaped combustion surface, from the picture, with great exactness and from this he calculated the quantity of gas coming out in unit of time. He confirmed the conclusion of E. Mallard, that an unequal velocity of combustion accompanies an unequal proportion of the two components contained in a mixture of explosive gases. The velocity increased almost in proportion to the content in combustible gas up to a maximum from which it again decreased proportionally. A diagram of the relations (Fig. 8) consists, when the velocity of propagation is made the ordinate and the per cent of combustible gas the abscissa, of two almost straight lines. The maximum velocity of propagation was reached when the combustible gas was about 10 per cent by volume in excess. If this excess was made greater the velocity of propagation again decreased and finally became so small that no explosion could be detected.

55. This relationship between the velocity of combustion of the gases and the ratio of their component parts explains the fact that there exists for every gaseous mixture, capable of undergoing a reaction, a definite upper and lower limit for the proportions of the component gases. These limits are so sharply defined for a given method of imparting initial velocity, such, for instance, as electric sparks, and under constant conditions of temperature, pressure and the like, that an easily combustible gaseous mixture may be made incombustible by a slight variation of these proportions. R. Bunsen* is authority for the following figures referring to mixtures of explosive gas and oxygen.

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* R. Bunsen, Gas. Method., 338; 1877.

	Incombustible, per cent volume.	Combustible, per cent volume.
Detonating gas	8.72	9.66
Oxygen	91.28	90.34

According to this table the mixture containing the excess of oxygen loses its combustibility when the volume of detonating gas sinks to 8.72 per cent, and becomes again combustible when this volume is raised to 9.66 per cent. The following table contains the limiting volume per cent for a number of other gases and easily volatile substances when mixed with air.*

TABLE 11. LIMITING PROPORTIONS FOR GASES AND VAPORS IN EXPLOSIVE MIXTURES WITH AIR.

	Per cent volume.
Hydrogen	9.5–66.5
Carbon monoxide	16.5–75
Water gas	12.5–66.5
Methane	6 –13
Illuminating gas	8 –19
Acetylene	3.5–52.5
Ethylene	4 –14.5
Ether	2.7– 7.7
Acetone	5 –12
Benzene	2.7– 6.3
Alcohol (96 per cent)	4 –13.7
Benzine	2.4– 4.9
Pentane	2.5– 4.8

56. The range of explosibility for such mixtures is, of course, dependent upon the experimental conditions, such, for instance, as the diameter of the explosion tubes, and especially upon those factors which influ-

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* H. Bunte and P. Eitner, J. Gas. Wasser., **44**, 835, 855; 1901: **45**, 1, 21, 69, 90, 112, 221, 244, 264; 1902.

ence both the initial velocity and the velocity of propagation of explosive reactions, such as kind of initial impulse, initial temperature and pressure.

A gaseous mixture which cannot be brought to explosion by means of electric sparks may, however, still be detonated with a detonator.* Investigations into the influence of the intensity of electric sparks upon the inflammability of explosive gaseous mixtures with air were made by H. Herwig.† He observed a considerable extension of the above-mentioned limits when increasing the electric current by increasing the battery from 1 to 4 cells. F. Emich‡ has also demonstrated that, under normal conditions of temperature and pressure, detonating gas is not detonated by induction sparks less than 0.22 millimeter in length.

Raising the initial temperature scarcely extends the maximum explosion limit, but sometimes extends the minimum limit considerably. H. Bunte and J. Roskowski § experimented with mixtures of hydrogen, carbon monoxide, methane and illuminating gas with oxygen, air and a mixture of 21 per cent oxygen and 79 per cent carbon dioxide and made determinations at 15°, 100°, 200° and 300° C. In the case of mixtures of these gases with air, for instance, the following table shows the shifting of the maximum volume per cent of the gas for each 100 degrees difference in temperature.

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* M. Berthelot, Force mat. exp., 1, 164; 1883.

† H. Herwig, Ann. Physik., **148**, 44; 1873.

‡ F. Emich, Sitzber. Wiener akad. Wiss., **16**, 10; 1897. See also, relative to the effect of variation of electric sparks and glowing wires in their ability to bring about detonation, A. de Hemptinne, Bull., Acad. Roy. Belg., **11**, 761; 1902, and Hamilton Hutchins, Proc. U. S. Naval Institute, **14**, 419; 1888.

§ H. Bunte and J. Roskowski, J. Gas. Wasser., 491, 524, 535, 553; 1890. J. Roskowski, Z. phys. Chem., **7**, 485; 1891.

TABLE 12. INFLUENCE OF TEMPERATURE UPON THE EXPLOSION LIMITS.

Explosion temperature, °C.	Hydrogen.	Carbon monoxide.	Methane.	Illuminating gas.
100	3.5	2.6	0.2	2.1
200	3.9	3.2	−0.2 (?)	2.0
300	7.2	−23.0 (?)	2.0	1.9

A fire-damp mixture consisting of methane and air comes to explosion in all proportions at high temperatures.* Increase of pressure shows the same effect. F. Heise† has passed an electric spark of constant length and intensity through a similar fire-damp mixture, first at atmospheric pressure and then at increased pressures. It became plain that under increasing pressures the explosion limits shifted towards that mixture which ordinarily explodes with greater difficulty. The difference was so great that it became noticeable at an increase in pressure corresponding to that in a mine shaft of from 700 to 800 meters in depth. A fall of temperature, on the other hand, narrows the explosion limits, and the explosive phenomenon finally ceases altogether when the pressure falls below a certain limit.‡

57. It is a well-known fact that explosive gaseous mixtures are made use of in internal-combustion engines for the accomplishment of mechanical work. This is done by burning a mixture of the vaporized or sprayed

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* E. Mallard and H. le Chatelier, Compt. rend., **91,** 825; 1880. H. le Chatelier and M. Boudouard, Compt. rend., **126,** 1510; 1898.

† F. Heise, Glückauf, **34,** 725; 1898.

‡ H. Herwig, Pogg. ann., **148,** 44; 1873. W. G. Mixter, Am. J. Sci., (4), **7,** 327; 1899. M. Berthelot and P. Vieille, Compt. rend., **128,** 777; 1899. A. de Hemptinne, Bull., Acad. Roy. Belg., 761; 1902. N. Teclu, J. prak. Chem., **75,** 212; 1907.

combustible substance and air in a closed space where the energy developed may be communicated to a movable piston which transforms its motion to a rotating one. The ignition is brought about either by electric sparks or by incandescent wires.

Very finely divided dust and solid combustible substances are comparable to explosive gaseous mixtures in respect to their power to burn or explode.* Experiments have shown that the presence of 10 grams of coal dust in one cubic meter of air may be explosive. The success of the experiment depends upon the fineness of the coal dust. According to v. Schwartz,† dust explosions have been observed with the following substances: Coal, soot, wood dust, cork dust, tanner's bark, grain, bran, malt, meal, starch, sugar, dextrin, cotton, wool, tow, metals, bronze, paint, resin, sulphur, naphthalene, celluloid and soap.

The following occurrences will suffice to show how these easily explosive gaseous or dust mixtures may give rise to unexpected and serious results. On the 30th of March, 1904, an explosion occurred at Prince's Dock, Glasgow, while loading several empty acetone casks, which had been shipped to the dock by rail and were to be loaded on the ship "Szeged." Two men were rolling a cask onto the ship, when an explosion occurred through which several persons were wounded, two fatally. The bung had probably been lost from the cask or had been taken out by the workmen, and the mixture of acetone and air in the cask had been ignited either accidentally or intentionally with a

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* Charles E. Munroe, Explosions caused by commonly occurring substances, J. Am. Chem. Soc., **21,** 317; 1899.

† v. Schwartz, Handb. Feuer. Exp., 64, 203; 1902. H. Stockmeier, Z. angew. Chem., **19,** 1665 (1906). O. Edelmann, Chem. Z., **30,** 925, 951 (1906).

match. Many burned matches were afterwards found scattered about the quay.*

A lady was having her hair washed with a cleaning preparation. An explosion suddenly occurred. The lady was wrapped in flames and the hair dresser was burned. It seems that the cleaning agent consisted of petroleum benzine of a very volatile and easily combustible nature. Although the cause of its ignition could not be established with certainty, yet experiences at benzine cleansing establishments † point to the fact that an electric spark from the lady's hair ignited the gas. The absence of light or fire in the room and neighboring rooms was proven beyond a doubt. The explosion itself was a result of the formation of an explosive mixture of air with benzine from the shampoo solution.‡

A most serious explosion of a combustible mixture, which wrecked an extensive grain mill, killed several persons, destroyed large stores of meal and grain, and demolished about forty buildings in the vicinity, occurred in St. Louis. The fire originated from some obscure source. The flame, or perhaps only a spark, soon reached the meal dust flying about in the mixing rooms and a violent explosion which completely wrecked the immense building immediately followed. The vibrations from the explosion were felt several miles away. On the other side of the street, two grain elevators, in which 20,000 barrels of meal and 200,000 bushels of grain were stored, immediately burst into flames.§

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* Ann. Rept. H. M. I. Exp., 58; 1904.

† M. M. Richter, Die Benzinbrande in den chemischen Waschereien, 1883, and Chem. Zentr., II, 1010; 1904.

‡ Ann. Report H. M. I. Exp., 59; 1897.

§ J. Phillips, The Handling of Dangerous Goods, 251; 1896. See also H. Weber, Dingler's pol. J., **227**, 407; 1878.

58. Although the experiments of G. Piobert, R. Bunsen, E. Mallard and others seem to prove that there exist characteristic, comparatively small velocities for the propagation of explosive processes, yet many observations and experiences, among which may be mentioned explosions of illuminating gas in gas pipes,* point to the fact that under certain conditions, not well understood, much greater velocities must obtain. In fact much greater velocities of propagation have been obtained in explosive systems by changing the experimental conditions, especially by the use of air-tight apparatus, whereby pressure and temperature can become important factors, as well as by the use of powerful agents, such as high-power electric sparks, and, above all, mercury fulminate detonators with which to initiate the reaction.

59. M. Berthelot† enclosed explosive oxygen-hydrogen gas in a thick-walled rubber tube 5 millimeters in diameter, one end of which was provided with two wire electrodes for firing the gas by an electric spark, and the other with an easily movable piston which could be made to register its motions with a pencil on a rotating registering cylinder. The velocities thus measured varied, according to the distance of the piston from the point of ignition and the intensity of the electric spark, between that of a few meters per second, obtained by R. Bunsen, up to about 3000 meters per second (Table 13).

The significance of the initial impulse as regards the velocity of the reaction as well as the propagation of the explosion is made very clear by these experiments.

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* H. Dixon, Phil. Trans., **184**, 97; 1893. See also H. le Chatelier, Grisou.

† M. Berthelot, Force mat. exp., I, 160; 1883. See also Compt. rend., **129**, 430; 1899.

TABLE 13. TRANSITION FROM DEFLAGRATION TO DETONATION.

Distance between piston and ignition point, meters.	Duration of the explosion, $\frac{\text{seconds}}{1000}$.	Average velocity.	
		In the whole length, meters.	Within a limited distance, meters.
0.02	0.275	72.7	72.7
0.05	0.342	146.2	448
0.50	0.541	924.4	2261
5.25	2.108	2491	3031
20.19	7.62	2649	2710
40.43	15.1	2679	2706

The velocities recorded proved to be influenced to a large extent by the intensity of the initiating spark, and, since this could not be held accurately to a definite intensity, no constant velocities could be obtained. However, by the use of mercury fulminate detonators, Berthelot obtained constant results. Far from coinciding with the low velocities of propagation of a few meters which had been determined up to that time, and which formed the lower velocity limits of explosions, these proved to be many thousand meters and to belong to the upper velocity limits.

60. The important fact that under certain conditions, such as by the use of electric sparks as the initial impulse, the explosive transformation can progress with various velocities, and that these can exist side by side, was further proved by A. von Oettingen and A. von Gernet.* The explosive gas was confined in a glass eudiometer, 400 millimeters long, and brought to explosion by small electric sparks. The explosion phenomena were photographed by the aid of a rotating mirror. Since the oxyhydrogen flame is poor in photo-

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* A. von Oettingen and A. von Gernet, Wied. Ann., **33**, 586; 1888.

graphically active rays of light the eudiometer tube was coated on the inside with cuprous chloride which was heated to a glow by the explosive process and thus made photographic reproduction possible. The photograph showed progressive waves which were repeatedly thrown back to the end of the eudiometer. The velocity of their propagation could be calculated from their shape and from the velocity of rotation of the mirror. In this way a series of velocities was obtained which could be plainly followed from the lowest to the highest limits. Later investigators, especially H. Dixon,* have given some credence to another interpretation of the results of these experiments (section 142).

61. Experience teaches that under conditions usually in force only one or the other limiting value of velocity of propagation obtains in explosive processes, and the corresponding phenomena are accordingly characterized either as deflagration, where the velocity of propagation is only a few meters, or as detonation, where the velocity reaches almost as many kilometers per second. Intermediate velocities have been obtained by M. Berthelot, H. Dixon† and others. It is further shown that the one form of explosion may go over to the other form under changing conditions and *vice versa.* A deflagration under rapidly rising pressure, as in firearms, for instance, can end with a detonation. On the other hand there are hindrances to the propagation of a detonation, whereby its high velocity may be so decreased that the transformation of the explosive system takes on the character of a deflagra-

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* H. Dixon, Phil. Trans., **200,** 315; 1903. A. Nägel, Mitt. Forsch. Ingen; **54,** 1, 1908.

† H. Dixon, Phil. Trans., **175,** 617; 1884.

tion. H. Dixon* observed that acetylene, enclosed in long narrow tubes, is not decomposed throughout its entire length even by the use of powerful detonators. The explosion was propagated only to a certain distance from the point of the initial impulse. Vapors of carbon bisulphide in air are completely decomposed under the same conditions, yet the velocity of propagation of the explosion was by no means constant throughout its entire length, but became gradually slower and slower. Similar phenomena have been observed in the case of liquid and solid explosives,† not only those composed of homogeneous, chemically simple substances, such as nitroglycerin and nitromannite, but also explosive mixtures of solid, heterogeneous substances, such as ammonium nitrate mixtures. The latter case disproves the theory previously expressed,‡ namely, that on account of insufficient surfaces of contact between the components (section 3), only the gradual transformation proceeding with a velocity of a few meters per second can take place, and that an explosive reaction propagated with a velocity of over a thousand meters per second cannot take place.

(*a*) *Influence of temperature.*

62. Compared with the high temperatures developed during the explosive process, the original temperature of an explosive system, especially in the case of gaseous

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* H. Dixon, J. Gas Lighting, 1893; Chem. News, **73**, 139; 1896. See also C. Mallard and H. le Chatelier, Compt. rend., **95**, 599, 1352; 1882. H. Biltz, Ber., **23**, 1378; 1893. C. E. Munroe. The Propagation of Explosions in Mixtures of Petroleum Vapor with Air in Tubes, Proc. Am. Phil. Soc. **49**, 203; 1910.

† M. Berthelot, Ann. chim. phys., (6), **6**, 556; 1885.

‡ See, for example, J. van't Hoff, Vorles. theor. phys. Chem., III, 101; 1898–1900.

mixtures, seems to have but a subordinate significance as regards the velocity of propagation of an explosive transformation. Nevertheless such an influence is noticeable, especially upon velocities of the lower order, where the loss of heat, through radiation and conduction, becomes of great consequence. E. Mallard and H. le Chatelier * found for a mixture of hydrogen and air, with 30 per cent of the former, which was ignited in a glass tube 1 meter long and 6 meters inner diameter, the following figures:

TABLE 14. INFLUENCE OF TEMPERATURE ON VELOCITY OF PROPAGATION.

Temperature of gas, °C.	Velocity, meters.
15	3.28
100	4.35

The difference in velocities is evidently sufficiently great for it to be said that a difference of initial temperature causes a noticeable shifting in the limits of the explosion (section 56).

63. With liquid and solid explosive substances an increase of initial temperature produces an increase of reaction velocity. This relation has been followed in the case of gunpowder by measurements of the velocity of the projectile and of the gas pressure. From measurements that have been made, W. Heydenreich † has calculated, for various kinds of powders, weapons and projectiles, that for every 1° C. increase in initial temperature the velocity of the projectile increases from 0.05 to 0.20 per cent and the gas pressure from 0.29 to 0.77 per

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* E. Mallard and H. le Chatelier, Ann. mines, (8), 4, 321; 1883.

† W. Heydenreich, Lehre vom Schuss, II, 38; 1898.

cent of the total. A more exact statement cannot be made, as it is hardly possible to separate the influence of temperature on the reaction velocity of powder from the other uncertain factors, such as the varying moisture content. Even a small collection of moisture on the surface of the powder grains[*] decreases to a considerable degree the velocity of propagation of the reaction, and a slight drying increases it.

64. As regards the influence of an increased temperature on the upper limits of the velocity of explosive reactions the above-mentioned determinations are still less certain. H. Dixon[†] determined the velocity of detonation of explosive gaseous mixtures at +10° C. and +100° C., and gave it as his opinion that the velocity decreased with increasing temperature.

TABLE 15. INFLUENCE OF TEMPERATURE ON THE VELOCITY OF DETONATION.

Initial temperature, °C.	Hydrogen and oxygen.		Ethylene and oxygen.	
	Average meters.	Number of experiments.	Average meters.	Number of experiments.
10	2821 $\begin{cases}+8\\-9\end{cases}$	5	2581 $\begin{cases}+25\\-19\end{cases}$	5
100	2790 $\begin{cases}+10\\-16\end{cases}$	8	2538 $\begin{cases}+10\\-6\end{cases}$	4

65. According to the experiments of the French Commission on Explosives,[‡] the velocity of propagation of explosion in the case of kieselguhr dynamite (75 per cent nitroglycerin) in lead tubes 6 millimeters in diameter varied between 1916 and 3180 meters,

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[*] A. W. Cronquist, Z. ges. Schiess. Sprengstoff, I, 106; 1906. W. Heydenreich, the same, I, 148; 1906.

[†] H. Dixon, Phil. Trans., **184**, 97; 1893.

[‡] Compt. rend., **100**, 314; 1885.

and the main factor that caused this variation was believed to be the varying temperatures of the dynamite. It was, however, more probably due to influences of another kind (section 72).

(*b*) *Influence of pressure.*

66. Although G. Piobert,* in his study on the velocity of explosion of black powder, ascribes no influence on the velocity of the propagation of the explosion to the varying pressure in the weapon, later investigators have recognized, for powder, the dependence of this velocity on the pressure and have sought to express it approximately in empirical laws. In the years 1862–65, San Roberto † measured the velocity of explosion in the case of black powder in the valley and on the top of the Alps, a difference in height corresponding to a difference in pressure of 317 millimeters of mercury. He filled thick-walled lead tubes of 17 millimeters inside diameter with black powder and drew them out to a diameter of from 3 to 4 millimeters in order to obtain a uniform powder core. Each tube was cut into 4 parts, 40 centimeters in length, and the time consumed in burning was measured. The results of these experiments appear in Table 16.

If v represents the velocity of the combustion of the powder grains, p the pressure at which the powder burns, and a a constant, applicable to the powder employed, the formula of San Roberto is expressed by

$$v = a \cdot p^{\gamma},$$

where $\gamma = \frac{2}{3}$. The exponent γ in course of time under-

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* G. Piobert, Traité d'Artillerie, 1839; Compt. rend., I, pt. 8; 1840.

† See M. Berthelot, Force mat. exp., I, 85; 1883. H. Brinck, Innere Ballistik, 76; 1906. E. Frankland, Phil. Trans., **151**, 629; 1861.

TABLE 16. INFLUENCE OF PRESSURE ON VELOCITY OF COMBUSTION.

Altitude, meters.	Air pressure, millimeters.	Time consumed in burning, seconds.
220	740.0	35
400	724.3	35.2
750	694.1	36.1
1720	618.7	38.8
1820	610.4	39.0
2650	559.4	41.5
3000	529.4	44

went various modifications, varying between $\frac{1}{4}$ and 1,* but it never expressed satisfactorily the relation between the velocity of combustion of the powder grains and the pressure which obtains, especially under conditions in force in firearms. The cause of this variation lies in the fact that investigators have accepted the assumption that the grains of black powder burn in concentric layers and that therefore during the process of combustion a proportion exists between the time consumed in burning and the thickness of the layer of powder burned.

67. P. Vieille† proved, in a suggestive work, that this hypothesis is, in general, not true for black powder, but is true for explosives, such as gelatinized nitrocellulose, which possess a nearly homogeneous character. He determined experimentally the velocity of combustion for various powders in the following manner. The powder was brought to ignition in a steel bomb (Fig. 9), and the velocity with which a steel

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* According to L. Roux and E. Sarrau, $\gamma = \frac{1}{2}$; according to H. Sébert, H. Hugoniot and Moisson, $\gamma = 1$; i.e., the velocity varies in direct proportion with the pressure.

† P. Vieille, Mem. poudr. salp., VI, 256; 1893. See also W. Wolff, Kriegstec., Z., 6, 1; 1903.

piston *E*, driven by the gases from the decomposed powder, compressed a soft copper cylinder *F*, and was registered on a rotating cylinder by means of the sharp-pointed extension *G*, gave the velocity of combustion. It appeared in these experiments that geometrically similar spherical or cubical powder grains, when the powder composition consisted of a gelatinized mass, burned completely in uniform time only when their lineal dimensions were proportional. All non-gelatinized explosives, especially the black powder then in use, burned under high pressure in a far less regular manner. Black gunpowder whose grains were 4 millimeters thick burned in only 0.0072 second, which was less time than the same mass in grains of 13 millimeters thickness. Another black gunpowder burned in nearly the same time, when the size of the grains were as widely different as 2 millimeters and 13 millimeters. If such powders burned in concentric layers, the time consumed in burning under the same conditions of composition, pressure and the like must be proportional to the size of the grains. A gelatinized nitrocellulose did in fact conduct itself in this manner. The grains (thin leaves) of 0.5 millimeter burned in 0.0043 second; those of 2 millimeters required 0.018 second. The dependence of veloc-

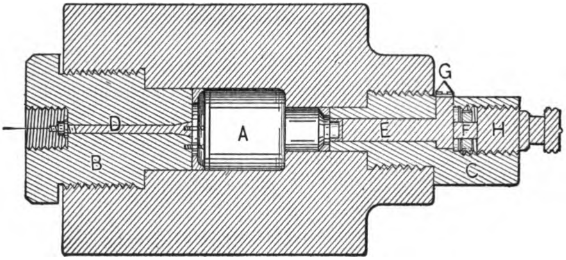

Fig. 9.

ity of combustion upon pressure in the case of gelatinized powders could be expressed in a potential function of the above-named (section 66) form, wherein γ varied between $\frac{5}{9}$ and $\frac{2}{3}$ according to the kind of powder. On account of the small number of experiments and types of powders which could be used in framing a conclusion there still remained a doubt whether the velocity of combustion is not simply proportional to the pressure so that the relation between the two could be just as correctly expressed by a linear function of the form

$$v = a + bp.$$

68. By the establishment of these facts, P. Vieille laid the foundation for the modern gelatinized smokeless gunpowder that, on account of its regular velocity of combustion within wide limits, allows a much higher utilization of its energy than was possible in the case of black powder without injuring the weapon to any material extent (sections 91 and 184). To what extent the velocity of combustion increases with pressure, in the case of both black powder and smokeless powder, may be seen from Table 17.*

The summary in Table 17 shows that the variation in the velocity of combustion with the pressure is characteristic for various types of powder. Under atmospheric pressure the powders mentioned fall into the following order in respect to their combustion velocity. Nitrocellulose powder is the slowest burning powder, then comes 40 per cent nitroglycerin powder, 58 per cent nitroglycerin powder, ordinary black powder, and finally brown prismatic powder,

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* Brinck, Inn. Ball., 119; 1906. See also W. Heydenreich, Lehre vom Schuss, II, 21; 1898. P. Vieille, Mem. poudr. salp., VII, 370; 1893. R. Liouville, Compt. rend., **140**, 708; 1905. J. E. Petavel, Phil. Trans., **205**, 357; 1905.

TABLE 17. VELOCITY OF COMBUSTION OF POWDER.

Pressure, atmospheres.	Black powder.		Nitrocellulose powder, cm./sec.	Nitroglycerin powder.	
	Gunpowder, cm./sec.	Brown prismatic, cm./sec.		40 per cent nitroglycerin, cm./sec.	58 per cent nitroglycerin, cm./sec.
1	0.80	0.90	0.08	0.27	0.5
500	6	4	5	10	15.5
1000	8	4.5	7.5	16.5	23
1500	9	5	10	21.5	29
2000	10	6	12	26	35
2500	.....	6.5	13.5	30	39
3000	.....	7	15	.....	42
3500	.....	.....	17	.....	46
4000	.....	.....	18	.....	49

which belongs to the type of powders burning the fastest. This order becomes reversed if the powders be arranged according to the magnitude of the exponential coefficient γ (section 66), which expresses the influence of pressure on the velocity of combustion. The combustion of powders of the black-powder type is accelerated only comparatively little by pressure, and on account of this property of black powder it has always been valued as being least injurious to the weapon. In comparing nitrocellulose and nitroglycerin powders we learn the fact, important from a ballistic standpoint, that although the latter burns more rapidly than the former, yet the influence of pressure on the variation in the velocity of combustion is generally smaller in the case of the latter. Many believe that this fact should indicate a great advantage of nitroglycerin over nitrocellulose powders.

69. There exists as much doubt in regard to the influence of the initial pressure exerted upon an explosive system on the higher limit of velocity of propagation of the explosion as in the case of the initial

temperature (section 64). M. Berthelot and P. Vieille* varied the initial pressure in the proportion of 1 : 3, and from the results of their experiments expressed the belief that the velocity of propagation of the explosion in combustible gaseous mixtures was independent of the pressure. Hydrogen and oxygen mixtures, for instance, gave them the following results:

TABLE 18. INFLUENCE OF PRESSURE ON VELOCITY OF DETONATION.

Initial pressure, millimeters.	Velocity, meters.
560	2763
760	2800
1260	2776
1580	2744

The gas was detonated in a caoutchouc tube, of 5 millimeters inner diameter and about 40 meters long, which was provided at the ends with stopcocks. The detonation was brought about by a small pellet of mercury fulminate, which in turn was detonated by an electric spark. The progressive explosion waves broke the electric current in two places by tearing strips of tin foil, and the time which elapsed between the two breaks was measured by means of a Boulengé chronograph. It should be mentioned, incidentally, that as far as the velocity of the explosion waves was concerned it appeared quite immaterial whether the tube was composed of caoutchouc, glass, lead or other material, and whether it was laid in a straight length or in curves or coils. Further, the inner diameter

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* M. Berthelot and P. Vieille, Compt. rend., **95**, 151, 199; 1882. See also M. Berthelot, Compt. rend., **94**, 149; 1882: and Force mat. exp., I, 150; 1883.

of the tube exerted a retarding influence only when it fell below 2 millimeters.

70. H. Dixon[*] repeated these experiments with greater exactness in that he took into account the circumstance that the point of the first breaking of the current was sometimes reached before the higher limit of the velocity of propagation was attained. He detected a slight increase of velocity of the explosion waves with increasing pressure.

TABLE 19. INFLUENCE OF PRESSURE ON THE VELOCITY OF EXPLOSIVES.

Initial pressure, millimeters.	Velocity of the explosion waves in explosive gases.	
	Average value, meters.	Number of experiments made.
200	2627 $\begin{Bmatrix}+9\\-8\end{Bmatrix}$	3
300	2705 $\begin{Bmatrix}+18\\-25\end{Bmatrix}$	5
500	2775 $\begin{Bmatrix}+9\\-11\end{Bmatrix}$	3
760	2821 $\begin{Bmatrix}+8\\-9\end{Bmatrix}$	5
1100	2856 $\begin{Bmatrix}+13\\-12\end{Bmatrix}$	6
1500	2872 $\begin{Bmatrix}+11\\-11\end{Bmatrix}$	6

The apparatus used by H. Dixon for this research is shown in Fig. 10,[†] where *AC* and *EF* are two steel tubes which are connected by a lead tube *D* about 75 meters in length. At *C* and *E* are the interrupters in the form of thin strips of silver foil, and at *B* two copper wires are inserted through which an electric current ignites the gaseous mixture by means of elec-

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[*] H. Dixon, Phil. Trans., **184**, 97; 1893. Ber, **38**, 2419; 1905.

[†] J. W. Mellor, Chem. Stat. Dyn., 452; 1904.

tric sparks. The whole apparatus is filled with the explosive gaseous mixture to be tested through the cocks *A* and *F*. When the explosion waves, starting at the point *B*, reach *C*, the first silver strip is broken and at the same instant the first stylus begins registering on an electric apparatus for this purpose. When the explosion has traversed the tube *D* and reached the second silver strip *E*, a second stylus is released and registers its mark on the apparatus. The time between the two breaks can be calculated from the impression of the styluses on a blackened tablet affixed to the registering apparatus which is rotated with a known velocity.

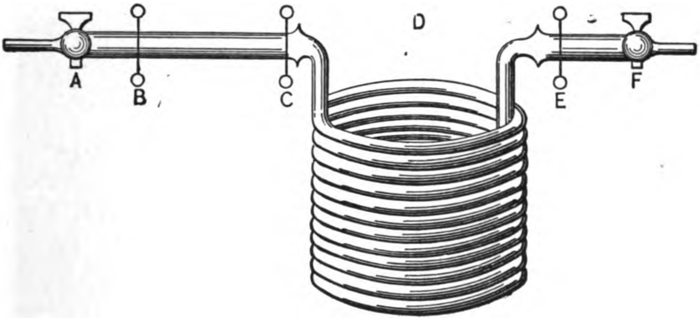

Fig. 10. Dixon's Device for Determining the Velocity of the Explosion Wave.

71. M. Berthelot and H. le Chatelier,* working together later in an investigation into the explosion velocity of acetylene under the considerably higher pressures of from 5 to 36 atmospheres, came to the same conclusion: that an increase of the explosion velocity occurs with increasing pressures. The acetylene was run into short glass tubes of from 2 to 6 millimeters inner diam-

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* M. Berthelot and H. le Chatelier, Compt. rend., **129,** 427; **1899: 130,** 1755; 1900.

eter and only 1 meter long, since greater lengths could not stand the pressure employed. The detonation was brought about by means of mercury fulminate. On account of the high lighting power of acetylene decomposing with the separation of carbon, no difficulty was experienced in registering the process by means of photography. The velocity of transmission of the explosion increased from 1000 to 1600 meters in round numbers, when the pressure exerted upon the acetylene was increased from 5 to 30 atmospheres.

72. After the velocity of transmission of explosion in gaseous systems under various conditions seemed to have been accurately determined, M. Berthelot and P. Vieille* extended these experiments to liquid and solid explosive substances. Observations on the influence of the initial pressure on the velocity of the transmission of the explosion were not included in the work or were frustrated in consequence of the concurrence of many unforeseen factors. Even a slight difference of temperature in the case of the liquid explosives nitroglycerin and methyl nitrate brought about an unequal detonation velocity (section 65). The two investigators attributed this to the change in the viscosity of such oily liquids. In contrast to experiences with gaseous mixtures, the material of which the explosion tubes were composed and the strength of their walls exercised an influence in the case of liquid explosives. It could not be determined with certainty from the observations whether or not the diameter of the tube influenced the velocity to be measured, yet this has recently been shown to be probable and was proved, especially for free lying cartridges having va-

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* M. Berthelot and P. Vieille, Ann. chim. phys., (6), **6**, 556; 1885: **23**, 485; 1891. Mem. poudr. salp., IV, 7; 1891.

rious diameters, by C. E. Bichel.* A number of cartridges of equal diameters were laid in a row (Fig. 11), so that a single unbroken cartridge 35 meters in length was formed.

The detonation velocity, measured by a Boulengé chronograph, proved, to a certain extent, to be dependent upon the diameter of the cartridges and increased with increasing diameter. The highest limit of velocity was reached in the case of nitroglycerin explosives with 30 millimeters, and in the case of ammonium nitrate explosives with 50 millimeters diameter of cartridge. The increase in the velocity of detonation with the diameter of the cartridge was determined by M. Dautriche† for cheddite (Table 22, No. 31).

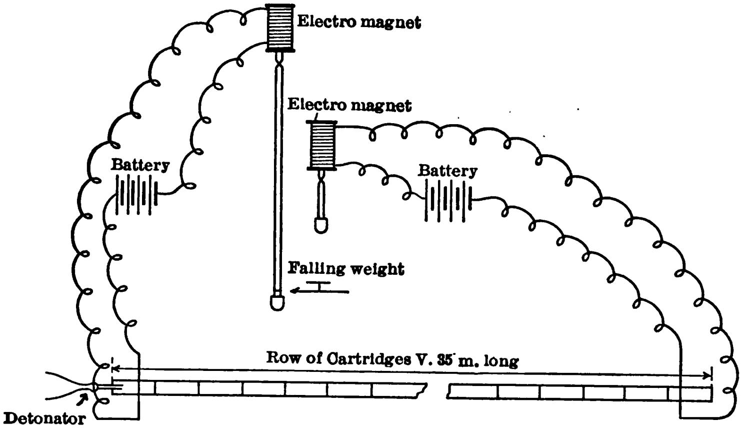

FIG. 11. Device for Determining the Rate of Detonation of Cartridges of Explosives.

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* C. E. Bichel, Z. Berg. Hütten. Salin., **50,** 669; 1902. Glückauf, **40,** 1040; 1904. See also H. Mettegang., Ber. Kon. angew. Chem., II, 322; 1903.

† M. Dautriche, Compt. rend., **143,** 641; 1906: **144,** 1030; 1907. See also Z. ges. Schiess Sprengstoffw., **74,** 313; 1907. Also A. M. Comey, 7th Int. Congress Applied Chem., III, B, 28; 1910: who confirmed the value of Dautriche's method and extended its application to the determination of the velocity of the detonation wave in air.

73. In the case of pulverulent explosives, where the interstices are filled with air, the volumetric density of the mass, that is, the ratio of the weight of the charge to its volume (cubic density), is of influence. While M. Berthelot and P. Vieille, *loc. cit.*, recognized only the increase in the velocity of propagation in explosions with an increase in volumetric density, M. Dautriche, *loc. cit.*, showed that when an explosive is compressed its detonation velocity is at first increased, but, by continued compression, a point is reached beyond which the velocity begins to decrease and this point is characteristic for each explosive substance. The descending branch of the corresponding curve appears to have the character of an asymptote. The method of measurement given by M. Dautriche is based upon the use of detonating fuses, of very accurately known velocity of propagation, in connection with an apparatus which records the point of meeting of two detonations coming from opposite directions. Two fuses *AB* and *AC* are laid down in a closed curve and so arranged that both may be fired by one and the same muffle-shaped detonating cap containing 1.5 grams of mercury fulminate. The other ends of the two fuses do not meet end to end but overlap each other a short distance. If both fuses are detonated with the same uniform velocity, a thing which is not difficult to attain, the two detonations must meet together in a point *S*, which is so situated that the lengths *ABS* and *ACS*, which are traversed in equal times by the detonation, are equal. If now a metal tube of definite length, filled with the explosive to be tested, is connected in one of the branches, and the meeting place, *S*, of the two detonations again determined, there is obtained a mark of the fuse which corresponds in its time of explosion to that of the column of

explosive employed. Since the detonation velocity of the fuse has been once for all definitely determined we obtain by this means the absolute velocity of detonation for the explosive in question. Dautriche found in this way the following figures for cheddite, consisting of 80 per cent potassium chlorate, 5 per cent castor oil, 13 per cent mononitronaphthalene and 2 per cent dinitrotoluol, using for the experiment a zinc tube 20 millimeters in diameter.

TABLE 20. INFLUENCE OF VOLUMETRIC DENSITY UPON THE VELOCITY OF DETONATION OF CHEDDITE.

Volumetric density......	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.38	1.52
Velocity of detonation, meters................	2100	2248	2430	2504	2550	2510	2360	2166	
Number of experiments..	5	5	4	4	4	4	4	1	Failure.
Average deflection......	20	52	14	19	31	37	42		

The following figures were obtained in the same way for dynamite consisting of 75 per cent nitroglycerin and 25 per cent kieselguhr.

TABLE 21. INFLUENCE OF VOLUMETRIC DENSITY UPON THE VELOCITY OF DETONATION OF GUHR DYNAMITE.

Volumetric density....	0.63	0.79	0.85	1.34	1.54	1.62	1.69	1.71	1.74
Velocity of detonation.	1991	2397	2563	3670	5230	6794	4207	2460	Failure

74. It is worthy of notice that gaseous mixtures composed of explosive and inert components show a behavior analogous to the above (section 73), in regard to the change in the detonation velocity with increasing concentration of the explosive component. Compare the corresponding curves (Figs. 12 and 13), one showing the relation between the velocity of detonation and density in the case of cheddite, and the other the

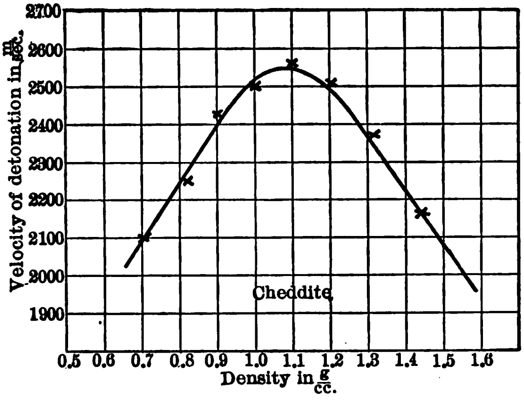

Fig. 12. Change of Rate of Detonation with Density in Solid Explosives.

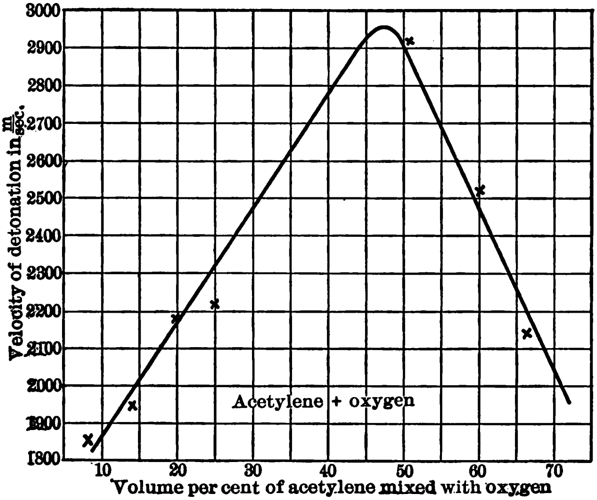

Fig. 13. Change of Rate of Detonation with Concentration in Gases.

velocity of detonation and the concentration of acetylene in its mixtures with oxygen.*

There appear here relations similar to those existing

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* H. le Chatelier, Compt. rend., **130**, 1757; 1900.

in the case of combustion propagated with low velocities.*

Just as this is confined within limited boundaries beyond which an explosive transformation can no longer take place, so the detonation potentiality ceases at an upper and a lower limit of concentration. There results in the case of explosives a "failure" (Versager) (section 15).

75. In Table 22 we have collated the reliable determinations of the velocity of detonation for a number of explosive systems.

(*c*) *Catalytic influences.*

76. H. Dixon† showed what a surprising influence a small quantity of water vapor has upon the velocity of propagation of the explosion in mixtures of carbon monoxide and oxygen ($2\,CO + O_2$) when the mixture is ignited by means of an electric spark (section 30). The influence of a detonator upon the velocity of the reaction at its upper limits (H. Dixon, *loc. cit.*) is somewhat similar to this, as may be seen from Table 23.

A distinct increase in the velocity of propagation is apparent with increasing moisture contents in the gas up to about 5.6 per cent, above which the diluting of the explosive gaseous mixture with inert water vapor begins to show its effect. When, in the place of water vapor, other gases which contained hydrogen were added, such, for instance, as H_2S, NH_3, HCl, C_2H_4, etc., so that

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* See also the velocity of oxidation dependent upon the oxygen pressure, for example in the case of Phosphorus, K. Ikeda, J. Coll. Science Imperial Univ., Japan, **6**, 43; 1893. T. Evans, Z. phys. Chem., **16**, 315; 1895.

† H. Dixon, Chem. News, **46**, 151; 1882: Phil. Trans., **175**, 617; 1884: **184**, 111; 1893. See also H. B. Baker, J. Chem. Soc., **65**, 611; 1894, and J. W. Mellor and E. J. Russell, do., **81**, 1272; 1902.

TABLE 22. VELOCITIES OF DETONATIONS.

No.	Name of the explosive system.	Composition of the explosive system.	Inner diam. of the rod or tube, mm.	Density.	Velocity, m./sec.	Literature.
	A. Gaseous Mixtures.					
1	....	$2H_2+O_2$	<10	....	2820	M. Berthelot, Sur la force des matieres explosives, I, 159; 1883. H. Dixon, Phil. Trans., **184**, 97, 161; 1893: **200**, 328; 1903.
2	....	H_2+N_2O	<10	....	2300	
3	....	H_2+Cl_2	<10	....	1730	
4	....	$2CO_2+O_2$	<10	....	1680	
5	....	$2CH_4+3O_2$	<10	....	2320	
6	....	$C_2H_4+2O_2$	<10	....	2360	
7	....	$2C_2H_2+5O_2$	<10	....	2390	
8	....	$C_2N_2+O_2$	<10	....	2730	
9	....	$C_2H_2+N_2O$	<10	....	2580	H. le Chatelier, Compt. rend., **130**, 1757; 1900.
10	....	C_2H_2+2NO	<10	....	2850	
	B. Liquid Explosives.					
11	Nitroglycerin....	$C_3H_5(NO_3)_3$	3–30	1.60	1000–1600	M. Berthelot, Ann. Chim. Phys., (6), **6**, 556; 1885: **23**, 485; 1891.
12	Methyl nitrate...	$CH_3.NO_3$	3	1.18	2100	
13	Panclastite......	$CS_2+N_2O_4$	3	1.35	4600–6600	
	C. Solid Explosives, Simple Compounds.					
14	Mercury fulminate.	$Hg(CNO)_2$	6.45	?	3920	C. E. Bichel, Glückauf, **41**, 1195; 1905.
15	Nitromannite....	$C_6H_8(NO_3)_6$	<4	1.53–1.58	6900–7100	F. Abel, Phil. Trans., **156**, 269; 1866: **157**, 181; 1867: **159**, 489; 1869: **164**, 337; 1874. M. Berthelot, Ann. Chim. Phys., (6), **6**, 556; 1885.
			<4	1.9	7700	
16	Nitrocellulose (dry).	$C_{24}H_{29}(NO_3)_{11}O_9$	2	0.69–0.73	3700–3800	
			<4	0.9	3900	
			2	1.17	4800	
			<4	1.2	4300	
			3.15	1.27	5400	
			<4	1.4	4800–6200	
17	Nitrocellulose (moist).	70% nitrocellulose.. 30% water.	31	?	5900–6100	
18	Nitrohydrocellulose.		<4	?	4900	
			<5.5	?	6100	
19	Nitrostarch.....	....	<4	1.1–1.2	5000	
			<4	1.35	5500	
20	Picric acid......	$C_6H_2(NO_2)_3OH$	30	1.55	7700–8200	C. E. Bichel, Glückauf, **40**, 1043; 1904.
21	Trinitrotoluene ..	$C_6H_2(NO_2)_3CH_3$	30	1.55	7200	
	D. Solid Explosives, Mixtures.					
22	Black powder....	75 Potassium nitrate. 13 Charcoal. 12 Sulphur.	30	1.04	300 no detonation.	
23	Guhr dynamite..	75 Nitroglycerin... 25 Kieselguhr.	3	?	2300–2800	M. Berthelot, Ann. Chim. Phys., (6), **6**, 556; 1885.
			6	?	1900–3200	
			31	?	5900–6600	F. Abel, as before. C. E. Bichel, Glückauf, **40**, 1043; 1904: Dautriche, Compt. rend., **143**, 643; 1906.
			30	1.52	6800	
			20	1.62	6800	

TABLE 22. — *Continued.*

No.	Name of the explosive system.	Composition of the explosive system.	Inner diam. of the rod or tube, mm.	Density.	Velocity, m./sec.	Literature.
	D. Solid Explosives, Mixtures (Cont'd).					
24	Explosive gelatin.	93 Nitroglycerin... 7 Collodion.	30	1.63	7700	C. E. Bichel, Glückauf, **40**, 1043; 1904.
25	Gelatin dynamite.	63.5 Nitroglycerin. 1.5 Collodion. 27 Sodium nitrate. 8 Sawdust.	30	1.67	7000	
26	Carbonite........	25 Nitroglycerin. 34 Potassium nitrate. 1 Barium nitrate. 38.5 Rye flour. 1.0 Tan bark. 0.5 Soda.	30	1.42	2700	
27	Ammonium carbonite.	82 Ammonium nitrate. 10 Potassium nitrate.	......	1.19	3100	
		4 Rye meal. 4 Gelatinized nitroglycerin.	30			
28	Donarite........	80 Ammonium nitrate. 12 Trinitrotoluene. 4 Rye meal. 4 Gelatinized nitroglycerin.	30	1.31	4100	
29	....	87 Ammonium nitrate.				F. Heise, Sprengstoffe und Zündung der Sprengschüsse 9. 1904.
		6 Ammonium sulphate.	40	1-1.2	2900	
		7 Dinitroglycerin.	50	1-1.2	3300	
30	....	92 Ammonium nitrate.	30	1-1.2	2900	
		8 Naphthalene....	40	1-1.2	3300	
			50	1-1.2	3700	
31	Cheddite........	80 Potassium chlorate. 5 Castor oil.				Dautriche, Compt. rend., **143**, 643; 1906.
		13 Mononitronaphthalene.	20	1.10	2550	
		2 Dinitrotoluene.	40	1.17	2900	

water could be formed in the reaction, a similar effect was noticed in every case, but not in other cases when no water was formed, as, for instance, with SO_2, N_2O, CCl_4, C_2N_2 and the like. Pure dry explosive mixtures of hydrogen and oxygen, on the other hand, showed the same velocity as moist.*

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* H. Dixon and L. Bradshaw, Proc. Roy. Soc., **79** [A], 234; 1906. Z. phys. Chem., **61**, 373; 1907.

TABLE 23. VELOCITY OF DETONATION OF MOIST CARBON MONOXIDE EXPLOSIVE MIXTURES.

Explosive carbon monoxide mixture, $2\,CO + O_2$.	Water vapor, per cent.	Detonation velocity in meters.	
		Detonated with detonator.	Detonated by electric sparks.
Dried.			
With P_2O_3	....	$1264\left\{\begin{matrix}+3\\-2\end{matrix}\right\}$ (2 determinations)	36
With H_2SO_4	....	$1305\left\{\begin{matrix}+15\\-16\end{matrix}\right\}$ (4 determinations)	119
Saturated with H_2O vapor.			
At 10° C	1.2	$1676\left\{\begin{matrix}+11\\-\ 6\end{matrix}\right\}$ (6 determinations)	175
At 20° C	2.3	$1703\left\{\begin{matrix}+15\\-18\end{matrix}\right\}$ (6 determinations)	...
At 28° C	3.7	$1713\left\{\begin{matrix}+13\\-11\end{matrix}\right\}$ (3 determinations)	...
At 25° C	5.6	$1738\left\{\begin{matrix}+12\\-12\end{matrix}\right\}$ (5 determinations)	244
At 45° C	9.5	$1693\left\{\begin{matrix}+\ 7\\-12\end{matrix}\right\}$ (3 determinations)	...
At 55° C	15.6	$1666\left\{\begin{matrix}+\ 8\\-16\end{matrix}\right\}$ (3 determinations)	...
At 60° C	20.0		317
At 65° C	24.9	$1526\left\{\begin{matrix}+8\\-7\end{matrix}\right\}$ (2 determinations)	...
At 75° C	38.4	$1266\left\{\begin{matrix}+6\\-6\end{matrix}\right\}$ (2 determinations)	...

77. The cause* of the accelerating influence of water vapor on the detonation of explosive carbon monoxide mixtures can probably be accounted for by the fact that the two reactions

$$CO + H_2O = CO_2 + H_2O \quad \text{and} \quad 2\,H_2 + O_2 = 2\,H_2O,$$

at the temperatures of the experiments, proceed more rapidly than the reaction

$$2\,CO + O_2 = 2\,CO_2,$$

which proceeds without the formation of water.

According to another conception,† the transitory formation and decomposition of hydrogen peroxide is regarded as an accelerating intermediate reaction.

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* H. Kühl, Z. phys. Chem., **44,** 385; 1903. P. Rohland, Chem. Ztg., **30,** 808; 1906. J. W. Mellor, Chem. stat. dyn., 300; 1904. E. Armstrong, Proc. Royal Soc., **40,** 287; 1886: **70,** 99; 1902: **74,** 86; 1904.

† M. Traube, Ber., **15,** 666; 1882: **18,** 1890; 1885: cf. also V. Meyer, Ber., **19,** 1099; 1886.

3. Explosion Waves.

78. Hardly anything is known with certainty in regard to the laws which govern the explosive transformations known as "explosion waves," or "detonation waves,"* which proceed with a velocity of thousands of meters in a second. Many investigators have attempted, both by theoretical and experimental methods, to establish a relation between these waves and better-known phenomena, such as sound waves.

79. According to M. Berthelot, a kind of parallel certainly exists between explosion waves and sound waves in homogeneous mixtures,† especially gases, since both proceed with uniform velocity, and these velocities are specific constants for each medium. The behavior of the two movements are analogous also in respect to many other circumstances, such, for instance, as the retardation of the velocity in consequence of friction, as in narrow tubes. On the other hand, there exist essential differences, as, indeed, are to be expected when we consider that the explosion waves owe their existence to a progressive chemical reaction, while the sound waves are created and propagated simply by physical means. Furthermore, simple, progressive, chemical reactions can certainly not produce the periodic changes of pressure which characterize sound. M. Berthelot, in another place, points out the further difference that the velocity of the progressing detonation is far greater than that of sound in the same medium. The detonation velocity of explosive gas (hydrogen and oxygen), for instance, is 2840 meters per second, while sound waves in the same medium

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* M. Berthelot, Force mat. exp., I, 134; 1883. Compt. rend., **93**, 21; 1881: **94**, 101, 149, 822; 1882: **95**, 151, 199; 1882.

† Charles E. Munroe, Am. J. Sci., (3), **36**, 48; 1888.

travel but 514 meters. An explosive gas of carbon monoxide and oxygen gave for the former a velocity of 1090 meters per second and for the latter only 328 meters, while sound waves in carbon dioxide, the product of this explosion, were only 264 meters. A general analogy between the two kinds of motion can, however, be drawn if we accept the theory of M. Berthelot, that the propagation of the detonation is caused by the impact of gas molecules whose kinetic energy appears as the sum of the total heat of the explosive reaction. If d be the density of the products of an explosion, the density of air being taken as 1, and T the temperature of explosion, i.e., the quotient of the heat of explosion divided by the average specific heat of the products of explosion under constant pressure, then v, the velocity of the explosion waves, is

$$v = 29{,}354\sqrt{\frac{T}{d}}.$$

For a mixture $2\,H_2 + O_2$, the detonation velocity was calculated at 2831 meters per second at 0° C. and 760 millimeters, while 2810 meters was found experimentally. The agreement between the calculated and the determined velocities for the mixture $CH_4 + 2\,O_2$ is not so good, 2427 meters being calculated as against 2287 meters found, while the calculation fails entirely in the case of $2\,CO + O_2$, 1941 meters being calculated and only 1089 meters found.

80. H. B. Dixon,* in his conclusions drawn from similar observations, assigns first importance to the circumstance that, during the explosion of a gaseous mixture, immediately adjoining the region in reaction is another region of very highly heated gas into which

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* H. B. Dixon, Phil. Trans., **184**, 97; 1893.

the explosion wave enters, and he calculated with what velocity a sound wave would be propagated through a gaseous mixture at such a high temperature. This method of calculation, applied in other cases, gives results which in many instances agree more closely with the observed velocities than those calculated by the formula of Berthelot, yet it shows some unexpectedly wide deviations which necessitate the further assumption of an incomplete reaction in the region just traversed by the explosion wave. This method of calculation gives for the mixture $2\,H_2 + O_2$ an explosion velocity of 3416 meters, while only 2821 meters was found. The results are as widely divergent in the case of the explosion of cyanogen and oxygen. In the former case the water, which is a product of the explosion, is dissociable, and makes an incomplete combustion possible, but this is not true in the latter case, where the deviation between observation and calculation is yet to be explained.

81. E. Jouguet* has developed a theory which is based on the calculations of B. Riemann† and H. Hugoniot,‡ on percussion waves of infinitely small magnitude of impulse of the second order. According to this theory explosion waves with constant velocity seem possible only on the condition that they be plane

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* E. Jouguet, Compt. rend., **138,** 1685; 1904: **139,** 121; 1904: **140,** 711; 1905: **142,** 1034; 1906: **144,** 415; 1907. See also A. Schuster, Phil. Trans., **184,** 152; 1893. D. L. Chapman, Phil. Mag., (5), **47,** 90; 1899. Crussard, Compt. rend., **144,** 417; 1907. Crussard and E. Jouguet, Compt. rend., **144,** 560; 1907. H. Mache, Ann. Phys., (4), **24,** 544; 1907.

† B. Riemann, Göttinger, Abhandlungen, **8,** 43; 1858.

‡ H. Hugoniot, J. Math. pures et appl., (4), **3,** 477; 1887: **4,** 153; 1888. See also W. Nernst, Physik. chem. Betrachtungen über den Verbrennungs prozess in den Gasmotoren, Z. Vereins Ingenieure, Berlin, 1905.

and not spherical. In fact all measurements thus far made have been of velocities in narrow tubes or small files where there is no possibility for the formation of the spherical detonation waves which are probably formed when large masses are exploded.

82. It is apparent from the foregoing discussion that the velocity of detonation, even in homogeneous gaseous mixtures, cannot readily be computed mathematically. P. Vieille* holds, as did M. Berthelot before him, that the observed limits for the velocity of propagation of explosive reactions are by no means constant quantities, especially in the case of pulverized, plastic or solid explosive substances or mixtures, but considers them as dependent upon more or less arbitrary experimental conditions and especially upon the varying density of the explosive system (section 73), which influences the gaseous products of explosion and consequently the velocity of the explosion waves. This velocity increases far more than proportionally with increasing density. If the density of the gaseous products of explosion could reach the theoretical maximum or the density of the original liquid or solid explosive, velocities far in advance of those previously measured would result. By the use of the formula

$$v = \sqrt{\frac{E \cdot \gamma}{d}},$$

in which E denotes the elasticity of the gaseous products of explosion under constant temperature; γ, the ratio of the specific heat of this medium under constant pressure to that at constant volume; d, the density of the same medium, P. Vieille has derived the follow-

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* P. Vieille, Mem. poudr. salp., IV, 20; 1891. See also R. Threlfall and Adair, Proc. Roy. Soc., **45**, 450; 1889: **46**, 496; 1890.

ing values for the velocity of propagation of explosion waves in compressed, dry guncotton.

TABLE 24. VIEILLE'S RELATION BETWEEN DENSITY AND VELOCITY OF DETONATION FOR GUNCOTTON.

Volumetric density.	Velocity in meters.
0.1	1,271
0.8	5,700
0.9	11,400
1.0 and over	to 8

Detonation velocities of more than 6000 meters per second have been observed (Table 22), for compressed guncotton with a density of 1.2 to 1.4, yet it is not certain to what extent these results have been influenced by errors in measurement. These deductions appear no longer to be in accordance with the facts in the light of the investigations of Dautriche (section 73), which show that the detonation velocity in pulverulent explosives such as cheddite and guhr dynamite by no means continues to increase with increasing density, but soon reaches a maximum and then begins to decrease.

83. The above-mentioned influence of the concentration on the velocity of propagation of an explosive reaction (section 73) is not surprising when we consider that in heterogeneous explosives the explosive substance alternates with another inert substance, such as air, on account of which the percussion waves must necessarily be discontinuous since they owe their existence to purely chemical causes.

M. Berthelot* was the first to conceive that the

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* M. Berthelot, Force mat. exp., I, 122; 1883.

explosion waves discovered by him can be separated into two different kinds of waves, viz., a purely chemical percussion wave, consisting of an uninterrupted transformation of chemical energy into heat and mechanical energy, and a second purely physical wave. The former is the true so-called explosion wave. The chemical percussion wave, once produced, propagates itself with constant velocity because it is supported by the continuous chemical reaction. The physical wave, on the contrary, continually decreases in intensity with the square of the distance (section 151), because its kinetic energy, which is due to the original chemical impulse, is scattered in the surrounding inert gases. If this view be accepted it appears possible that both kinds of waves and, therefore, their velocities also, must coincide to a greater or less degree, according to the character and dimensions of the inert matter filling the interstices of heterogeneous mixtures (see also "Impact of Explosions" and the deadening influence of air, section 154).

CHAPTER III.

EXPLOSIONS PRESSURE.

84. Explosive transformations are always characterized by their ability to perform a large amount of mechanical work in an extremely short time. The energy transformed can be transmitted only by those decomposition products which are in the form of gas or vapor, since, except that which appears as heat, only those products are able to do this which absorb the energy liberated by the exothermal reaction, in the form of elastic force. The greater the velocity with which the chemical transformation is initiated and propagated the less is the amount of heat which is lost to the energy of expansion through radiation and conduction. Even under the most unfavorable conditions, as in the case of relatively slow explosive reactions, so much expansive energy is transmitted to the gases that the surrounding medium experiences a corresponding pressure. An intimate relationship exists, therefore, between the velocity of the explosive reaction and the pressure exerted by the products of the explosion. It is at least doubtful whether the velocity of the expansive energy is at first identical with the initial velocity of the reaction or with the propagation of the explosion once begun, for in the case of the expansion of gases a transportation of matter takes place, while in the explosion waves there occurs a change of chemical condition. If, however, the velocity with which the gases expand in the first

instant is not equal to the velocity of detonation, then the kinetic energy of the gases will not be equal to the product of half the mass of these gases by the square of the velocity of detonation (section 90) as it should be.

85. Something definite has been learned with regard to the pressure of the gaseous products of explosion in the first stage of the explosive reaction, i.e., in the region between the initiation of the explosive reaction and the beginning of the expansion, so far at least as gaseous explosive systems are concerned. We are dealing here with pressures which do not greatly exceed the measurable pressure of explosion which is transmitted to the containing walls. In the case of solid and fluid explosives, this pressure is so great that it can only be approximately determined by experimental methods. It is estimated at thousands of atmospheres. According to calculation it must reach an infinite value,* especially in case the so-called "covolume of the explosive" is equal to or greater than the volume of the substance before the explosion, in which case the molecule itself is assumed to be incompressible. One molecule of mercury fulminate, for instance, undergoes explosive decomposition, according to the equation

$$Hg(CNO)_2 = 2\,CO + N_2 + Hg,$$

into four molecules of gas which at 0 degree and 760 millimeters of pressure occupy a thousand times the space occupied by the original substance. If, now, these four molecules of gas should be compressed, their volume would decrease in proportion as the pressure increased, but only to a certain point where the molecules actually come in contact with each other. This

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* E. Sarrau, Mem. poudr. salp., V, 125; 1892: VII, 225; 1894.

volume, although it is greater than the volume of the molecule of mercury fulminate, cannot be further decreased. It represents the lower limiting volume of the new-formed molecules and is called the covolume of the mercury fulminate.* E. Sarrau † has deduced the covolume of the gases most often formed in explosions, such as carbon dioxide, nitrogen, hydrogen, etc., from the investigations of E. H. Amagat ‡ on their compressibility, and found that it amounts in round numbers to $\frac{1}{1000}$ of the volume of the gas at 0 degree and 760 millimeters. This value of the covolume can be used as an experimentally given value. Nevertheless, it must not be forgotten that the calculation of the covolume gives only a purely theoretical approximation which may possibly differ considerably from the actual. That every resistance, the strongest casing, the hardest rock, must be broken by a practically infinitely great pressure cannot be doubted, and the pressure of the explosive, especially at high densities of loading, may be imagined.

86. All experimental determinations of explosion pressures are in reality calculated upon the second stage of the explosive reaction; that is, upon conditions in force after expansion has begun and indeed often after it has progressed to a considerable extent. The gases liberated within an inclosed space by the explosion press against the resisting walls, and it is the pressure thus developed which increases more or less rapidly at the maximum thus reached, or, in a narrower sense, the explosion pressure, which is measured. The veloc-

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* It would be more correct to call this the covolume of the products of explosion.

† E. Sarrau, Compt. rend., **94**, 639, 718, 845; 1882.

‡ Condensed in Ann. chim. phys., **29**, 68; 1893.

ity of the expansion of the gases is not measured. In general, this is unknown. It is known only that at the first instant of the explosion it is very great, perhaps even greater than the velocity of the explosion waves (section 84), and that at the end of the expansion it sinks to zero.

1. Rate of Increase of Pressure.

87. When an explosive reaction takes place in a closed, inflexible space, such as an explosion bomb, the velocity of the increase of pressure is given by the following relation between time and pressure (Fig. 14).

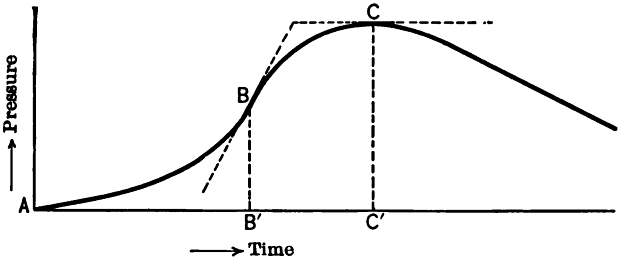

Fig. 14. Rate of Increase of Pressure.

The increase in pressure begins at the point A immediately after the first contact of the expanding gas with the walls of the containing vessel and it progresses with increasing velocity. The turning point B represents the maximum of the velocity of pressure increase, while the ordinate BB' represents the pressure of the explosion itself. The velocity of the pressure increase becomes again smaller after this and sinks to zero at the point C, where the tangent runs parallel to the abscissa and the pressure of explosion has reached its maximum CC'. The velocity of the pressure increase then becomes negative, and the pressure of the explosion decreases to the limiting value set by the experimental conditions of density of loading, temperature and the like.

88. The more or less steep course of this pressure curve, which is expressed by the quotients $\frac{BB'}{AB'}$, or $\frac{CC'}{AC'}$, stands in close relationship to that characteristic of explosive systems which has been called *brisance.* We speak of the *brisance* of an explosive reaction when the surrounding inert substances, which a relatively slowly increasing pressure (of explosion) would have moved forward as a whole, or in large pieces, and in the prescribed direction, lose their form entirely and are blown to fragments. Explosive systems which possess brisance are usually characterized by the fact that they are often able to exercise their full explosive effect when lying unconfined or confined only by a weak covering such as tinfoil, or under other similar conditions. The range of the effects of brisance is supposed to be largely confined to the immediate neighborhood of the explosion and it therefore exerts its greatest influence upon the medium with which it is in direct contact.

89. Although the methods in use for testing the brisance of an explosive substance are not entirely satisfactory from the practical standpoint, yet several properties have been selected as more or less characteristic for use in ascertaining the degree of brisance of an explosive. The following may be mentioned as the most important of these:*

(*a*) The substance to be tested is packed into a

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* Ph. Hess, Mitt. Art. Geniew., **10,** 139; 1879. Z. angew. Chem., **17,** 545; 1904. C. Beckerhinn, Mitt. Art. Geniew., **8,** 71; 1877. M. v. Förster, Versuche mit komprimieter Schiesswolle, 1883–86. F. Heise, Spreng. Zünd. Spreng., 37; 1904; Mem. poudr. salp., I, 120, 1882–83: IX, 29; 1897: XII, 232; 1903–04.

cartridge and laid on an iron plate, a wooden board, a lead cylinder (Fig. 15) or some similar substance and exploded by means of a detonator. The brisance is judged from the size and extent of the compression or shattered region caused by the explosion.

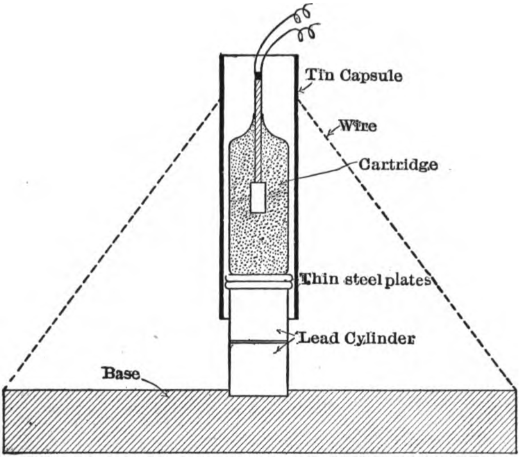

FIG. 15. Determining Brisance through Compression of Lead Cylinders.

The following is the most general method used for the testing of brisance, especially that of substances loaded into cartridges. A lead plate 45 millimeters square and 4 millimeters thick is laid on a steel ring. The cartridge to be tested is set on this plate and brought to explosion by means of a fuse which is carried through a ring above the cartridge in order to hold it firmly in a vertical position. The cartridge, on exploding, hollows out the lead plate and the excavation thus formed, together with the further traces of the explosion, presents to the eye a picture of the degree of brisance and an indication of the probability that the substance may be used as a primer. The photographs of four such lead plates, which have been used with substances of varying degrees of brisance, are shown in Fig. 16. Plate I was completely pierced by a powerful cartridge. Plate II was just penetrated by a weaker cartridge. On both plates may be seen the marks, in the form of diverging rays, caused by the cartridge which was itself completely blown to dust. On Plates III and IV, weak (moist) cartridges have left only slight traces and a number of diverging rays which, by their partly rough and deeper scratches, show that the copper capsule was not fully blown to dust.

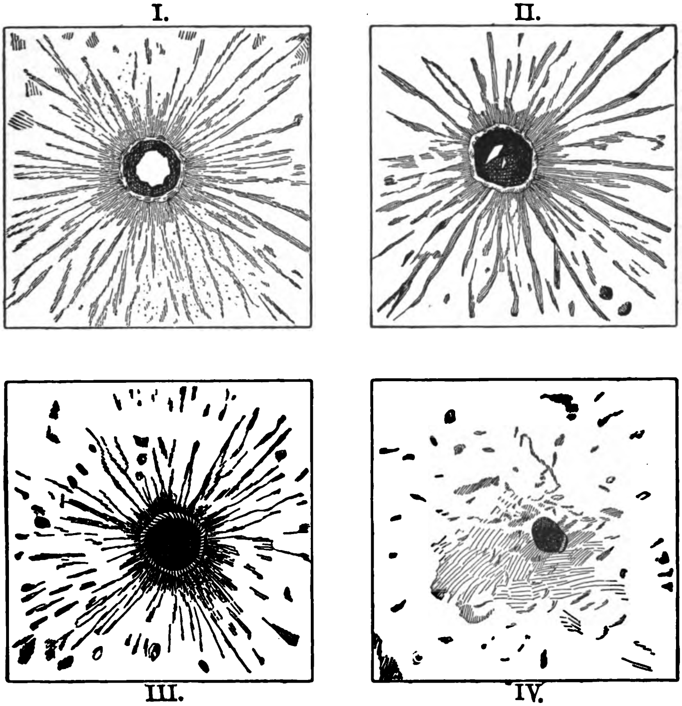

FIG. 16. Action of Detonators of Various Degrees of Brisance on Lead Plates.

(*b*) Ten grams of the substance to be tested, in the form of a cartridge, are placed on a small tripod of definite height and detonated by means of a detonator. The pressure of the explosion gases, progressing in radial direction, is transmitted through the intervening space to a steel plate which n turn transmits the impulse to a cylinder of soft copper or lead by means of a steel punch. The size of the puncture made on the cylinder

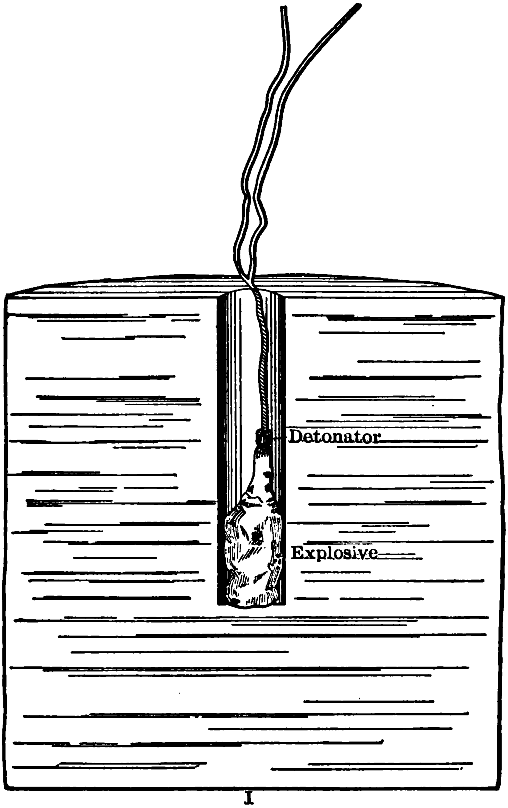

FIG. 17. Trauzl Lead Blocks before Firing in Them. Shown in Section.

serves as a measure of the brisance of the explosive. Since the explosive does not come into actual contact with the measuring apparatus, the brisance, as it is described above (section 88), is only partly measured.

(*c*) The substance to be tested is exploded within a massive lead cylinder of definite dimensions provided with a hole bored into its center which is likewise of definitely known dimensions (Trauzl Lead Block Test). Ten grams of the explosive, provided with a detonator, are placed in this hole, the remaining space is filled with dry sand and the charge exploded by aid of a fuse. A bottle-shaped cavity within the block results, the volume of which is measured and compared with the volume of the original cavity in the lead block. In Fig. 17, the halves of two such Trauzl

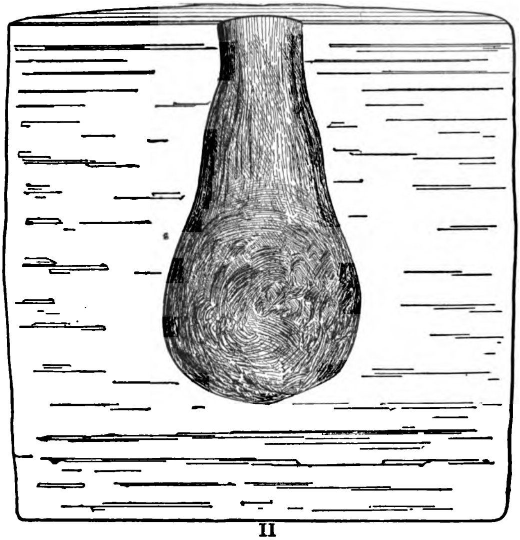

FIG. 17. Trauzl Lead Blocks after Firing in Them. Shown in Section.

lead blocks are given, showing in (I) the load before the explosion, and in (II) the space caused by the explosion, in which case the previous contents of the hole have been completely blown to powder.

The experiment shows that in general the more brisant (section 88) an explosive is, the more of its available energy is used in hollowing out the lead block. Mercury fulminate accordingly produces a very large hole in comparison to its small total energy, while black powder and gelatinized smokeless powder produce comparatively small holes whose appearance and form indicate that the gases of explosion are developed more slowly and have more time to escape through the loose sand with which the canal was filled. The results of tests with Trauzl lead blocks* are set forth in Table 25.

(*d*) The substance to be tested is placed in a bomb, exploded by means of a detonator, and the pieces into which the bomb is blown are counted.

90. It is yet an open question how far these and other similar empirical methods for measuring the relative brisance of various explosives are to be relied upon. So many factors enter into the idea expressed by the term brisance, such as velocity of combustion and detonation, heat of explosion, specific and volumetric density, specific gas volume and the like, that a more exact expression cannot be employed. Many technicists† are of the opinion that the detonation velocity is the main factor determining the brisance of an explosive system, and in fact a high velocity of transformation

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* For detailed method, see Charles E. Munroe, U. S. Naval Institute Proceedings, **5**, 25; 1879: **36**, 805; 1910.

† H. Mettegang, Ber. Kon. angew. Chem., II, 322; 1903. See also C. E. Bichel, Glückauf, **41**, 469; 1905. R. Threlfall, Phil. Mag., (5), **21**, 174; 1886.

TABLE 25. BRISANCE OF SEVERAL EXPLOSIVES.

No.	Designation.	Space hollowed* out in lead block, cubic centimeters.	Relative value, according to the hollowed space.	Relative value according to the energy set free.
1	Nitromannite..........	650	125	136
2	Nitroglycerin..........	600	115	120
3	Explosive gelatin (8 per cent collodion)......	520	100	100
4	Guncotton (13 per cent N)................	420	81	123
5	Gelatin dynamite (60 per cent nitroglycerin)...	410	79	132
6	Guhr dynamite (75 per cent nitroglycerin)...	350	67	85
7	Collodion cotton (12 per cent N)..............	250	48	108
8	Picric acid.............	300	58	118
9	Ammonium nitrate explosive..............	300	58	95
10	Nitroglycerin powder (40 per cent nitroglycerin)............	150	29	37
11	Guncotton powder.....	150	29	54
12	Mercury fulminate.....	150	29	116
13	Black powder..........	30	6	15

* After deduction of 61 cubic centimeters for the original bore hole and 17 cubic centimeters for the 2-gram detonator.

is an important condition for the appearance of this phenomenon. It does not, however, seem to be capable of proof that there exists a complete agreement between the detonation velocity of a given explosive and the brisant effects produced by its explosion, such as the puncturing of metal cylinders, hollowing out of lead blocks, transmission of initial effect from cartridge to cartridge through intervening space and so on. M. Dautriche* measured both the velocity of detonation of dynamite No. 1 (75 per cent nitroglycerin, 25 per cent kieselguhr) of various densities and the punctures caused by the explosion of 20 grams of such

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* M. Dautriche, Compt. rend., **144**, 1030; 1907.

dynamites on lead cylinders of 36 millimeters diameter and 72 millimeters height (Fig. 15) and found that the maximum puncture did not in the least correspond to the maximum velocity of detonation. While this velocity varied in the ratio of 1 : 3 the corresponding punctures in the lead cylinder varied only between 1 and 2. The hollow formed in the Trauzl lead block by the explosion of 10 grams of dynamites of various densities showed likewise an independence of the corresponding detonation velocities within wide limits.

It is known also that the velocity of detonation of gaseous systems may very nearly equal that of specifically brisant explosives and still give no evidence of brisance. A mixture of hydrogen and oxygen, as an example of the former, shows a velocity of 2800 meters per second, while ammonia carbonite, as an example of the latter, has a velocity of 3000 meters. Here it is evident that the lack of density in gaseous systems prevents brisant effects; hence such systems may safely serve as a motor force, as in the familiar gas motors. It seems evident that the specific or volumetric density and the degree of brisance bear a certain dependent relation to each other. A further example along this line is the small degree of brisance in the volumetrically light nitrocellulose in comparison with the denser nitroglycerin, although the former has the greater detonation velocity (Table 22).

C. E. Bichel* has proposed to use the product of half the mass of the products of explosion and the square of the velocity of detonation as an explosives' unit. This idea is based on the conception that the expanding gases go out from the place of the explosion with the

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* C. E. Bichel, Glückauf, **41**, 465; 1905. Z. ges. Schiess Sprengstoffw., **3**, 341; 1908.

velocity of propagation of the detonation, i.e., the velocity of the explosion waves. What we call "explosion waves" is not in reality actual motion, but is a virtual one, similar to sound waves, it being simply a propagation of a changed condition, and unlike air waves in a storm, where the air masses themselves are in motion (section 84).

M. Berthelot* has used the larger or smaller degree of dissociation in the products of explosion in explaining the different degrees of brisance of many explosives. The especially high brisance of mercury fulminate, nitrogen chloride, etc., whose products of explosion (N_2, CO, Hg, Cl_2) present no marked dissociation at the highest temperatures, even under the most favorable conditions, was explained from this viewpoint.

91. The following methods of determining the velocity of the development of pressure presuppose a relatively great expansion of the gases of explosion at the start (section 86), and therefore can give no definite information in regard to the phase of the reaction in which brisant effects predominate. All attempts to follow this stage of pressure development are defeated by the insurmountable difficulty of constructing a measuring instrument which will not be shattered. Notwithstanding this difficulty the experiments which have been carried out with available apparatus point to the important fact that brisance is not a definite, unchangeable characteristic of several noticeable types of explosive substances, but that the expedients which are resorted to to decrease the velocity of explosive reactions so that they may be regulated, such, especially, as suitable initial impulses and changes in the physical condition of the explosive substance, also increase or

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* M. Berthelot, Force mat. exp., II, 177; 1883.

diminish the brisance. To what extent this has become possible may be seen in the use of guncotton and nitroglycerin as propellants. These components of modern smokeless powder, which belong properly to the brisant explosives, undergo such a lowering of their velocity of explosion in the gelatinizing processes of manufacture, without, however, influencing their energy content, that the end product has almost completely lost the brisant character (section 68). Earlier attempts to draw a sharp line between brisant and nonbrisant explosives now appear impracticable.

92. The velocity of pressure increase in explosive reactions is recognized as the most important factor in their use in firearms, both with respect to the preservation of the piece and the guidance and propulsion of the projectile. The kinetic energy resident in the projectile from a firearm is the result, not of one single impulse, but of a continuous series of impulses which act upon the projectile from its place of rest till the time it leaves the muzzle, and this energy may be greater as a result of many moderate impulses than from a few strong impulses and many weak ones.* In the right-angled system of coördinates (Fig. 18), if the distances traversed by a projectile in its course *OE* be expressed as the abscissas (*OA*, *OB*) and the impulses acting upon it as the ordinates (*OL*, *AM*, *BN*, *EV*), then the surface (*OLMNVE*) will represent the total work done upon the projectile by the powder and hence the kinetic energy that the projectile possesses at the moment it leaves the muzzle.

Suppose that, instead of the impulses of various intensities, one continuous, constant impulse of medium intensity had acted on the projectile, and that the sur-

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* J. S. v. Romocki, Gesch. Exp. II, 14; 1896.

face (work) (*OHFE*) be equal to the surface (work) (*OLMNVE*), then the projectile will have received the same kinetic energy in both cases. It needs no discussion, however, to show in which case the barrel of the weapon, upon which the same pressure is constantly exerted as upon the projectile itself, is subject to the most severe strain. The ideal conditions denoted by the line *HF* cannot be obtained in practice, but that denoted by *LMINV* is very favorable. We are generally quite satisfied with pressures such as are expressed by curve II, while the most unfavorable case is shown by curve III where the gas pressure has reached its maximum before the projectile has moved from its position of rest.

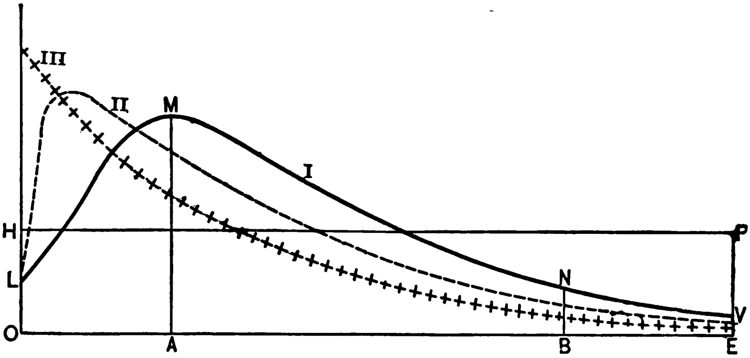

FIG. 18. Gas Pressures shown by Pressure Gauge in Firing Trials.

93. The recoil measure, proposed by H. Sébert * and in a modified form still in use to-day, is an apparatus by which the velocity of pressure increase in guns may be followed more closely. It is based, in principle,

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* H. Sébert, Les appareils Marcel-Deprez pour la measure des pressions des gaz de la poudre, 1875; Mitt. Art. Geniew., **10**, 363; 1879. See also W. Heydenreich, Lehre vom Schuss, I, 24; 1898.

upon the law of the preservation of the center of gravity, according to which the separate parts of a system of bodies, rigidly bound together, shift their positions as soon as their relationship becomes slightly changed in consequence of some inner force, and become so adjusted that the center of gravity of the whole system retains its position. According to this principle if a projectile of weight G be propelled by a powder charge of weight L from a cannon of weight R mounted on a sliding carriage of weight S, so that the whole system may rebound with minimum friction exactly in the direction of the axis of the bore, then, up to the time of the exit of the projectile from the mouth of the cannon, the distance traversed at any given time by the cannon and carriage, on the one hand, w_R, and by the projectile on the other, w_G, must stand in such relation to each other that the center of gravity of cannon, carriage, projectile and charge together remain in the same place as before the shot. This is the case as soon as the following proportion is fulfilled:

$$w_G : w_R = \left(R + S + \frac{L}{2}\right) : \left(G + \frac{L}{2}\right).$$

Hence as soon as the distances traversed by the cannon and carriage within definite intervals of time are measured, the distances traversed by the projectile in the same intervals of time can be calculated and from these data the gas pressure which prevails at the time noted.

94. P. Vieille* has made use of a method for measuring the velocity with which the explosive pressure increases in gaseous mixtures, which consists essentially

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* P. Vieille, Compt. rend., 95. 1280; 1882. Mem. poudr. salp., X, 177; 1899.

in the registration of the movement of a piston of known mass and diameter. The acceleration due to the influence of the expanding gases can be deduced from the law of the movement of the piston and consequently that of the force which acts upon it in the various stages of its movement. A wrought-iron container of about four liters contents is filled with the explosive gaseous mixture under atmospheric pressure and this is brought to explosion by electric sparks. The pressure developed acts upon a piston of about fifteen millimeters diameter, which is provided with a registering point by which its movement may be recorded on a revolving drum covered with soot. The registering point of the piston is connected with an electric circuit, and at the moment of the ignition of the gases a spark springs from the registering point to the drum, producing a distinct white spot which marks the beginning of the motion. Since the stroke of the piston is only five millimeters, the reading of the diagram must be made with a microscope. The velocity of revolution of the drum at the moment of the explosion is noted by a tuning fork of known oscillations, which oscillations are registered on the drum as wave lines.

95. In the case of liquid or solid explosives much greater pressures may be developed than with gases, and for the registration of these a very strong walled explosions bomb provided with a Noble compression apparatus is used.

The explosion chamber *E* is inclosed in the steel cylinder *S*. This space is not usually more than thirty cubic centimeters in volume and accordingly only small quantities of explosive can be used. The chamber is closed at its upper end by a screw *K*, through which runs an insulated pin *Z*. At the other end is a tight-fitting,

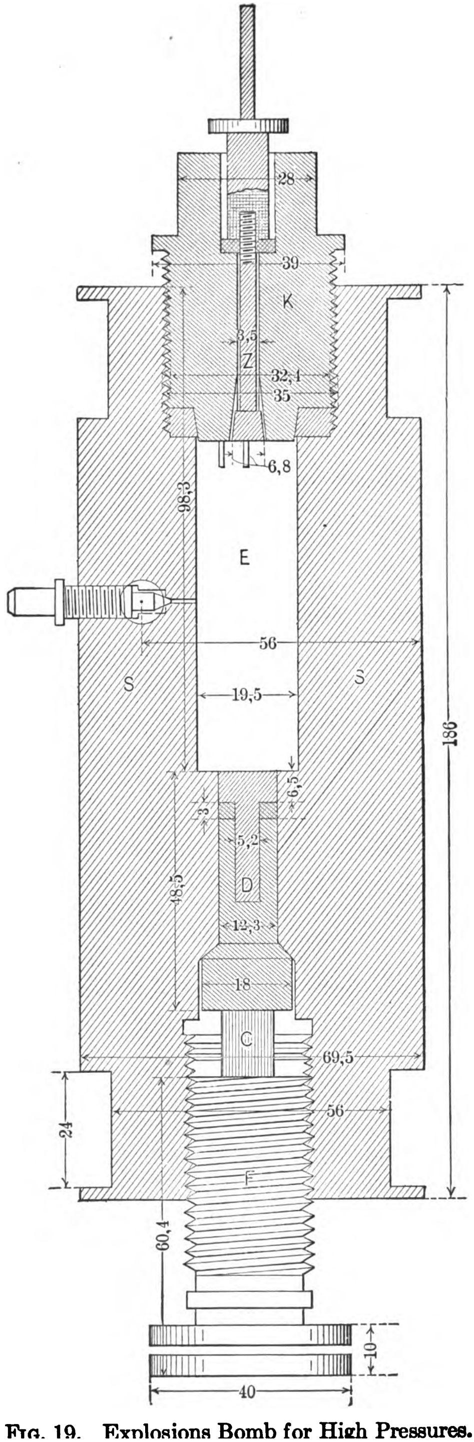

Fig. 19. Explosions Bomb for High Pressures.

movable piston *D*, behind which is the registering apparatus. The ignition is brought about by a thin iron or platinum wire connected at its two ends with the insulated pin *Z* and the screw *K*, and heated to glowing by an electric current. The registering apparatus* consists of a cylinder of soft copper *C* of from 13 to 15 millimeters in length, and from 8 to 10 millimeters in diameter (section 105), with polished end surfaces. This cylinder is inserted between the above-mentioned movable piston and a second screw *F*, which closes the under end of the cylinder. In the case of the experiments of E. Sarrau and P. Vieille† herein described, a stylus was fastened at the side of the piston and this stylus registered the movement of the piston on a revolving blackened drum so soon as the explosive pressure had compressed the copper cylinder. The velocity of revolution of the drum is determined here also by the help of a vibrating tuning fork. A slight divergence from these arrangements was made, in which the movable piston was connected directly with the tuning fork, one prong

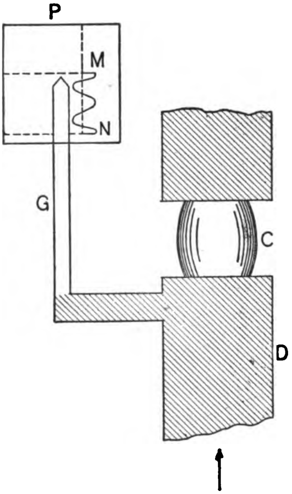

FIG. 20. Registration Device.

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* Gen. Rodman, U. S. A., Reports of Experiments, Boston, 1861. W. E. Woodbridge, On measurement of pressure of fired gunpowder in its practical applications, Am. J. Sci., (2), **22,** 153; 1856. F. A. P. Barnard, On the explosive force of gunpowder, Am. J. Sci., (2), **36,** 241; 1863. B. F. Craig, Products from the combustion of gunpowder under different pressures, Am. J. Sci., (2), **31,** 429; 1861.

† E. Sarrau and P. Vieille, Mem. poudr. salp., I, 383; 1882–83.

of which registered the vibrations (5000 per second) on a blackened surface *P* (Fig. 20).

The movement of the piston, brought about by the explosion and communicated to the surface through the point of the prong of the tuning fork, traced the wave line *abcdefg* (Fig. 21).

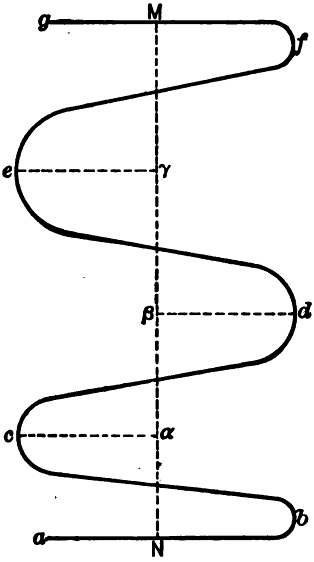

FIG. 21. Tracing of the Wave.

The total shortening of the copper cylinder *C* is equal to the line *MN*, and the shortenings corresponding to the time intervals of 1, 2, . . . 5 thousandths of a second are given by the lengths $N\alpha$, $N\beta$. The apparatus can, of course, register increasing pressures only, and hence gives the course of the pressure curve only to its maximum (Fig. 14, *CC′*).

96. With this apparatus, E. Sarrau and P. Vieille investigated a number of explosives with regard to their brisance under various conditions and were able to follow, in its gradations, the difference between the relatively slow burning black powder and the rapidly burning explosives nitrocellulose, nitrostarch and potassium picrate, after these had been strongly compressed. Guncotton, nitrostarch and potassium picrate exploded in pulverulent form with much greater velocity than even the most rapidly burning black powder in the form of dust. While the rise of pressure to its maximum, in the case of the first-named substances, occupied less than 0.0004 second, in the case of black powder this

amounted to at least 0.0015 second. The velocity of the rise of pressure with black powder could be regulated within wide limits by compression. A preparation which in finest dust form burned within 0.0015 second required 0.0057 second as grained powder and 0.084 second after it was compressed. These times are in the proportion of about 1: 56. On the other hand, no considerable retardation of pressure rise could be obtained in a closed space by the compression of guncotton or potassium picrate. The latter showed differences only between 0.00036 and 0.00060 second in the length of time required to reach the maximum pressure when in dust form and when in very strongly compressed blocks. Nitrocellulose under like conditions showed differences between 0.00045 and 0.00110 second, i.e., at most a retardation in the proportion of 1: 2 (Fig. 22). According to these experiments, the use of the two last-named substances for charges in firearms seemed hopeless. It was not then known that a considerable retardation and regulation in general of the velocity of explosion was possible even in the case of brisant substances.

97. J. E. Petavel* asserted, in criticism of the method used by E. Sarrau and P. Vieille for the measurement of the velocity of pressure increase (section 95), that small changes of pressure cannot be accurately measured by the compression piston and copper disk on account of their too great moment of inertia. He suggested that the elastic deformations which the walls of the explosions bomb sustains with increasing pressure be used as an indicator of the pressures and that these be registered by means of a suitable lever adjustment. A small mirror was fastened to the lever arm, and the re-

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* J. E. Petavel, Phil. Trans., **205**, 357; 1905.

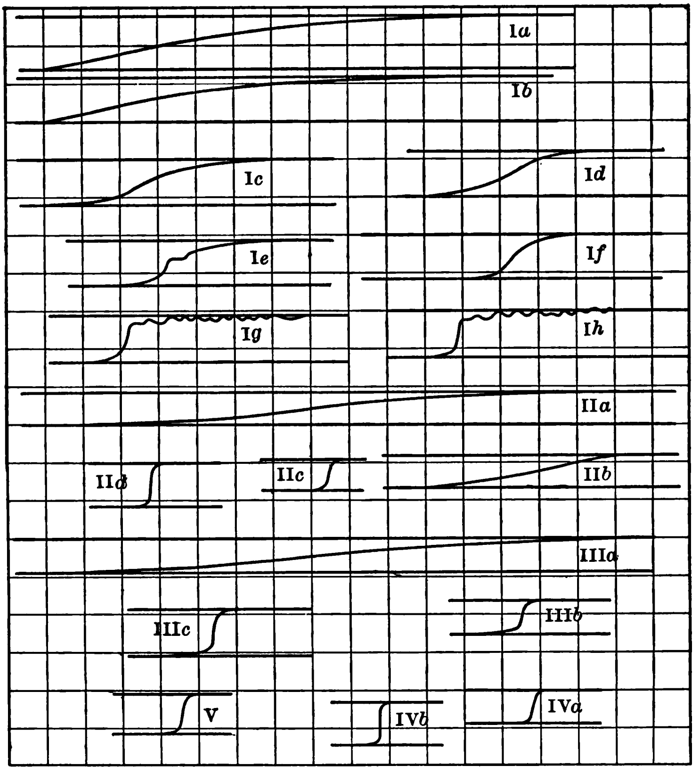

FIG. 22. Pressure Curves obtained by Sarrau and Vieille for Various Explosives.

I. Gunpowder, $\Delta = 0.70$ (*a*, *b*, compressed; *c*, *d*, fragments; *e*, *f*, grains; *g*, *h*, dust).
II. Nitrocellulose, $\Delta = 0.22$ (*a*, compressed; *b*, fragments; *c*, flakes; *d*, dust).
III. Nitrostarch, $\Delta = 0.22$ (*a*, compressed; *b*, powdered; *c*, dust).
IV. Potassium picrate, $\Delta = 0.30$ (*a*, compressed; *b*, powdered).
V. Dynamite, $\Delta = 0.30$.

Remarks. The time dimensions for I*a* and I*b* are reduced one-fifth. The abscissas represent time and the ordinates represent the degree of compression of copper cylinders.

flected beam of light from this mirror, as it was deflected during the explosion, was thrown on a rapidly moving photographic film. In this way, pressure curves were obtained whose ordinates corresponded to the deflection of the mirror, i.e., directly proportional to the pressures obtaining at that instant in the bomb when the abscissas gave the corresponding times. Experiments were first carried out with this apparatus on the English military powder cordite whose properties were otherwise well known through the works of A. Noble.*

98. C. E. Bichel† used an apparatus for similar experiments which permitted of comparatively large quantities of explosive, such as whole cartridges, being used. The explosions bomb consisted of a cylindrical steel block 80 centimeters in length and 50 centimeters in diameter. This rested on a solid base of masonry and was held firmly in place by two bands. The chamber for the explosive, of which 100 grams was the maximum load, had a content of 15 liters and was evacuated before the explosion. A spring indicator, such as is used for measuring the steam pressure in steam engines, was fixed in a perpendicular position above the charge. A stylus connected with the spring registered a diagram on a drum revolved by clockwork. With comparatively small velocities of detonation, such as are given by ammonium nitrate mixtures, the pressure curve drawn by the indicator was a gently ascending line; with high velocities, as with dynamite, this was a rapidly ascending line. Further relationships between velocity of detonation and velocity of pressure increase

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* A. Noble, Artillery and Explosives, 1906.

† C. E. Bichel, Z. Berg. Hütten Salin., **50**, 669; 1902. Engl. Pat., 3023 (1896). See also R. Blochmann, Dingler's pol. J., **318**, 232; 1903.

could not be drawn, principally on account of the fact that, out of regard for the measuring apparatus and the durability of the bomb, loads with very low charging densities only could be exploded, as a rule only $\frac{1}{150}$.

99. The development of pressure in the explosions bomb generally took place regularly and not by fits and starts. Yet this is easily to be accounted for, as P. Vieille* has indicated, by the fact that in such vessels the charge of explosive is usually distributed in an approximately uniform manner. If, however, the explosion occurs in a tubular container where the load might be unsymmetrical, as it would be if compressed at one end, then the pressure development and pressure distribution could be irregular. In such a case the gaseous products of explosion might, during their formation, oscillate back and forth along the main axis of the tube and develop enormously high pressures. P. Vieille observed such periodical rises of pressure by the help of a steel tube of 1 meter length, 60 millimeters outer diameter and 22 millimeters inner diameter, each end of which was provided with identically similar pressure devices. On the side near one end was a screw to which was connected the platinum or iron wire used to ignite the charge by means of an electric current. The movement of the copper cylinder (section 95), as it was compressed by the explosions pressure, was measured at each end, both for magnitude and velocity, by means of a stylus and a revolving drum. If the charge, consisting, for example, of guncotton leaf powder for the Lebel gun, was distributed throughout the entire length of the tube with a density of 0.2, then a pressure of 2400 atmospheres was registered at each end. The same pressure was observed in the explo-

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* P. Vieille, Mem. poudr. salp., III, 177; 1890.

sions bomb where the powder was piled together. If now the same charge was compressed at the end of the tube where ignition occurred, then a pressure of from 4000 to 5000 atmospheres was developed at the opposite end and the returning reflected pressure wave could still produce pressures of more than 3000 atmospheres. It could be observed from the registering apparatus that the pressure waves oscillated back and forth and were reflected from the two ends of the tube. It was also confirmed, through observations and occurrences, that a similar phenomenon is possible in firearms, where the conditions are generally not unfavorable to it, since with the progressing projectile the burned powder comes to lie more and more constantly to one side.*

2. THE MAXIMUM EXPLOSIONS PRESSURE.

100. The older statements of B. Robins (1742), B. Rumford† (1792) and others, in regard to the highest pressures proceeding from explosive reactions, especially in firearms, are not much more than comparative estimates.‡ Attention was very early directed towards obtaining some more reliable method for measuring the pressure of explosions, and it is known that in recent times (since Rodman, 1857), the science of ballistics has made greater progress the more energetically it has been attempted to overcome the difficulties in the way of measuring high gas pressures of brief duration. The estimation of maximum pressures in bombs is recognized as a valuable essential in judging in general the technical value and potential energy of explosives,

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* A. Noble, Art. Exp., **80**, 497, 1906; cf. also J. E. Petavel, Phil. Trans., **205**, 357; 1905: H. Dixon, Phil. Trans., **200**, 338; 1903.

† Benjamin Thompson (Count Rumford), Phil. Trans., **71**, 229; 1781: **87**, 222; 1797.

‡ J. Kotrtsch, Mitt. Art. Geniew., **4**, 155; 1873.

especially under conditions obtaining in practice. It is not to be overlooked that our knowledge of the characteristics of gaseous bodies is considerably enlarged by such investigations. In this way we first obtained a knowledge of the influence of pressure on the degree of dissociation and the chemical balancing action of gases, the change in the specific heat under the influence of very high temperatures and the like.

101. The maximum pressure arising from the explosion of gaseous mixtures was first measured by R. Bunsen.* The vessel containing the explosive gas mixture *A* (Fig. 23), which was 1.7 centimeters in diameter and 8.15 centimeters high, was closed by a ground glass plate which was pressed down by a weighted arm *H*. Ignition was brought about by electric sparks. When the pressure caused by the combustion or explosion of the gas was less than that exerted by the lever arm on the glass plate, the gas burned quietly. When it was

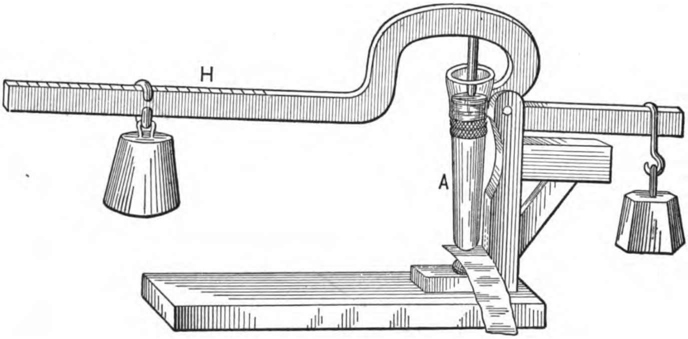

FIG. 23. Bunsen's Apparatus for Measuring the Maximum Pressure produced in the Explosion of Gaseous Mixtures.

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* R. Bunsen, Gasometrische Methoden, 319; 1877. See also G. A. Hirn, Polyt. Zentral., 1861.

greater, the water above the cover was thrown upward with a loud report. The pressure limits at which combustion took place quietly, on the one hand, and accompanied by loud report, on the other, could be so closely determined that the average might properly be regarded as the desired pressure. In this way there was obtained for a mixture of carbon monoxide and oxygen, with quiet burning, a pressure of 10.2 atmospheres; with explosion, a pressure of 10.4 atmospheres — an average of 10.12 atmospheres. The pressure in the mixture itself was 11.12 atmospheres.

102. E. Mallard and H. le Chatelier* attempted to ascertain for the French commission on fire damp the maximum pressure which occurs when the chemical union of methane with oxygen is accompanied by explosion. They used a bomb of about four liters' capacity. Ignition was brought about by a strong electric spark in the middle of the bomb. For registering the pressure they used a Bourdon spring manometer which consisted of an elliptical tube wound spirally on its axis and provided with an index hand on its closed end. This hand registered its deflection on a blackened paper strip wound on a uniformly revolving drum. The manometer tube which was made of brass and connected with the bottom of the bomb by means of a stopcock was completely filled with water which just covered the bottom of the bomb. A tuning fork of a known number of oscillations registered its vibrations on the same paper that received the pressure curves. The curves registered furnished a clue to the degree to which the products of the explosion were cooled on the metal walls of the container and also a measure for the maximum pressure. The fire-damp mixture, consisting of

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* E. Mallard and H. le Chatelier, Ann. mines, (8), **4**, 379; 1883.

1 volume methane + 2 volumes oxygen + 9 volumes air, gave an explosion pressure of nearly 6.5 atmospheres — a value which fully explains the powerful mechanical effects which usually accompany explosions of fire damp.

103. M. Berthelot and P. Vieille* measured the explosion pressures of gaseous mixtures by the method used earlier by P. Vieille (section 94), in which the movement of a piston of known cross section and mass was acted upon by the explosion pressure. These investigators took into account the cooling influence of the metal walls, which causes a lowering of the highest pressures, in that they carried on the experiments in containers of various dimensions (0.3, 1.5 and 4 liters); the highest maximum pressures being observed in the largest container. The maximum explosion pressure which M. Berthelot and P. Vieille noted in these experiments was 26 atmospheres with the mixture $C_2N_2 + 2\ N_2O$, which was run into the explosion chamber under atmospheric pressure. There were in all forty-two different explosive mixtures investigated, among which were such series as oxygen or nitrogen monoxide (N_2O) mixed with cyanogen, acetylene, ethylene, ethane, methyl ether or ethyl ether, all of which seemed well suited for systematic comparisons. Especial attention was directed towards isomeric mixtures which varied in their original components, but which contained the same elements in the same proportions and gave the same products on explosion. From comparison of the pressures obtained with these various

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* M. Berthelot and P. Vieille, Compt. rend., **98**, 545, 601, 705; 1884. See also A. Langen, Mitt. Forsch. Ingen., Vol. 8; 1903. D. Clerk, Proc. Inst. Civil Engineers, **85**, III, 1; 1885–86. A good résumé is found in F. Habers' Thermodynamics of Technical Gas Reactions, London, p. 226; 1908. See also M. Pier, Z. phys. Chem., **62**, 397; 1908.

mixtures the investigators came to the conclusion that, up to the high temperatures of from 3000° to 4000° C., the maximum pressure increases in proportion to the molecular density of the gaseous system, but that the specific heats are independent of pressure.

104. B. Lean and W. A. Bone,* in experiments to determine the maximum pressure of gaseous mixtures, assumed that the actual pressure is considerably higher than the measured one when this is measured by the movement of a body of relatively large mass (section 97). They accordingly proceeded as follows: The explosive mixture was contained in a lead tube of about two liters' capacity, to which a closed glass tube of from 10 to 25 cubic centimeters' capacity was connected by means of a steel stopcock. The glass tube was filled with air or some other inert gas and was connected with the lead tube, an instant before the explosion, by opening the stopcock. The air in the glass tube was compressed in a corresponding degree to the explosion pressure in the lead tube, and it was assumed, in view of the short duration of the explosion, that the compression took place adiabatically; or, at any rate, that no considerable diffusion of the gas being compressed into the compressed gas took place during the explosion. The depth to which the flame penetrated into the glass tube was determined by photographic means. The maximum pressure developed from the mixture $2H_2 + O_2$ was calculated to be 20.7 atmospheres, about twice as high as had been found by earlier investigators. This apparently doubtful result has received no further confirmation.

105. The maximum pressure exerted by a solid or liquid explosive upon the walls of an inclosing space is

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* B. Lean and W. A. Bone, Chem. News, **66**, 101; 1892.

evidently a function of the density of loading, i.e., of the quotient of the weight of the charge in grams divided by the inclosing space in cubic centimeters. The determination of the density of loading often becomes necessary in the technical use of explosives under similar circumstances, as, for instance, in a blast hole or in firearms, because it is important to obtain the maximum available effect. The density chosen is usually determined in such cases by practical experience, but it may also be obtained beforehand by experiments with the explosions bomb, so far as the law which governs the relation between maximum pressure and density of loading is known. A. Noble and F. Abel* have carried out along this line one of the most important investigations in the field of the chemistry of explosives. They used for their purpose an extremely strong bomb which could be used with 1 kilogram of black powder to the liter of content, and they determined the prevailing maximum pressure with the help of the compression apparatus suggested by A. Noble in the year 1867. The essential feature of this apparatus is, as above described (section 95), a small copper cylinder which is placed between a movable piston of known cross section and a solid support, and the pressure is deduced from the magnitude of its compression. Before these cylinders are used in the measurements, determinations are made, with similar cylinders, of the magnitude of the compressions ϵ, ϵ^1, ϵ^2 . . . , caused by the static pressures of the known weights G, G^1, G^2 . . . , and a table is constructed from which the corresponding values of ϵ and G may be read. It has been demonstrated, particularly by E. Sarrau and P.

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* A. Noble and F. Abel, Phil. Trans., **165**, 12; 1875: 171, 203; 1880. Mitt. Art. Geniew., **8**, 333; 1877.

Vieille,* that these tables may also be used for the determination of pressures developed by an explosive in a closed space, although the compressions thus obtained take place with much greater velocity. By subjecting such copper cylinders, 13 millimeters in height and 8 millimeters in diameter, in a lever press to pressures which gradually increased to the maximum, these two investigators ascertained that, so long as the height of the cylinder did not diminish more than 5.5 millimeters, the relation between this decrease in height ϵ in millimeters and the pressure of the weight G in kilograms can be expressed by the equation

$$G = k_0 + k\epsilon,$$

in which k_0 and k are two constants determined as 541 and 535 respectively. In order then to determine how far this conclusion could be applied to conditions in force in an explosion it was necessary to take account of the influence of the velocity of the pressure developed. Two limiting cases are conceivable in the time relations between pressure development and the movement of the piston which compresses the copper cylinder:

(*a*) The velocity of the development of pressure is so small and the piston so little that the latter is set into motion immediately after the beginning of the active pressure and comes to a standstill when the maximum pressure P is reached. (*b*) The velocity of the development of pressure is so large and the mass of the piston so considerable that the latter does not begin to move until the maximum pressure is reached. In this case

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* E. Sarrau and P. Vieille, Mem. poudr. salp., I, 356; 1882. P. Vieille, Mem. poudr. salp., V, 12; 1892. A. Indra, Mitt. Art. Geniew., **31,** 841, 967; 1900: **32,** 121; 1901. L. Wltavsky, the same, **39,** 232; 1908. Siegl, Ermittelung von Gasspannungen, 1904. See also J. S. von Romocki, Gesch. Exp., II, 82; 1895–96.

the whole distance of the movement of the piston, though short, is to be regarded as traversed under the influence of the maximum pressure. All other cases lie between these two limits. If ϕ denote the varying magnitude ϵ of the compression, as a function of the varying times considered, and P the pressure, then the above-mentioned expression becomes

$$P = k_0 + k\frac{\epsilon}{1+\phi},$$

and the value of ϕ is 0 in the first case and 1 in the second case. In order to determine the maximum pressure P, for any observed compression ϵ, it is necessary first of all to know the value of ϕ which can be determined experimentally from a number of determinations in which the velocity of the pressure development and the mass of the piston are varied in known proportions. In the case of black powder the decrease in the height of the copper cylinder appeared to depend upon the density of the powder alone, and not upon the mass of the piston or the velocity of the pressure development. The first-mentioned case can be used in this instance in calculating the maximum pressure. With nitroglycerin the two limiting cases could be very closely approximated by varying the mass of the piston. When the piston weighed four kilograms the value of ϕ very closely approached 0, and ϵ was almost twice as great as when the piston weighed but a few grams.

Guncotton in the form of flakes conformed to the second case only; the time that elapsed between the beginning of the movement of the piston and the development of the maximum pressure was too small to be measured, and only half of the decrease in the copper cylinder was considered in calculating the maximum pressure.

106. The experiments of A. Noble and F. Abel revealed a distinct relation between maximum pressure and the density of loading, and demonstrated that the pressure always increases more rapidly than the density of loading (Fig. 24).* Suppose that about one-half of the powder was not gasified. The results obtained may be expressed by the formula

$$P = \frac{2640 \cdot \delta}{1 - 0.6 \cdot \delta},$$

where δ denotes the density of loading, calculated on the part of the charge converted to gaseous form.

This formula has been proven applicable also to explosive systems which are completely converted to gas. In this case the density of the products of explosion is identical with the density of loading, Δ. For nitroglycerin, for instance, the corresponding formula is

$$P = \frac{9280 \cdot \Delta}{1 - 0.723\ \Delta}.$$

The coefficients, 2640 for black powder and 9280 for nitroglycerin, are constants for the explosive in question and are often expressed by the letter f. The coefficients 0.6 and 0.723 are also characteristics for the explosive system and represent the space within the containing vessel which is not available for the expansion of the gases because it is occupied by the volume of the molecules which form the solid residue and the gaseous products of explosion (covolume) (section 85). This value is denoted by α, and the general formula

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* F. Häusser, Mitt. Forsch. Ingen., 31, 1905, has furnished analogous information for gaseous explosive systems.

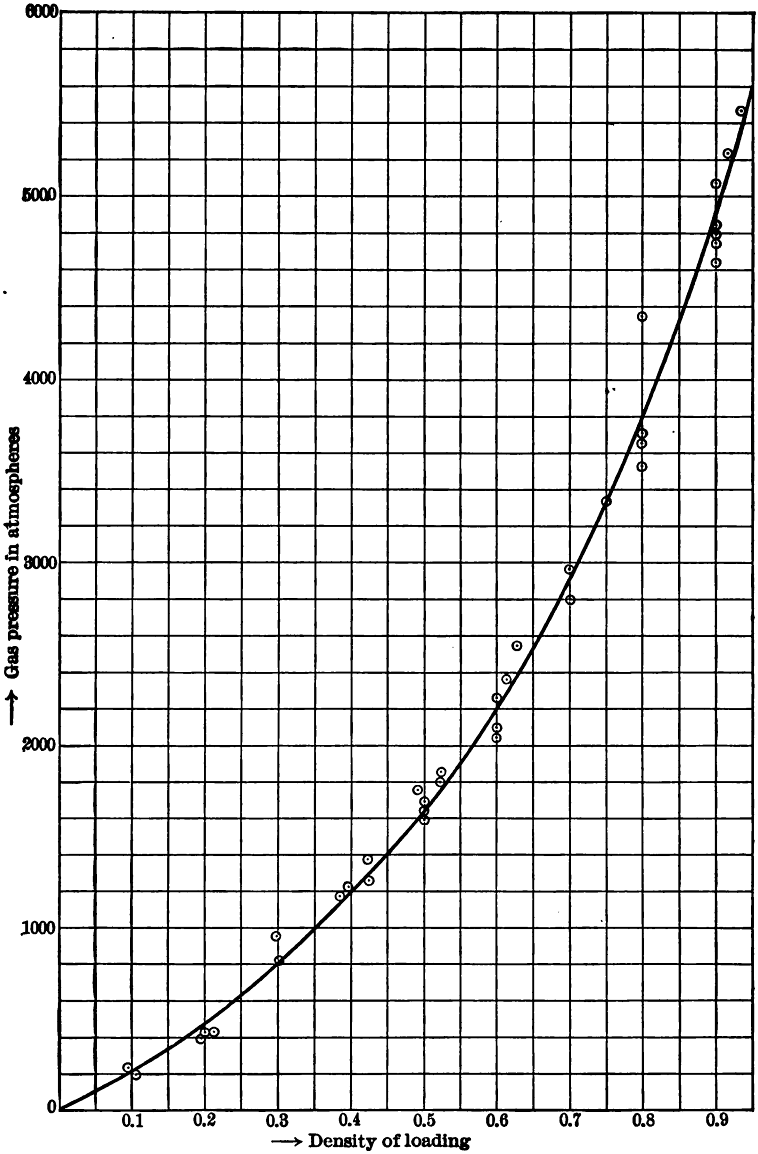

FIG. 24. Relations between the Density of Loading and the Maximum Pressure for Gunpowder.

expressing the relation between pressure of explosion and density of loading is then

$$P = \frac{f \cdot \Delta}{1 - \alpha\Delta}.$$

107. The theory of the problems here discussed is founded upon the Clausius' form of the Van der Waal formula for gases and vapors:

$$P = \frac{RT}{V - \alpha} - \frac{\phi(T)}{(V - \beta)^2}.$$

P denotes the pressure exerted upon the unit of surface by the unit of weight of a gas or gaseous mixture with the characteristic gas constant R, in the volume V, at the absolute temperature T. α is the covolume, β a constant based upon the cohesion of the gases. The function $\phi(T)$ is of such a nature that its value decreases very rapidly with increasing T, and hence the second member of the expression for P, unlike the first, more and more approaches zero, its limiting value, the larger the value of T becomes. At the high temperatures which obtain in explosive reactions the second member may be completely disregarded, so that in this case the formula for unit weight becomes

$$P = \frac{R \cdot T}{V - \alpha}.$$

This formula expresses the maximum pressure which the products of the explosion of the unit weight of a powder in the volume V exert upon the unit of surface. The product RT is identical with the above-mentioned constant f (section 106). The maximum pressure, which any given quantity of an explosive W in the volume V exerts, is then

$$P = \frac{fW}{V - \alpha W}.$$

If, finally, the density of loading (section 105) $\frac{W}{V} = \Delta$ be brought into the formula, we have the general form of the expression for the relation between explosion pressure and density of loading mentioned in section 106.

f and α are often called the Abel constants of explosives because F. Abel first recognized these constants for the maximum pressure of the products of an explosion and introduced them as characteristics of these products. To ascertain their magnitudes for any given explosive the values of P corresponding to the various values of Δ are first determined experimentally in the explosions bomb. Should more than two experiments be carried out they may be used directly for the determination in question; that is, if the above formula (section 106) be given the form

$$\frac{P}{\Delta} = f + \alpha \cdot P,$$

it then represents a straight line with P as abscissae and $\frac{P}{\Delta}$ as ordinates. The magnitude f is the initial ordinate for $P = 0$, and α is the tangent angle of this straight line with the abscissa. In this way the two Abel constants may easily be ascertained graphically.

108. M. Berthelot has characterized the pressure P, which the above-described method gives when the density of loading $\Delta = 1$, as the *specific pressure* of the given explosive. According to the investigations of the French commission on explosives,* the specific pressure seems to be the most practicable of all the characteristic theoretical magnitudes of explosives for use as a

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* See also J. Daniel, Dict. mat. exp., 658; 1902.

suitable comparative standard of the actual effect produced by the explosive.

109. The maximum pressures for a large number of explosives have been determined for various densities of loading by the method described by A. Noble and F. Abel. In this connection prominence should be given to the works of M. Berthelot and P. Vieille[*] on diazobenzene nitrate and mercury fulminate; of E. Sarrau and P. Vieille[†] on nitrocellulose, nitroglycerin, nitromannite and potassium picrate, and of W. Macnab and E. Ristori[‡] on nitroglycerin cubical powder. Exhaustive experiments have also been made by A. Noble[§] on the behavior of guncotton, cordite, Rottweiler nitro-

TABLE 26. RELATION BETWEEN DENSITY OF LOADING AND MAXIMUM PRESSURE FOR SEVERAL EXPLOSIVES.

(In Atmospheres per Cubic Centimeter.)

Density of loading.	Black powder.	Nitro-glycerin.	Gun-cotton.	Picric acid.	Ammonium nitrate.	Mercury fulminate.
0.1	336	1,098	1,061	983	542	468
0.2	708	2,351	2,343	2,174	1,217	966
0.3	1,123	3,847	3,921	3,650	2,077	1,501
0.4	1,587	5,640	5,912	5,523	3,211	2,072
0.5	2,112	7,829	8,502	7,982	4,779	2,686
0.6	2,708	10,560	12,000	11,350	7,082	3,347
0.7	3,393	14,060	17,020	16,240	10,800	4,062
0.8	4,201	21,520	24,810	24,030	17,870	4,952
0.9	5,126	25,270	38,500	38,310	36,250	5,683
1.0	6,236	35,010	......	......	......	6,602
1.2	9,255	......	......	......	......	8,726
1.4	14,130	......	......	......	......	11,320
1.6	29,340	......	......	......	......	14,560
1.8	......	......	......	......	......	18,790
2.0	......	......	......	......	......	24,350
2.4	......	......	......	......	......	43,970

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[*] M. Berthelot and P. Vieille, Mem. poudr. salp., I, 99; 1882, and II, 3; 1884–89.

[†] E. Sarrau and P. Vieille, the same, II, 126; 1884–89.

[‡] W. Macnab and E. Ristori, Proc. Roy. Soc., **56**, 8; 1894.

[§] A. Noble, Art. Exp., 472; 1906.

cellulose gunpowder and several other newer types of powder. The most important results of this work, so far as they concern the relationship between density of loading and maximum pressure, are collected in Table 26. It is to be emphasized, however, that this table gives only those numbers that have been calculated for the higher pressures of loading, from a maximum pressure of about 6000 atmospheres upward. Direct determinations of the maximum pressure for the density of loading l, i.e., the specific pressure, have so far been possible only in the case of black powder (section 105).

CHAPTER IV.

TEMPERATURE OF EXPLOSIONS.

110. By temperature of explosion or temperature of combustion in the theoretical sense is to be understood that temperature to which the products of explosion can be heated by the heat developed during the reaction. If the heat of explosion in an explosive system amounts to Q calories for constant volume, and the average specific heat of the products of its explosion be represented by c, then the rise of temperature t is given by the formula:

$$t = \frac{Q}{c}.$$

111. It remains for the future to develop a method for the accurate determination of the average specific heats of the products of explosion at the high temperature obtaining in such reactions. R. Bunsen and L. Schischkoff * founded their determination of the temperature of the combustion of black powder upon the assumption that the specific heat of the gases was independent of the temperature. Putting the heat of explosion of black powder Q at 620 calories, and the average specific heat of the products of its combustion, calculated at constant volume, at $c = 0.185$, they found the temperature of its combustion according to the above formula to be

$$t = \frac{620}{0.185} = 3350^\circ \text{ C}.$$

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* R. Bunsen and L. Schischkoff, Ann. Phys. Chem., **102**, 321; 1857. See also A. Noble and F. Abel, Phil. Trans., **165**, 12; 1875: **171**, 203; 1880.

In a similar manner they obtained for the temperature of explosion of guncotton between 5000 and 6000 degrees and for nitroglycerin between 7000 and 8000 degrees. The credibility of such high temperatures is doubtful on several grounds.* According to later experiments the average specific heat c of the gaseous mixture is in fact not a constant but a function of the temperature, and indeed a function increasing not inconsiderably with increasing temperature. Assuming that the value of c for each temperature is given in the expression, $c = a + bt$, in which a and b denote empirically determined magnitudes, then we obtain for Q the equation

$$Q = at + bt^2,$$

and for t, the temperature sought,

$$t = \frac{-a + \sqrt{a^2 + 4b \cdot Q}}{2b}.$$

The constants a and b for the separate gases are variously given by different authors. The following values were deduced by E. Mallard and H. le Chatelier† from their experiments on the pressure of explosion:

For CO_2, SO_2	$c = 6.26 + 0.0037\,t$;
For H_2O	$c = 5.61 + 0.0033\,t$;
For N_2, H_2, O_2, CO	$c = 4.80 + 0.0006\,t$.

If the relative quantities in which the given gaseous products of an explosive reaction appear be denoted by

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* N. Wuich, Mitt. Art. Geniew., **22**, 67; 1891. A. Noble (Phil. Trans., 206) has recently calculated the temperatures of explosion for nitroglycerin powders at approximately 5000 degrees, assuming the specific heats of the gases of explosion as constants (with the single exception of CO_2). F. W. Jones in Arms and Explosives, 1907–08, shows the admissibility of such an assumption.

† E. Mallard and H. le Chatelier, Ann. mines (8), **4**, 379; 1883. See also F. Haber, Thermodyn. Gasreak., 191; 1905. English edition, 208; 1908. W. Nernst, Theo. Chem., 46; 1907.

$\alpha, \beta, \gamma, \delta \ldots$, then the constants a and b are denoted by the expressions:

$$a = 6.26\,\alpha + 5.61\,\beta + 4.8\,(\gamma + \delta \ldots),$$
$$b = 0.0037\,\alpha + 0.0033\,\beta + 0.0006\,(\gamma + \delta \ldots),$$

and the temperature of explosion, for instance of guncotton, when it decomposes according to the equation $C_{24}H_{29}O_{42}N_{11} = 12\,CO_2 + 6\,H_2O + 12\,CO + 8.5\,H_2 + 5.5\,N_2$, is $t = 2710°$. Nitroglycerin by this method of calculation gives $t = 3470°$. If the heat of explosion of an explosive system consisting of several components be not known it can be calculated by the thermochemical method proposed by M. Berthelot* (section 6). The theoretical temperature of explosion may also be thus calculated.† According as the water, which appears in the products of explosion, is regarded as liquid water or as water vapor (which seems more convenient), different results are obtained for the temperature of explosion which may differ very considerably from each other in explosives of the ammonium nitrate type.

112. Frequent use is made of the above method of calculation in many countries where coal mines are worked, particularly in France, Spain and, until recently, Belgium, because of the significance which is attributed to the theoretical temperature of explosion as giving a clue to the safety of the explosive in the presence of fire damp. This is supported by the results of an exhaustive investigation carried on by E. Mallard and H. le Chatelier,‡ in 1880–82, into the height of the

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* For a detailed account of this method with applications to permissible explosives see Investigations of Explosives used in Coal Mines, Bull. 15, U. S. Bureau of Mines, 16; 1912.

† H. Schmerber, Lemploi des explosifs, 16; 1900.

‡ E. Mallard and H. le Chatelier, Ann. mines, (8), **4**, 379; 1883. See also F. Haber, Thermodyn. Gasreak., 181; 1905. English edition, 208; 1908. W. Nernst, Theo. Chem., 46; 1907.

temperature necessary for the ignition of fire damp. These two physicists discovered that a fire damp must be heated to 650° C. and that this temperature must be maintained at least 10 seconds before an ignition takes place (section 37). In consequence of this retardation in ignition it is possible to use explosives whose temperature of explosion far exceeds 650° C. The French fire-damp commission came to the conclusion that the calculated temperature of an explosion may reach 2200° C. without igniting a fire damp of a certain composition. This principle has been put into actual practice in France and Belgium by manufacturing explosive mixtures whose calculated temperatures of explosion lie below the above-mentioned maximum and by using in coal mines such explosives only.*

113. The principle of the temperature of explosion, t, which has been elucidated by the above discussion, is related to the maximum pressure, P, as expressed in the following equation:

$$P = \frac{V_2}{V_1}\left(1 + \frac{t}{273}\right),$$

where V_1 and V_2 indicate the respective volumes of the given explosives before and of the gaseous reaction products after the explosion, when reduced to 0 degree and 760 millimeters. The space which is occupied by the gases generated, at 0 degree and 760 millimeters, by 1 gram of the explosive, expressed in cubic centimeters, is generally a constant dependent only upon the composition of the gases of explosion and hence characteristic. In analogy with the definition of specific weight this

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* W. Eschweiler, Ber. Kon. angew. Chem., II, 303; 1903. F. Heise, Spreng. Zünd. Spreng., 68; 1904. C. E. Bichel, Z. ges. Schiess Sprengstoffw., **2**, 169; 1907.

is called the specific gas volume of an explosive system. This volume can easily be determined by the use of a suitable gas meter,* after the explosion has been carried out in a bomb, where the pressure of explosion may also be measured in case it is desired to calculate t.

E. Mallard and H. le Chatelier † have, by a similar formula, calculated the temperatures of explosion of explosive gaseous mixtures from the measurements of their corresponding maximum pressures and find them in excellent agreement with the thermochemical calculation. Such an agreement is, of course, not to be expected in the case of solid and liquid explosives on account of the not inconsiderable influence of the density of loading (section 106), and more especially of the covolume which, at the high temperatures obtaining, limits the jurisdiction of the Gay-Lussac-Mariotte law.

114. M. Berthelot ‡ proposed to use the product of the specific gas volume by the rise of temperature, $V_0 \cdot t = \frac{V_0 \cdot Q}{c}$, as a relative measure for the mechanical work done by the explosive, or in cases where the products of explosion have approximately like specific heats, the expression $V_0 \cdot Q$, which he calls the *characteristic product of the explosive.*

That the character of many explosive systems is determined to a considerable extent by the two characteristics expressed by the relations between the volumes and temperatures which accompany an explosive reaction is plainly shown by the data in Table 27, where the volumes before and after the explosion are given in the first and second columns, and the volume

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* E. Sarrau and P. Vieille, Mem. poudr. salp., II, 126; 1884–89.

† E. Mallard and H. le Chatelier, Compt. rend., **93**, 962, 1014; 1881.

‡ M. Berthelot, Force mat. exp., I, 64; 1883.

TABLE 27. PRODUCTS OF VOLUME FACTOR AND HEAT FACTOR FOR SEVERAL EXPLOSIVES.

Explosive system.	Volume factor.			Heat factor.		Product of volume factor and heat factor.
	V_1.	V_2.	$\frac{V_2}{V_1}$.	$\frac{t}{°C.}$.	$1+\frac{t}{273}$.	
	cc.	cc.	cc.			
A. Solid Explosives:						
Black powder..........	0.59*	280	*470*	2700	*10.9*	5,100
Guhr dynamite (75 per cent)................	0.62*	535	*860*	3100	*12.3*	10,600
Explosive gelatin.......	0.60	720	*1200*	3500	*13.8*	16,600
Ammonium nitrate explosive (82.5 per cent NH_4NO_3, 17.5 per cent dinitrobenzene)................	0.62	900	*1450*	2300	*9.4*	13,600
B. Gaseous Mixtures:						
$2H_2+O_2=2H_2O$.......	3	2	*0.66*	2500 to 3500	*13.8*	9 to 25
$2CO+O_2=2CO_2$.......	3	2	*0.66*			
$C_2N_2+O_2=2CO+N_2$...	2	3	*1.5*			
$C_2N_2+2O_2=2CO_2+N_2$.	3	3	*1.0*			
$C_2N_2+2N_2O$ $=2CO+3N_2$......	3	5	*1.66*			

* Considering the parts not converted into gas.

factor $\frac{V_2}{V_1}$ in the third. In the fourth column the usual rise of temperature $t = \frac{Q}{c}$ is assumed, and from this the heat factor $\left(1 + \frac{t}{273}\right)$ is derived and placed in the fifth column. The sixth column contains the product of columns three and five as a comparative value for the pressure of explosion *P*. It appears from this table that the technology of explosives in its previous development has proceeded along the line of a continual increase of the volume factor $\frac{V_2}{V_1}$, and in some cases even at the expense of the heat factor $\left(1 + \frac{t}{273}\right)$, as is shown in the case of the explosives containing ammonium nitrate. It may also be seen why the gaseous explosive systems have had no success as explosive agents in competition with the liquid or solid explosives, for, while in the case of the latter substances the factor $\frac{V_2}{V_1}$ reaches into the thousands, in the case of the former this is in the neighborhood of one.

The work that explosive gaseous mixtures produce is due almost entirely to the heat developed, and this is of a like magnitude in the two groups. It has often been proposed to compress an explosive gaseous mixture with a view to decreasing its volume and increasing its energy, but even this expedient, aside from other disadvantages, does not fully eliminate the difficulty. One liter of hydrogen and oxygen explosive gas, compressed to 100 atmospheres, furnishes only 204 calories, while one liter of black powder furnishes 1150 calories. Yet even with the knowledge of the "characteristic product" of explosives, practical experience shows that we are by no means in possession of a sufficiently reliable method of measuring this. A grave objection to Berthelot's proposal to base the measure of the power of an explosive on the product of the number of heat units developed by the specific gas volume is that the velocity with which the gases of explosion are developed is not taken into account. One of the consequences of this, as may be seen from Table 28,* is that mercury fulminate stands at the bottom of the list, even below black powder; that explosive gelatin appears about six times as effective as black powder; and that dyna-

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* W. Will, Z. Elektrochem., **12**, 560; 1906. In this table the specific volume is calculated on 1 kilogram of the explosive, and the water in the products of explosion in the form of vapor. The heat of explosion, however, is calculated on liquid water.

mite and ammonium nitrate explosives appear as equal in effectiveness. These disparities could be largely modified by consideration of the velocity factor.

TABLE 28. SPECIFIC VOLUME, CALCULATED TEMPERATURE OF EXPLOSION AND CHARACTERISTIC PRODUCT FOR SEVERAL EXPLOSIVES.

No.	Explosive system.	Specific volume, L.	Calculated temperature of explosion, °C.	Characteristic product.	
				$V_0 \cdot Q$.	Relative value.*
1	Explosive gelatin (7 per cent collodion)...	710	3540	1,164,000	100
2	Nitroglycerin.........	712	3470	1,125,000	97
3	Nitromannite.........	723	3430	1,099,000	95
4	Dynamite (75 per cent)	628	3160	810,000	70
5	Nitroglycerin powder (40 per cent)........	840	2900	1,084,000	93
6	Guncotton (13 per cent N)................	859	2710	945,000	81
7	Guncotton powder.....	830	2400	747,000	64
8	Collodion cotton (12 per cent N).........	974	1940	711,000	61
9	Ammonium nitrate explosive (NH_4NO_3 with 10 per cent of nitronaphthalene)...	925	2120	860,000	74
10	Picric acid...........	877	2430	710,000	61
11	Black powder.........	285	2770	195,000	17
12	Ammonium nitrate....	937	2120	590,000	50
13	Mercury fulminate....	314	3530	129,000	11

* Explosive gelatin counted as 100.

115. In addition to the calculation of the temperature of explosion from the heat of explosion or the maximum pressure developed, when the specific heat is known, a third method has recently been discovered which is based on an analytical determination of the amount of an endothermal compound formed during the explosion, as for instance the amount of NO formed in an explosion of hydrogen explosive gas in the presence of air. If the thermodynamic relation between the

temperature and the equilibrium constant of the given endothermic compound is known, and if the explosion is carried out under conditions which insure that the equilibrium is not materially altered during the period of the cooling of the explosion products to ordinary temperatures, then we have all the necessary data for a calculation of the temperature which at least must have obtained during the explosion. This is a problem which is closely connected with that of the determination of the equilibrium concentration at high temperatures investigated especially by W. Nernst* (section 134).

116. We have not yet succeeded directly in measuring, in any reliable way, the rise of temperature which accompanies explosive processes. Even the most delicate pyrometric devices, such as thermocouples, prove inadequate when dealing with changes of temperature following so closely upon each other. On this account we are still in doubt as to the maximum temperatures which actually obtain in explosive processes. They are undoubtedly higher than our instruments show, but on the other hand are certainly lower than those calculated by thermochemical methods which must be based on the ideal maximum of an exothermal reaction proceeding without loss of heat.

117. W. Macnab† has attempted to obtain at least a clue to the relative magnitude of the maximum temperatures developed by the explosion of various smokeless powders. Within the bomb, in which the powder was brought to explosion, there was arranged

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* W. Nernst, Theo. Chem., 676; 1907. Z. anorg. Chem., **45**, 126; 1905. K. Finckh, the same, **45**, 116; 1905.

† W. Macnab and E. Ristori, Proc. Roy. Soc., **66**, 221; 1900. See also W. Macnab and A. E. Leighton, J. Soc. Chem. Ind., **23**, 298; 1904.

the (platinum) — (platinum-rhodium) junction of a le Chatelier pyrometer, and the deflection of the galvanometer needle was fixed on a rapidly moving photographic film by a reflected beam of light. The curved lines thus obtained were then the result of the combined movement of the beam of light and that of the photographic film. A comparison of the deflection thus obtained in the galvanometer with the heat of explosion obtained in a calorimetric bomb shows a close agreement in the results of the two methods.

TABLE 29. RELATION BETWEEN HEAT OF EXPLOSION AND MEASURED TEMPERATURE RISE.

		Heat of explosion in calories.	Deflection of the galvanometer needle in millimeters.
Nitrocellulose powder	Containing saltpeter.	742	106
		745	123
		755	135
		762	136
		786	137
		807	139
	Free from saltpeter	845	150
		896	160
		1014	161
Nitroglycerin powder		1031	168
		1253	191
		1286	204

118. Many attempts have been made to determine the temperatures developed by the combustion of various powders by placing in the cartridges wires of varying thicknesses composed of platinum or other difficultly fusible substance and observing which thickness of wire was just melted on explosion of the charge. A. Noble,[*] for instance, brought to explosion in a bomb three kilograms of guncotton having a density of loading

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[*] A. Noble and F. Abel, Phil. Trans., **165**, 1; 1875. A. Noble, Art. exp., **171**, 230, 414; 1906. A. Noble, Fifty Years of Explosives, 28; 1907.

of 0.28, and having within the charge a small bundle of osmium. After the explosion the walls of the bomb were scraped and the pieces of osmium examined. Since it was discovered that at least a part of the osmium found had gone into the metal walls by a kind of sublimation, A. Noble estimated the temperature as far above that of the melting point of osmium (2500° C.), —perhaps about 3200° C. In a similar experiment with cordite when a small bundle of carbon electrodes was placed within the powder charge, melted carbon in the form of diamond was found in the residue from the explosion. According to W. Crookes' experiments the melting point of carbon lies somewhat above 4000° C.

119. To determine relatively the temperature of explosion the hot gases from the explosion are allowed to strike through narrow tubes and the radius within which a melting of the tube walls takes place is observed. P. Vieille* used for his experiments a small explosions bomb (Fig. 25), which, besides the usual compression cylinder *B* and electric primer *A*, was provided with a third side-screw *C*, which carried a metal cylinder *D*.

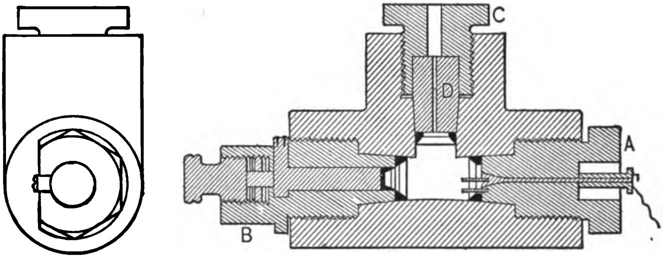

FIG. 25. Vieille's Bomb for Ascertaining the Erosive Action of Explosives.

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* P. Vieille, Mem. poudr. salp., XI, 157; 1901. See also A. Noble, Art. Exp., 470; 1906.

This cylinder was 40 millimeters in height by 22 millimeters in thickness, and it was provided with a central canal, 1 millimeter wide, through which the gases could escape after the charge was fired. This cylinder was cleaned and weighed before and after the explosion, and its loss in weight, which, according to the explosive used and the pressure developed, might amount to several per cent, was taken as an indication of the thermal intensity of the gases developed. The erosion in the canal varied also with the character of the metal of which the cylinder *D* was made. Platinum suffered the least loss; aluminum, zinc and like metals much greater losses. There occurred not only a melting of the metal, but a simultaneous blowing out and scattering of the melted metal by the powerful gas pressure. Under similar experimental conditions, especially of explosions pressure, the cylinder lost most in weight from explosive gelatin, nitromannite and powders containing nitroglycerin. Nitrocellulose powders caused a medium loss of weight, and nitroguanidine and black powder only a small loss. These experiments showed also the same gradation for the temperature of the gases of explosion from the various substances tested as had been calculated before from thermochemical data.

120. It has long been known that the wear and tear on a gun barrel bears a certain relation to the temperature which obtains during the combustion of the powder. In proportion as the heat of explosion of gelatinized powders is decreased by the addition of such substances as tannin,* vaseline† and the like, erosions

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* F. Abel and J. Dewar, D. R. P. Nr., 53294, of Aug. 6, 1889.

† W. Macnab and E. Ristori, Mitt. Art. Geniew., **26**, 93; 1895. See also A. Frank, Chem. Ztg., 939; 1907.

in the explosion chamber and the bore of the gun are decreased. The statement of Monni,* that the damage to the metal is lessened by an addition of carbon to the powder charge, is less noteworthy from the standpoint of the proposed addition than on account of the implied opinion as to the cause of the erosion in firearms. The carbon dioxide contained in the explosion products acts upon the steel of the gun barrel, taking out its carbon in accordance with the reaction

$$CO_2 + C = 2\,CO,$$

and consequently causing a porosity in the steel. Hence, if the burning out of the metal in firearms is to be prevented, it is most important to lower the amount of carbon dioxide in the decomposition gases. Suppose the composition of the gas, produced, for instance, by ballistite, be represented by the general expression

$$\alpha CO_2 + \beta CO + \gamma H_2O + \delta H_2 + \epsilon N_2,$$

then the quantity of carbon necessary to change all the CO_2 to CO is at least α, and the gas becomes

$$(2\,\alpha + \beta)\,CO + \gamma H_2O + \delta H_2 + \epsilon N_2.$$

Now since the number of calories produced by the formation of carbon monoxide from carbon is considerably less than by the formation of carbon dioxide it is comprehensible that, as is pointed out by P. Vieille, a ballistite with an addition of carbon up to 19 per cent will produce considerably less erosion than a ballistite without this addition (section 119).

If, further, the phenomenon of burning out in firearms may be regarded as analogous to that brought about artificially in experiments with explosions in

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* Monni, Z. ges. Schiess Sprengstoffw., I, 305; 1906. V. Recchi, *loc. cit.*, I, 285; 1906.

bombs with narrow outlet canals (section 119), then, reasoning from the results obtained in these experiments, we would expect a carbon enrichment of the metal of the gun barrel rather than a lessening in carbon contents. According to P. Vieille* the inner walls of an explosions bomb undergo a kind of cementation and acquire a higher degree of hardness than they originally possessed — a fact which he ascribed to the separation on the surface of the bomb of carbon as a dissociation product of the gases in contact with highly heated iron. The steel not only becomes harder, but microscopic examination of the surface has shown that the original pearlite (with approximately 0.9 per cent carbon) is gradually changed into hardenite, and at the same time the per cent of carbon in the steel increases. Along with these chemico-physical changes there occurs a lowering of the melting point of the steel and consequently a reduced power of resistance towards the hot gases of explosion. The test of P. Vieille (section 119) has been used in an American steel works,† to determine the power of resistance of various kinds of steel to the high temperature produced by the explosion of smokeless powder. The powder was packed in the explosion chamber of a heavy armor-piercing shell. The gases developed by the explosion escaped through a canal in the base screw. The powder charge used was 1.475 kilograms and the diameter of the canal about 4 millimeters. Table 30 shows that

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* P. Vieille, Mem. poudr. salp., XI, 209; 1901. See also H. v. Jüptner, Grundzüge der Siderologie, III, 1, 36; 1904. E. Bauer and A. Glaessner, Z. phys. Chem., **43**, 354; 1903. R. Schenck and F. Zimmermann, Ber., **36**, 1231; 1903. R. Schenck and W. Heller, the same, **38**, 2132; 1906. Z. Elektrochem., **10**, 397; 1904. R. Schenck, H. Semiller and V. Falcke, Ber., **40**, 1704; 1904.

† Z. ges. Schiess Sprengstoffw., 211; 1907.

wrought iron, Martin, tungsten and nickel steel offer about the same resistance to erosion from the explosion gases of smokeless powder; that the 20 per cent nickel steel shows a considerably greater erosion; and finally that manganese bronze cannot be used at all in contact with highly heated explosion gases. According to P. Siwy* about $\frac{1}{3}$ kilogram of iron escapes into the air with every shot from an efficient 28-centimeter gun. The iron may easily be detected in the gases from the explosion.

TABLE 30. EROSIONS FROM EXPLOSION GASES.

Material	Maximum pressure in atmospheres.	Cross section of the canal.		
		Before the experiment, square millimeters.	After the experiment.	
			Square millimeters.	Times the original diameter.
Wrought iron	2200–2300	12.38	55.14	4.5
Martin steel	2200–2300	12.38	55.44	4.5
3 per cent tungsten steel	2200–2300	12.38	55.14	4.5
Martin steel, 3 per cent tungsten	2200–2300	12.38	58.63	4.7
3 per cent nickel steel	2200–2300	12.38	62.07	5.0
20 per cent nickel steel	2200–2300	12.38	72.69	5.9
Manganese bronze	2200–2300	12.38	284.88	23.0

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* P. Siwy, Z. ges. Schiess Sprengstoffw., **3**, 67; 1908. See also T. Cwik, Mitt. Art. Geniew., 124; 1908.

CHAPTER V.

THE GASES FROM EXPLOSIVE REACTIONS.

121. The gaseous products of an explosive reaction are almost the sole material carriers of the energy set free by the reaction. The principal gases thus produced are carbon dioxide, water and nitrogen; occasionally carbon monoxide, hydrogen and methane; and in exceptional cases, nitric oxide, hydrogen cyanide and hydrogen sulphide. It is a well-known fact that some of these gases possess poisonous properties; others, such as carbon monoxide, hydrogen and methane, form explosive mixtures with air (section 55), and these properties must be considered in selecting explosives in mining and for artillery purposes.*

122. The composition of the gaseous products of explosion at the moment of the explosion, i.e., before the cooling of the expanding gases brings about any significant changes, is determined principally by the chemical composition and physical condition of the explosive system itself, but the influence exerted by the character of the initiation and the propagation of the explosive reaction often modifies the products to a marked degree. The chemical composition of the reaction products can generally be anticipated only when the system contains sufficient oxygen for a complete combustion of the carbon and hydrogen present to carbon dioxide and water. This condition can be ful-

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* Wappler, Jahrbuch f. d. Berg — und. Hüttenwes. im. Kgr. Sachsen, 31; 1887. Z. ges. Schiess Sprengstoffw., **2**, 261, 265; 1907.

filled both by chemical compounds, such as nitroglycerin (equation 1) and ammonium nitrate (equation 2), or by properly chosen mixtures, such as saltpeter, sulphur and carbon, mixed in the proportion by weight of 84:8 : 8 (equation 3).

Eq. 1. $2\,C_3H_5(NO_3)_3 = \overset{6}{\cancel{}}CO_2 + 5\,H_2O + 3\,N_2 + \frac{1}{2}\,O_2.$

Eq. 2. $NH_4.NO_3 = 2\,H_2O + N_2 + \frac{1}{2}\,O_2.$

Eq. 3. $10\,KNO_3 + 3\,S + 8\,C = 2\,K_2CO_3 + 3\,K_2SO_4 + 6\,CO_2 + 5\,N_2.$

If, in spite of an excess of oxygen, products of an incomplete transformation occur, particularly nitric oxide, it is probably due to an insufficient initial impulse, interrupted propagation of the explosive reaction or similar irregularities. Such incomplete transformations frequently occur in practice, as, for instance, in the so-called "blown out" shots.*

123. If, on the other hand, an explosive system contains too little oxygen to oxidize all the carbon to carbon dioxide and all the hydrogen to water, either a part of these elements remains unoxidized or the oxidation is arrested at the point of formation of some intermediate oxidation product (section 7). In such cases the actual composition of the gases at the moment of explosion is dependent upon the chemical equilibrium of the various determining factors, and, eventually, also when equilibrium is not reached at the temperature of explosion and consequently varies on cooling, upon the very high reaction velocities which usually obtain at the temperature of explosion and on cooling.† Picric acid and many other nitro compounds, several ammonium nitrate explosives and more especially all

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* F. Heise, Glückauf, 146; 1898. Dautriche, Z. ges. Schiess Sprengstoffw., **3**, 161; 1908.

† See W. Nernst, Theoret. Chemie, 674; 1907.

the nitration grades of cellulose, as well as the majority of gelatinized gunpowders, belong to such explosive systems. Therefore the equations for the decomposition of explosives in these groups, which are often seen in literature, cannot be regarded as expressing the actual transformation that occurs. As an example of this we may take the usual equation representing the explosive decomposition of picric acid,*

$$2\,C_6H_2(NO_2)_3OH = CO_2 + H_2O + 11\,CO + 2\,H_2 + 3\,N_2.$$

According to this equation the explosion gases of picric acid contain not less than 2 molecules of H_2 (besides 11 molecules of CO and 1 molecule of H_2O) to each molecule of CO_2. Such a ratio between carbon dioxide and hydrogen can exist only in the absence of every possibility of reaction. Even a slight addition of heat causes a further reaction, limited of course by the other reaction products, and an additional quantity of CO and H_2O is formed somewhat as represented by the equation:

$$x\,CO_2 + y\,H_2 = (x - a)\,CO_2 + a\,CO + (y - b)\,H_2 + b\,H_2O.$$

The extremely high temperatures that obtain in explosive reactions, of course, increase the effectiveness of these secondary reactions. To what extent this reaction actually occurs at the moment of the explosion depends upon the law of mass action and the velocity and equilibrium factors which obtain under the given conditions. The high temperature of transformation during the explosive reaction and also the accompanying rise of pressure are to be mentioned as of especial significance in this relation.†

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* L. Gody, Mat. exp., 410; 1896. F. Heise, Spreng-Zünd. Spreng., 112; 1904.

† In this connection consult especially F. Haber, Thermodyn. Gasreak., 103, 288; 1905. English edition, 121, 308; 1908.

124. The results of the analysis of the gases of explosion available apply, of course, to their condition after cooling to room temperatures and not to the conditions existing at the temperature of the explosion. Water vapor has condensed to water; substances, which can exist together only at high temperatures, have entered into reaction with each other during the cooling; and the equilibrium which was established at the moment of the explosion has been very considerably altered. In this way we may explain, for example, the fact that the explosion of hydrogen and oxygen in a eudiometer shows a quantitative formation of water, although at the maximum temperature of the explosion a considerable part of the hydrogen and oxygen existed together in an uncombined state. Under the existing conditions the velocity with which the gases cool is not so great as to enable the equilibrium between water vapor, hydrogen and oxygen, which was established at the maximum temperature of explosion, to remain the same after the cooling. To what extent this possibility of the variation of equilibrium prevents an insight into the condition of equilibrium in the gases of explosion at the moment of the explosion itself is a question which at the present time is frequently discussed and until now has been answered only in few cases and then only for low pressures.*

Influence of the Pressure of Explosion upon the Composition of the Gases.

125. The first experiments of A. Noble and F. Abel† were directed towards ascertaining the influence of the

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* See in this connection the previously mentioned comprehensive works of F. Haber and W. Nernst.

† A. Noble and F. Abel, Phil. Trans., **165**, 12; 1875: **171**, 203; 1880.

density of loading upon the composition of the gases resulting from the explosion. They exploded black powder of different origins and compositions in explosion bombs under varying densities of loading (section 105). With increasing density of loading, i.e., with increasing explosion pressure, there occurred a fairly regular increase of CO_2 and a corresponding decrease in CO.

126. The influence of the explosion pressure is much more noticeable in the case of cellulose nitrates (to which the highest nitrated guncottons belong), which substances are relatively poorer in oxygen than black powder, in which the components are mixed in such proportions as to bring about a more or less complete oxidation of the combustible elements. E. Sarrau and P. Vieille* used for such experiments explosion bombs filled with nitrogen, whose inner walls were plated with platinum to avoid any influence which the surface might exert upon the composition of the gases. The same care was exercised regarding the method of firing the charge after they had proved, by a special series of experiments, that the same explosion products resulted from a charge fired with mercury fulminate as from one fired electrically. When a cellulose nitrate of 13.5 per cent nitrogen content was fired in the bomb under a density of loading of $\Delta = 0.01$ to $\Delta = 0.3$, corresponding to the maximum explosion pressures of $P = 100$ to $P = 4000$ atmospheres, the results (in volume per cent), as shown in Table 31, were obtained.

The influence of pressure (Fig. 24), rapidly increasing with increasing density of loading, may be recognized in the continual increase of CO_2 accom-

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* E. Sarrau and P. Vieille, Mem. poudr. salp., II, 126, 337; 1884–85.

TABLE 31. GASES FROM THE EXPLOSION OF NITROCELLULOSE UNDER VARYING PRESSURES.

Gases without, H_2O.	Density of loading, Δ.			
	0.0098	0.023	0.2	0.3
CO_2	21.71	24.89	28.66	30.35
CO	49.31	42.77	37.08	34.22
CH_4	.....	0.14	0.52	1.62
H_2	12.66	16.05	18.42	17.36
N_2	16.38	16.32	15.32	15.85

panied by a corresponding decrease in CO. Hydrogen increases also with increasing pressure at low densities of loading, and at high densities again decreases constantly. The beginning of the formation of methane and its continual increase is noticeable. These results were completely verified in similar experiments by A. Noble and F. Abel,* on the varying composition of the gases resulting from the explosion of guncotton (Fig. 26) and gelatinized powders,† for different maximum pressures, and also by the Dynamit-Actiengesellschaft vormals, Alfred Noble et Co., on a number of technically important explosives.‡

127. The last-named work is especially noticeable, because it emphasizes the importance of the density of loading as a means of judging the degree of safety of explosives in the presence of fire damp. It had previously been frequently overlooked that many explosives used in mines containing fire damp, such especially as the peculiarly constituted carbonite, when fired under high loading pressures, produce gases essentially different from those produced under lower pressures, and

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* A. Noble and F. Abel, Proc. Roy. Soc., **56**, 205; 1894.

† A. Noble, Phil. Trans., **205**, 201; 1905: **206**, 453; 1906.

‡ Z. ges. Schiess Sprengstoffw., **1**, 1; 1906.

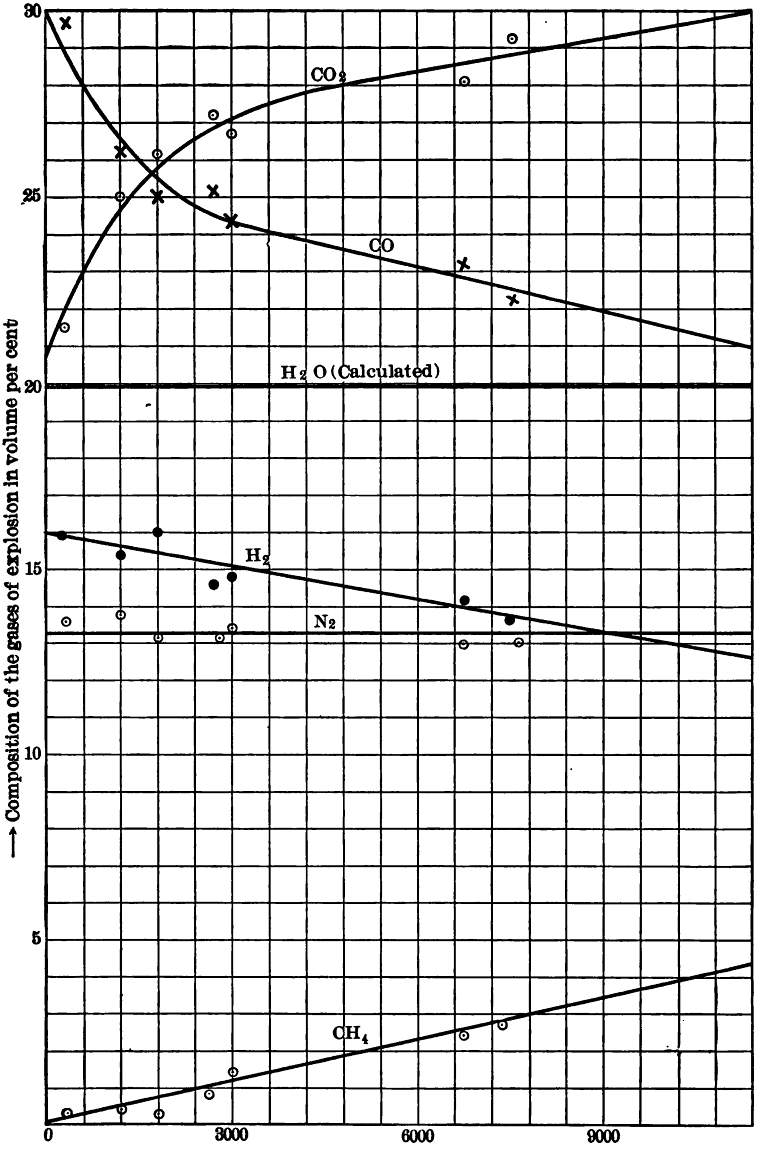

FIG. 26. Relation between the Maximum Pressure and the Evolution of Explosions Gas, for Guncotton.

that consequently conclusions as to the cause of their high degree of safety in the presence of fire damp (section 220) were without reliable foundation so long as they were based on the results of analyses of the gases obtained under low loading pressures. Although the French fire-damp commission had designated all explosives which contain combustible components in the gases of their decomposition as dangerous for use in the presence of fire damp, H. Broockmann,* on the contrary, pointed to the high percentages of carbon monoxide and hydrogen in the gases of carbonites as the most probable cause of their safety in the presence of fire damp. He did not, however, take into consideration the unexpectedly great influence of the density of loading on the character of the decomposition of this kind of explosives, and especially the increased quantities of methane found in the gases under high pressures, whose tardiness of ignition (section 37) the above-mentioned commission had recognized, and which would certainly be a factor in the unusually high degree of safety shown by carbonites in the presence of fire damp.

128. The formation of methane at high temperatures and under high pressures, which had been quite generally neglected earlier, was the subject of a more careful investigation by E. Sarrau and P. Vieille incidentally to a study of picric acid, the gases from which are influenced to an unusual degree by the explosions pressures as is shown in Table 32.

According to the supposition of E. Sarrau and P. Vieille, the composition of the gaseous end products of nitrocellulose, picric acid and similar substances which lack sufficient oxygen for complete oxidation, may be

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* F. Heise, Spreng. Zünd. Spreng., 82; 1904.

TABLE 32. GASES FROM PICRIC ACID UNDER VARYING PRESSURE OF EXPLOSION.

Gases without H_2O.	Density of loading, Δ.		
	0.1	0.3	0.5
CO_2	7.61	15.40	20.55
CO	61.56	54.34	48.80
CH_4	1.19	5.75	7.83
H_2	12.52	6.31	3.06
N_2	17.12	18.20	19.76

regarded as the result of two reaction processes as follows:

$$\text{(Eq. 1)} \quad CO + H_2O = CO_2 + H_2, \text{ and}$$
$$\text{(Eq. 2)} \quad 2\,CO + 2\,H_2 = CO_2 + CH_4.$$

So long as high temperatures obtain both take place with such great velocity that the given chemical system is in a state of equilibrium at any given instant. The higher the corresponding pressure the more is the equilibrium shifted, according to well-known laws, towards that side which is accompanied by a decrease in volume (equation 2).

If it were possible to increase the density of loading, $\Delta = 0.5$, which is limited by the rigidity of the bomb, to, say, $\Delta = 1.0$, corresponding to a pressure of more than 40,000 atmospheres, then the most highly condensed molecules, CO_2 and CH_4, would appear* as the predominant end products of the explosive reaction of such substances; i.e., the equation representing the decomposition of picric acid would be quite different from that obtained by previous experiments.

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* H. le Chatelier, Ann. mines, (8), **13**, 157; 1888. See, on the equilibrium of CH_4, M. Mayer and V. Altmayer, Ber., **40**, 2134; 1907. H. v. Wartenberg, Z. phys. Chem., **63**, 269; 1908. F. Haber-Lamb, Thermodynamics of Technical Reactions, London, 345; 1907.

129. In connection with the question as to the character of the gases of explosion arises the question as to whether dissociation phenomena occur to any considerable extent in explosive reactions. Carbon dioxide and water are the principal end products which are capable of dissociation. As regards the conduct of carbon dioxide at high temperatures it has been shown that the reaction

$$2\,CO_2 \leftrightarrows 2\,CO + O_2$$

is first noticeable, under atmospheric pressure, above 2000° C.* The quantity of carbon monoxide formed at this temperature under a pressure of 6 atmospheres was estimated by E. Mallard and H. le Chatelier† to be less than 5 per cent of the carbon dioxide present. The last-named investigator assembled the scattered material on the dissociation of carbon dioxide at various temperatures and pressures, classified it according to the law of chemical equilibrium for homogeneous gas systems, and obtained results which correspond satisfactorily with the data obtained from various other sources.‡ The unexpectedly great influence of pressure in minimizing the degree of dissociation may be seen from the following table compiled by W. Nernst and H. v. Wartenberg.§

Table 33 gives percentages of degree of dissociation, or the number of molecules of CO_2 which are decomposed into CO and O_2 from 100 original molecules.

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* E. Mallard and H. le Chatelier, Compt. rend., **91,** 825; 1880: **93,** 145, 962, 1014, 1076; 1881. F. Haber, Thermodyn. Gasreak., 147; 1905.

† H. Sainte-Claire Deville, Compt. rend., **56,** 195, 729; 1863. See also W. Nernst, Z. Elektrochemie, **9,** 625; 1903.

‡ H. le Chatelier, Z. phys. Chem., **2,** 782; 1888.

§ W. Nernst and H. v. Wartenberg, Z. phys. Chem., **56,** 548; 1906. W. Nernst, Theo. Chem., 680; 1907.

Thus, for instance, at 10 atmospheres and 2227° C., 7.08 per cent of the original CO_2 is decomposed into CO and O_2.

TABLE 33. INFLUENCE OF PRESSURE ON THE DEGREE OF DISSOCIATION OF CARBON DIOXIDE.

Temperature, °C.	10 atmospheres.	1 atmosphere.	0.1 atmosphere.	0.01 atmosphere.
727	$7{,}31.10^{-6}$	$1{,}58.10^{-5}$	$3{,}40.10^{-5}$	$7{,}31.10^{-5}$
1227	$1{,}88.10^{-2}$	$4{,}06.10^{-2}$	$8{,}72.10^{-2}$	0,19
1727	0,82	1,77	3,73	7,88
2227	7,08	15,8	30,7	53,0

According to the above, a not inconsiderable dissociation of carbon dioxide is to be expected so long as the pressure is below 100 atmospheres, as is the case in the explosive transformations in gaseous mixtures. If, however, this pressure rises into the thousands of atmospheres, as is the case with solid and liquid explosives under high densities of loading or when loose explosives are detonated with a detonator, then the conditions for any appreciable dissociation, namely, low pressure and a correspondingly high temperature, are not fulfilled. To the extent to which the original high pressure sinks the temperature also falls, in consequence of the expansion of the gases and radiation of heat, so that at no time and in no place are the conditions necessary for an appreciable dissociation given. This fact is not without practical significance. When, for instance, a considerable charge is fired from an M/88 gun, the temperature and pressure of the powder gases are distributed along the barrel of the gun somewhat in the following manner.*

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* Hirsch, Kriegstech. Z., 9, 226; 1906.

TABLE 34. TEMPERATURE AND PRESSURE OF THE POWDER GASES IN THE GUN.

Part of gun barrel, millimeters.	Temperature of the powder gases, °C.	Pressure of the powder gases, kilograms per square centimeter.
200	1426	1385
300	1202	834
400	1060	577
500	965	434
600	877	339
693 (mouth)	818	280

The temperature of the powder gases immediately before their exit from the mouth of the gun may, under certain conditions, be still higher than here given, perhaps exceed 1000° C. Since, however, the pressure at this place amounts to several hundred atmospheres, it follows that the degree of dissociation of the carbon dioxide in the whole barrel is small and by no means considerable enough to be taken into consideration in constructive or ballistic calculations.

We possess likewise but little information in regard to the dissociation of water at high temperatures under the influence of high pressures, yet there can be no essential difference between this and carbon dioxide. According to R. Bunsen, H. St.-Cl. Deville, W. Nernst and other investigators, a temperature of at least 2000° C. at atmospheric pressure is necessary for a beginning of the reaction

$$2\,H_2O \rightarrow 2\,H_2 + O_2.$$

E. Mallard and H. le Chatelier in another place estimated the dissociation of water under a pressure of 10 atmospheres, and at the temperature of the explosion of hydrogen and oxygen mixtures (3500° C.) at about 40 per cent, a ratio which would correspond with that of carbon dioxide under similar conditions. The work of W. Nernst and H. v. Wartenberg,* although it includes but a small part of the field, may sufficiently illustrate the conditions which exist.

TABLE 35. INFLUENCE OF PRESSURE ON THE DISSOCIATION OF WATER VAPOR.

Temperature, °C.	10 atmospheres.	1 atmosphere.	0.1 atmosphere.	0.01 atmosphere.
727	$1,39.10^{-5}$	$3,00.10^{-5}$	$6,46.10^{-5}$	$1,39.10^{-4}$
1227	$1,03.10^{-2}$	$2,21.10^{-2}$	$4,76.10^{-2}$	0,10
1727	0,27	0,59	1,26	2,70
2227	1.98	3,98	8,16	16,6

In summing up the present condition of this question it may be said that the dissociation phenomena play no important rôle in a number of explosive reactions because of the high pressure which prevails in these reactions and which prevents decomposition into a greater number of molecules; and that at present there is no necessity for taking the dissociation of the reaction products into consideration, especially in the case of those explosive reactions which are important from a technical and ballistic standpoint, although under other conditions this effect might not be inconsiderable.†

2. INFLUENCE OF TEMPERATURE ON THE COMPOSITION OF THE GASES.

130. If a chemical system be heated while its volume is held constant, a shifting of equilibrium takes place

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* W. Nernst and H. v. Wartenberg, Z. phys. Chem., **56**, 513; 1906. W. Nernst, Theo. Chemie, 680; 1907. See also L. Löwenstein, Z. phys. Chem., **54**, 715; 1906.

† M. Berthelot, Force mat. exp., I, 59; 1883. See also P. Vielle, Mem. poudr. salp., VI, 285; 1893. Crussard and E. Jouquet, Compt. rend., **144**, 560; 1907.

towards that side at which the reaction goes on with absorption of heat.* In the reaction

$$CO + H_2O = CO_2 + H_2,$$

heat is liberated. This heat development is, however, dependent upon the temperature and becomes smaller with rising temperatures because the specific heats of $CO + H_2O$ are smaller than those of $CO_2 + H_2$. Becoming smaller and smaller as the temperature increases it must finally, at still higher temperatures, become zero and then take a negative value. At that state of equilibrium when the heat development changes the sign preceding its factor from + to − and it goes over into a heat absorption, the equilibrium's constant $K = \frac{CO \cdot H_2O}{CO_2 \cdot H_2}$, which had previously been increasing more and more slowly, must have reached its maximum and beyond that point must again decrease.† How this value of K changes with the temperature may be seen from the following table compiled by F. Haber.‡

TABLE 36. CHANGES IN THE CONSTANT OF EQUILIBRIUM WITH THE TEMPERATURE $K = \frac{CO \cdot H_2O}{CO_2 \cdot H_2}$.

Temperature, °C.	$K = \frac{CO \cdot H_2O}{CO_2 \cdot H_2}$.
686	0.52
886	1.19
1086	2.04
1405	3.48
1600	4.24

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* H. le Chatelier, Ann. mines, (8), **13**, 157; 1888. See also J. van't Hoff., Dyn. chim., 161; 1884.

† A. Horstmann, Ann., **190**, 228; 1877. See also W. Ostwald, Lehrb. allg. Chem., 1896–1902, II, 2; Part I, 945.

‡ F. Haber, Thermodyn. Gasreak., **126**, 292; 1905. English edition, **143**, 310; 1908.

This change of the equilibrium constant with the temperature for the reaction so often occurring in explosive processes,

$$CO + H_2O \rightleftarrows CO_2 + H_2,$$

was determined by C. Hoitsema [*] from experimental material collected by W. Macnab and E. Ristori,[†] in connection with calorimetric tests of gelatinized smokeless gunpowder. The calculation of C. Hoitsema can, however, be true only in case the ratio of the two gases, after it has once been established at a temperature of about 3000° C. at the moment of explosion, remains the same on cooling. But it is improbable that this cooling should take place quickly enough to stabilize the composition of the gases attained at such high temperature (section 124).

In fact F. Haber [‡] in the light of newer material, especially that of O. Hahn, has calculated the equilibrium very carefully and shown that Hoitsema's maximum for K is not demonstrable. The further study of the reaction processes here mentioned between CO and H_2O will prove especially valuable in explaining the little-understood chemical reactions which take place in firearms from the moment the maximum gas pressure is attained to that of the exit of the gases from the barrel. In such work it must, however, be remembered that consideration must be given to the accompanying reaction that takes place under the influence of the high pressure (section 128),

$$2\,CO + 2\,H_2 \rightleftarrows CO_2 + CH_4,$$

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[*] C. Hoitsema, Z. phys. Chem., **25**, 686; 1898.

[†] W. Macnab and E. Ristori, Mitt. Art. Geniew., **26**, 93; 1895.

[‡] F. Haber, Sec. 123. O. Hahn, Z. phys. Chem., **44**, 513; 1903: **48**, 735; 1904.

the equilibrium proportions of which are naturally but little known and could not, therefore, have entered into the calculation in the above-mentioned study of Hoitsema's.

131. O. Boudouard* investigated the velocity with which the equilibrium between CO_2, CO, H_2 and H_2O is established at high temperatures. He filled an evacuated vessel, containing platinum as the contact substance, with carbon dioxide and hydrogen. After long heating the gases were drawn out and analyzed. From his results he concluded that at 850° C. equilibrium was established after heating three hours, and at 1100° C. after but one-half hour. His apparatus, however, did not allow a definite result to be obtained because its walls became pervious to carbon monoxide and hydrogen at the long-continued high heating.

132. At temperatures of from 2000° to 4000° C., which are reached in explosive reactions, equilibrium is undoubtedly established instantaneously.† The velocity of reaction in the first stage of cooling will still be so great that the equilibrium can conform to the falling temperature (section 124). But whether this additional shifting is of sufficient importance to cause the composition of the gaseous mixture after cooling to differ materially from the equilibrium at the temperature of explosion appears, from the analytical material at hand, doubtful. For instance, the gases from picric acid, with the appreciable amount of methane which they acquired under great pressure (section 128), have evidently undergone but little change from their original

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* O. Boudouard, Bull. soc. chim., Paris, (3), **25**, 484; 1901.

† See also F. Haber and F. Richardt, Z. anorg. Chem., I, 38; 1903. F. Haber, Thermodyn. Gasreak., 291; 1905. English edition, 1908, p. 309; Chem. Ztg. No. 69, 1908.

composition. Equilibrium must in this case have remained "frozen in," so to speak, at a high temperature when high pressures were still in force. This is evident from the fact that the gaseous mixture reacts at high temperatures, in the absence of a corresponding pressure increase, with a decrease in methane contents, even to the vanishing point. According to experiments of M. Berthelot,* methane is not stable when heated in quartz vessels to 1300° C., and this result is verified by the investigations of M. Mayer and V. Altmayer,† on the equilibrium of methane. The last-named investigators have followed the balance represented by the equation

$$C + 2\,H_2 \rightleftarrows CH_4$$

quantitatively under atmospheric pressure, determined the equilibrium from both sides, i.e., of CH_4 and of $C + 2\,H_2$, within the temperature limits of 470° to 620° C., and calculated from the data thus obtained the composition of the gases representing the equilibrium within the temperatures 250° to 850° C. at a pressure of one atmosphere. It becomes apparent from these calculations that at 850 degrees only 1.5 per cent CH_4 is stable, while at 250 degrees the formation of methane goes on almost to the end of the above equation. The experimental material at hand is not yet sufficient to permit of any definite conclusions being drawn as to the equilibrium of methane in the presence of other products of explosions, such as CO, CO_2 and H_2O, especially under pressures which approach 1000 atmospheres.

133. The fact that endothermic compounds are formed in many explosive reactions is in accordance

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* M. Berthelot, Ann. chim. phys., **6**, 183; 1905.

† M. Mayer and V. Altmayer, Ber., **40**, 2144; 1907.

with the above-mentioned (section 130) thermodynamic principle, viz., that when the temperature is raised, equilibrium is shifted towards that side of the equation which takes up heat. And, further, since equilibrium is very quickly established (section 124) at very high temperatures, which obtain in explosions, it is logical to conclude that, as a rule, those compounds which can possibly be formed at such temperatures will be formed in quantities very closely approximating the condition of equilibrium. Thus appreciable quantities of carbon monoxide are formed in the explosion of hydrogen and oxygen mixtures in the presence of air, as R. Bunsen * earlier observed. He exploded such mixtures in eudiometers in the presence of air and found that 100 volumes of air exploded with

64,31 volumes explosive mixture leave behind 99.90 volumes air;
78,76 volumes explosive mixture leave behind 99.43 volumes air;
97,84 volumes explosive mixture leave behind 96.92 volumes air;
226,04 volumes explosive mixture leave behind 88.56 volumes air.

We can calculate from these figures the per cents of nitric oxide which were formed during the explosion. It must be remembered that the nitrogen dioxide $(NO)_2$ formed immediately combined with the excess of air to form nitrogen tetroxide $(NO_2)_2$. This formation of nitrogen tetroxide uses up $\frac{1}{2}$ volume of O_2 for each volume of NO, so that two-thirds of the loss that occurs in the gas volume corresponds to the volume of the nitrogen dioxide formed. This calculation carried out gives for the above relations as NO contents of the air in volume per cents,

0,07	0,38	2,05	7,63

respectively.

If these figures are sufficiently trustworthy they

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* R. Bunsen, Gas. Method., 71; 1877.

establish the fact that explosive reactions may, under certain conditions, cause the formation of an appreciable quantity of oxides of nitrogen from the air.

134. The work of K. Finckh* was devoted to the elucidation of this problem. He investigated the formation both of nitrogen dioxide and hydrogen peroxide. It is reasoned on thermodynamic grounds that a considerable quantity of hydrogen peroxide is to be expected at the temperature of the explosion of hydrogen and oxygen mixtures, even if equilibrium were not immediately established. The experiments, however, showed only very small quantities of hydrogen peroxide, — far less than the quantity corresponding to the calculated equilibrium. K. Finckh concluded from this that the hydrogen peroxide formed at the moment of the explosion was rapidly decomposed during the cooling of the gases, and that it is not admissible, at least in this particular case, to draw any conclusion regarding the equilibrium at the moment of the explosion from the analysis of the end products. W. Nernst,† who applied a mathematical calculation to the case of the formation of nitrogen dioxide on the explosion of hydrogen and oxygen mixtures with air, comes also to the same conclusion. From the work of A. Finckh, in another place, a mixture of 95 parts of hydrogen and oxygen mixture with 100 parts of air gave a content of 1.8 per cent NO; W. Nernst calculated the corresponding explosion temperature from the pressure measurements of A. Langen‡ as 2310° C. Since the equilibrium concentration

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* K. Finckh, Z. anorg. Chem., **45,** 116; 1905.

† W. Nernst, Z. anorg. Chem., **45,** 126; 1905. See also W. Nernst, Theo. Chem., 674; 1907. K. Arndt, Technische Anwendungen der physikalischen Chemie, I, 1907.

‡ A. Langen, Forschungsarbeiten aus dem Gebiete des Ingenieurwesen, Vol. 8, 1903.

for this temperature, calculated according to W. Nernst, equals 2.05 per cent NO, either the quantity of nitrogen dioxide formed by the explosion did not conform to the equilibrium at that temperature or it afterwards decreased in volume according to the reaction

$$N_2 + O_2 \rightleftarrows 2\,NO.$$

K. Finckh found, at most, 2.3 per cent of NO for a mixture of 120 parts hydrogen explosive gas with 100 parts air; W. Nernst calculated the temperature of explosion (section 115) at 2400 degrees, which corresponds to a content of 2.23 per cent NO. In this case it is possible that the concentration of the NO at the equilibrium of the explosion temperature remained constant during the cooling.

CHAPTER VI.

EXPLOSIONS BY INFLUENCE.

135. Coincident with the more or less well understood phenomena which affect the immediate vicinity of an explosion, there occurs a phenomenon of a different sort which is able to exercise its influence to much greater distances. Whether this is due to the rapidly increasing pressure of gases developed with very great velocity or whether it is simply a phenomenon accompanying the high temperature, and comparable to the burning out, melting and such like, is still a question. According to late experimental and theoretical investigations a kind of wave movement originates in the sudden disturbance of equilibrium which is communicated to the surrounding medium, whether air or other gases, water or the ground. These waves have, in common with the explosion waves (section 78), a high intensity and great velocity but differ from the latter in that they rapidly lose their distinguishing character with increasing distance from the place of their origin and are finally transformed into ordinary sound waves.

136. The existence of a kind of force that exerts its influence at a distance has long been suspected from observations on black powder explosions,* though not absolutely proved. F. Abel† and especially J. Trauzl‡ first proved, without doubt, the existence of such an

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* J. Daniel, Dict. mat. exp., 291; 1902.

† M. Berthelot, Force mat. exp., II, 231; 1883.

‡ P. Chalon, Exp. mod., 269; 1899.

influence when they showed that submarine mines charged with guncotton are able to cause the explosion of other similar mines at such a distance as to make it seem impossible that any small particles or hot gases, penetrating through the intervening water, could have caused the second explosion. This method of bringing about an explosive reaction is known as detonation by influence.* Originally feared as a dangerous phenomenon accompanying great explosions, this kind of detonation has gradually won practical significance and now plays an important part in explosive technique.† It is now required of explosives to be used as blasting agents that, among other things, they shall readily communicate the explosion from one cartridge to another, even when a short space intervenes between the two.

It is also of commercial interest that an idea be obtained of the distances to which the explosive impact may exert its influence in one way or another. A magazine with 13,500 kilograms of guncotton exploded in Stowmarket, England, on Aug. 11, 1871. The noise of the explosion was heard to a distance of from 45 to 50 kilometers. The explosive impulse shook window panes at a distance of 11 kilometers and in a few instances is said to have broken them. At a distance of 8 kilometers an iron bar, with which a door was barred, was bent by the sudden pressure exerted against the door. Several window frames were broken at a distance of 1600 meters. Up to a distance of 400 meters and even in some cases as far as 1200 meters, weak walls were overthrown, church window mullions were fractured,

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* M. Berthelot, Force mat. exp., 1883, I, 117; II, 231. Also George F. Barker *in re* U. S. Blasting Oil Co. *vs.* George M. Mowbray *et al*, Circuit Court of U. S.; 1874.

† Charles E. Munroe, J. Am. Chem. Soc., **25**, 10; 1893.

gables were broken and similar injuries caused. As a rule, serious injury to property was confined to a distance of from 400 to 450 meters. At distances of from 250 to 350 meters several country houses were almost completely demolished. All factory buildings to a distance of 50 meters from the magazine were entirely destroyed. It is apparent from this that even in cases of very great explosions the area of serious injury is comparatively small, and it seems that a distance of 500 meters offers sufficient protection from the consequences of an explosion.*

137. According to W. Wolff † the mechanism of this phenomenon is somewhat as follows: An area of intense compression followed immediately by an area of rarefaction is produced at the point where the strongly compressed gases of explosion, in the first stages of the explosive reaction, meet the surrounding medium, — for example air, — in consequence of the strong resistance which the latter offers in the first instant against the diffusion of the former. Both these conditions are maintained in conformity with the laws of longitudinal wave movements. The explosion gases themselves are projected only a relatively short distance in this process. What is actually propagated and, in great explosions, causes destruction at such distances as above described, is a succession of wave movements, one positive pressure impulse proceeding away from the explosion center (the explosive impulse in a narrower sense), and a corresponding negative pressure impulse proceeding towards the explosion center which moves with the same velocity towards this center as the positive force

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* For American Table of Distances see Rept. Chief Insp. Bureau for Safe Trans. of Explosives and Other Dangerous Articles, **4**, 65; 1911.

† W. Wolff, Ann. Phys. Chem., **69**, 329; 1899.

moves in the opposite direction. W. Wolff affirms that this interpretation offers a satisfactory explanation of the oft-repeated observation in many reports on accidental explosions, namely, that, in addition to the direct effects of the explosions,—in directions away from the center of explosion,—indirect effects have been noticed where wreckage, window panes and the like were thrown towards the center of the explosion, exactly as if they had been sucked in in that direction. A current of air from the explosion outwards and *vice versa,* as is often supposed to occur,* is not at all necessary to explain these facts.

O. Guttmann† emphasizes the analogy between the method by which the explosive effect is produced and the phenomenon observed when a series of elastic balls is struck at one point. If such an elastic ball strikes another similar ball of the same size lying exactly in a line with the direction of the impact, the force of the impact is transmitted to the second ball and the first one remains at rest. In a series of several balls so placed only the last one is projected. The impulse is propagated through the entire series. In a similar manner the impulse of an explosion is propagated through the ground. This explains the fact that wooden posts, which have been sunk in sand embankments to prevent landslides, often project over a meter above ground after an explosion. The following occurrence lends additional credence to this view: On April 21, 1901, a fearful explosion was caused, in the Elektron Chemical Factory at Griesheim, by a fire which broke out in the picric acid magazine. Twenty-four persons were killed, a large number of workmen

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* Mitt. Art. Geniew., 1147; 1904.

† O. Guttmann, Z. ges. Schiess Sprengstoffw., **3**, 266; 1908.

were injured and much damage was done to property in the vicinity of the factory. The cause of the fire was not established. It had been burning about 20 minutes when an explosion suddenly occurred, immediately followed by another and greater one. The contents of the stone trough in which the picric acid was washed had exploded, as was afterwards discovered from pieces of the stoneware thrown out by the force of the explosion. It is supposed that this explosion was caused by the falling of some iron parts of the roof into picric acid which had become dried and heated to a high temperature by the fire. It is possible that the picric acid came in contact with red-hot iron or stone. It is noticeable that the immediate effect of the explosion was small compared with the destructive effect of the impulse which was exerted in a direction towards the center of the explosion. A large part of the building walls within a radius of from 30 to 50 meters were thrown inwards towards the explosion, the roofs were likewise thrown in that direction and the whole inner arrangements were shattered.*

138. Photographs of the compression waves (section 60) which occur in the air or in other gases, especially those taken by the methods devised by H. le Chatelier † and H. B. Dixon,‡ leave no doubt of the wavelike character of the explosive impulse. In the experiments of H. B. Dixon the explosive gaseous mixture was contained in a thick-walled glass tube *R* (Figs. 27 to 29), and could be ignited at *Z* by a strong electric spark. The light produced by the explosion

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* Ann. Rept. H. M. I. Exp., 471; 1901.

† H. le Chatelier, Compt. rend., **130**, 1755; 1900: **131**, 30; 1900.

‡ H. B. Dixon, Phil. Trans., **200**, 315; 1903. Ber. Chem. Ges., **38**, 2419; 1905.

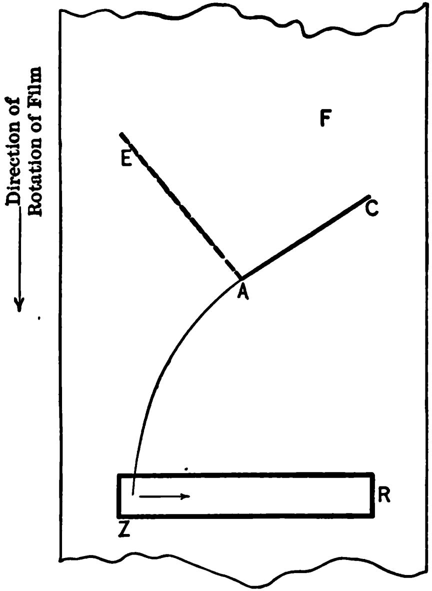

Fig. 27.

Z Point of Ignition
AC Explosion Wave
AE Explosion Impulse.

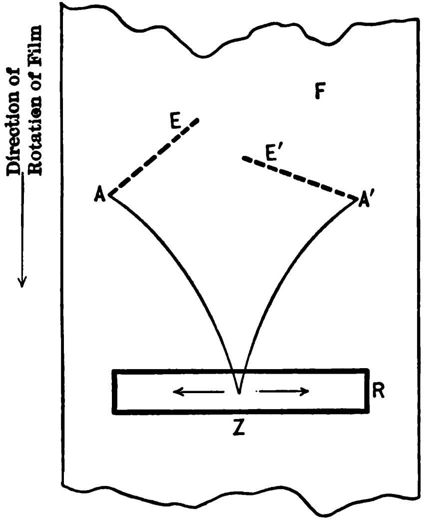

Fig. 28.

Z Point of Ignition
AE, A′E′ Explosion Impulses

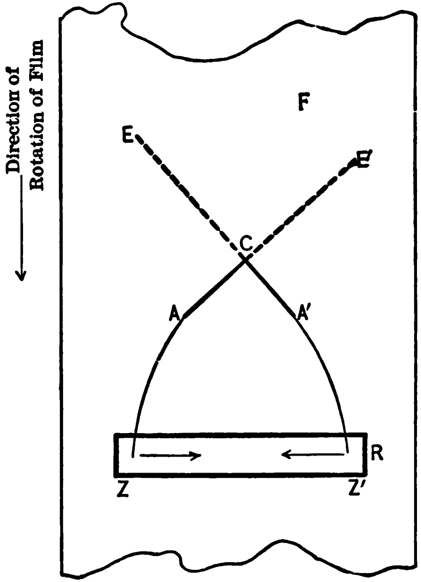

Fig. 29.

Z,Z′ Point of Ignition
AC, A′C Explosion Waves
CE, CE′ Explosion Impulses

Directions of the Explosive Movements are Indicated by the Arrows in the Rectangles.

was photographed on a rapidly moving photographic film *F*. The lines thus obtained were the result of the combined movement of a point of light proceeding in a horizontal direction (for instance, in Fig. 27, from left to right) and the film moving from above downwards. According to the results of these experiments the development of the explosive impulse is dependent principally upon the following conditions:

1. The point at which an explosion wave is formed becomes also the starting point of a series of waves which are propagated backwards through the burned gases (le Chatelier's "onde rétrograde," Dixon's "retonation wave"). In Fig. 27 *Z* is the point of ignition from which the combustion proceeds outwards with increasing velocity until suddenly at *A* the explosion wave sets in which projects the explosive impulse *AE* backwards.

2. If the explosion waves strike against an immovable wall or any other obstruction in the direction of its propagation this becomes the starting point of a wave series which is propagated backwards through the burned gas (le Chatelier's "onde réfléchie," Dixon's "reflexion wave"). In Fig. 28 the combustion has progressed with increasing velocity to the ends of the glass tube *R*, and at *A* and *A'* has initiated the explosive impulses *AE* and *A'E'*.

3. The meeting point of two explosion waves traveling towards each other becomes the starting point for two wave series, each of which is propagated backwards through the burned gas (le Chatelier's "onde prolongée," Dixon's "collision wave"). In Fig. 29 the explosion waves *AC* and *A'C* starting at *A* and *A'*, respectively, meet at the point *C*, which becomes the starting point for the explosive impulses *CE* and *CE'*.

It seems that occasionally the phenomenon of the explosion impulse has been confounded with the similar phenomenon of the explosion wave, which is characterized by constant propagation velocity for a given medium.* All photographs of the explosion impulse show very plainly the decrease of its velocity with increasing distance from the starting point. If, however, the question in the literature refers to definite propagation velocities of the explosive impulse, it must refer to that comparatively short space which as a rule can only be investigated by photographic apparatus.

Besides the wave series here mentioned which have exceedingly small oscillation amplitudes, other visible oscillatory mass movements have been observed whose velocity to some extent is considerably less than that of sound (section 90).

139. Physical-chemical experiments relating to the existence of the explosion impulse are very limited and are naturally attended with special difficulties when dealing with the phenomena accompanying great explosions. Nevertheless, we know that the velocity and intensity of the explosion impulse are the factors that are mainly responsible for the transmission of explosion influence at great distances.

1. Velocity of the Explosion Impulse.

140. E. Mach† exploded a small quantity of nitrogen iodide by touching it lightly with a wooden rod, and measured the velocity of the propagation of the

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* See, e.g., W. Nernst, Physik-chem. Betrachtungen über den Verbrennungsprozess in den Gasmotoren. Z. Vereins deutsch. Ingen., 25; 1905.

† E. Mach, Wiener Akad. Ber., 75; 1877.

air waves thus caused in the vicinity of the explosion. The following table gives the results of this experiment:

TABLE 37. VELOCITY OF THE EXPLOSION IMPULSE.

Distance from the source, millimeters.	Velocity, meters.
80	756
137	540
254	453
400	516
977	373

The waves took on the normal velocity of sound in air (340 meters) at a distance of several meters from the source. The results of this experiment were so surprising that for a long time their correctness was doubted, especially since other investigators, who, however, did not use an explosive as the source of the air waves, found only normal velocities. It is now known that the supposed sound waves observed by Mach, with their enormously high but rapidly decreasing velocities, were in reality the phenomena of the explosion impulse whose destructive effects at great distances had long been observed in explosions of large quantities of powder and other explosive substances.

141. P. Vieille* conducted a more exact experimental investigation of this explosion impulse. He observed in his study of the velocity of the propagation of explosion phenomena in explosive gaseous mixtures (section 94), that a wave movement traversed the explosive mixture with great velocity even when the mixture itself was not raised to the point of combustion, but acted simply as an inert medium through which the phe-

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* P. Vieille, Mem. poudr. salp., X, 177; 1899.

nomena produced by the explosion of the detonator were propagated. The original high velocity of this kind of explosion waves decreased so rapidly with the distance from the detonator that they could no longer be detected at the end of a tube several meters in length. P. Vieille used for this experiment strong steel tubes of 22 millimeters inner diameter, 25 millimeters thickness of walls and up to 32 meters in length. At each end, and sometimes in side-tubes, easily movable, close-fitting pistons, whose movements were registered as previously described (section 94) by a stylus on a rotating cylinder, were placed. A small detonator containing 0.63 gram of mercury fulminate, exploded by an incandescent wire, usually served as the source of the explosion impulse. The following table gives the result of these experiments when the tube was filled with air under atmospheric pressure.

TABLE 38. VELOCITY OF THE EXPLOSION IMPULSE.

Distance from source, centimeters.	Velocity, meters.
32.6	1073
53.2	1015
131.1	969
235.9	821
386.4	575

The velocity of the explosion impulse was still higher than the normal sound wave at a distance of 16 meters from the source. As might have been expected the velocity was influenced by the quantity of explosive detonated. P. Vieille gives the velocities shown in Table 39 for a distance of 113 centimeters from the source.

The velocity of the explosion impulse is also influenced to a great extent by the chemical nature as well

TABLE 39. VELOCITY OF THE EXPLOSION IMPULSE.

Charge in the detonator, grams.	Velocity, meters.
0.04	524
0.63	1151

as the density of the medium in which the explosion occurs. In gaseous mediums a considerable decrease of velocity was noticed with increasing pressures.

TABLE 40. VELOCITY OF THE EXPLOSION IMPULSE WITH VARYING PRESSURE.*

Velocity at 113 centimeters distance.	In hydrogen, meters.	In air, meters.	In CO_2, meters.
1 atmosphere pressure	2104	1041	814
22 atmospheres pressure	1555	576	363
Normal velocity	1319	340	281

* Charge, 0.63 gram mercury fulminate.

It might have been foreseen that the capsule in which the fulminate was exploded must also be of significance if the phenomenon in question was actually a propagation of wave movements. It is remarkable that P. Vieille obtained the highest velocities, under otherwise similar conditions, when the fulminate was inclosed in carton paper. The usual copper capsules produced almost the same influence as the paper. Weaker capsules made of silk, paper, or quills, and also much stronger ones made of sheet iron, gave regularly lower velocities for the explosion impulse.

The difference observed in Table 41 is not caused by the fact that the gases from the detonation acquire an unequal tension within the capsule (even a few kilograms excess pressure shatters a copper capsule) but

TABLE 41. SPECIFIC POWER OF THE ATMOSPHERE TO DEADEN THE EXPLOSION IMPULSE.

Distance, centimeters.	Mercury fulminate charge	
	In carton paper, meters.	In sheet iron, meters.
113	1144	931
386	805	634

more probably is caused by the deadening effect of the atmosphere upon the compression waves which have been developed.

142. H. Dixon* first succeeded in recognizing in explosive gaseous mixtures compression waves whose velocity of propagation was not essentially less than that of explosion waves produced in the same medium at the same time. He used the following method in obtaining these results: An explosion was produced by means of an electric spark at one end of a closed glass tube filled with the explosive gas. This traversed the entire length of the tube with the detonation velocity. The tube had a branch (Fig. 30), so that the explosion wave,

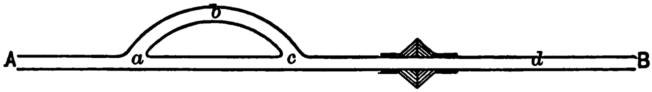

FIG. 30. Dixon's Apparatus for Generating Sound Waves whose Velocities approached that of Detonation Waves.

traveling from *A* towards *B*, had to traverse the bent part *abc* as well as the straight tube from *a* to *c*. When the wave, which is traversing this straight tube from *a* to *c*, passes the point *c*, it enters partly into the branch tube and meets the branch wave traversing the longer

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* H. Dixon, Phil. Trans., **200**, 315; 1903.

portion *abc*. There results from this collision a compression wave which is propagated in both directions towards *A* and *B* This wave follows close on the explosion wave traveling towards *B* in the part *d*, and both are photographed on a rotating film about 1 meter from the point *c* (section 138). The velocity of the detonation wave in the mixture $C_2N_2 + O_2$ was calculated at 2320 meters, the velocity of the sound wave following it at 1635 meters. The high temperature and the high pressure following the detonation wave, perhaps also the forward movement of the entire gas mass, produced conditions under which an ordinary compression wave could also be propagated with a velocity approaching a detonation wave.

143. H. le Chatelier* measured the propagation velocity of the compression waves attending explosion impulses in gaseous mixtures under various conditions of initiation and formation (section 138). The gas was detonated in tubes 1 meter long and 5 millimeters in diameter by means of a small 0.05 gram mercury fulminate capsule or a strong electric spark. The measurement of the velocity of the impulse waves was facilitated by the circumstances that the gas became luminous at the point of greatest compression (section 60), so that a photographic registration was made possible on a film moving rapidly in a direction at right angles to the direction of propagation of the impulse wave. In this manner the velocities were determined that are shown in Table 42.

While ordinary sound waves can cross each other without change of velocity, the explosion impulse suffers a considerable loss in velocity under corresponding conditions as also by reflection from a resisting

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* H. le Chatelier, Compt. rend., **130,** 1755; 1900: **131,** 30; 1900.

TABLE 42. VELOCITY OF COMPRESSION WAVES.

Velocity.	$C_2H_2 + O_2$, meters.	$C_2H_2 + 2\ NO$, meters.	$2\ CO + O_2$, meters.
1. Of the explosion waves...	2990	2850	1900
2. Of the explosion impulses:			
(*a*) "Onde rétrograde".	2300	1140	....
(*b*) "Onde réfléchie"...	2250	1350	1000
(*c*) "Onde prolongée"..	2050	....	....

obstacle in its path. H. le Chatelier finds (in another place) for the velocity of the explosion impulse in the mixture $C_2H_2 + O_2$:

At the point of formation....................	2300 meters.
After the first reflection......................	1350 meters.
After one crossing............................	1080 meters.
After two crossings...........................	980 meters.

144. The above (section 73) method for the estimation of the velocity of explosion waves by means of detonating fuses was used by M. Dautriche* also in determining the velocity of the explosion impulse in the air. Explosive cartridges weighing 100 grams were used as the source of energy. A dynamite whose detonation velocity had been estimated at 7000 meters per second gave a velocity of wave impulse at a distance of 5 centimeters from the nearest point of the cartridge of 3000 meters. A cheddite whose detonation velocity was 3000 meters gave 950 meters under similar conditions.

145. Experiments conducted on a large scale in various places, in which as much as 1500 kilograms of explosive (gelatin dynamite) were detonated at one time, furnished a valuable confirmation and extension of previous results obtained along this line with small quantities of explosives. An apparatus which was

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* M. Dautriche, Compt. rend., **144**, 1030; 1907; also A. M. Comey, 7th Int. Cong. App. Chem., III b, **28**; 1910.

originally designed for measuring the velocity of projectiles, but which seemed suitable also for the powerful dynamic forces met with in explosions, was used in Cummersdorf * for measuring the velocity of explosion impulses. This apparatus consisted of electric contacts which were opened or closed by means of a metallic membrane as soon as it was struck by an impulse, such, for instance, as the advance wave of a projectile. The making and breaking of the contact was registered as usual on a rotating drum by means of a stylus which was set in motion by an electromagnet connected in the circuit. The velocity of concussions in the immediate vicinity of the explosion was not measured because of the danger of shattering the apparatus. They must be very great, however, since measurements at a distance of 50 meters showed velocities of about 800 meters, and even at 250 meters the waves had not yet been reduced to the normal velocity of sound waves. Simultaneous with these air waves, similar concussion waves, whose velocities were considerably higher than that of the air waves at an equal distance from the explosion, were observed in the sandy soil of the field used for the experiments. In order to determine the velocity of these waves a registering apparatus was set up a half meter below the surface of the earth. This apparatus could register horizontal earth movements, but was not influenced by the direct action of the air waves nor the movements of the immediate surface of the ground caused by these.

146. The French Explosives Commission † used, for the measurement of the velocity of the explosion im-

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* E. Müller, Verh. d. Ver. Beförd. Gewerbfl., 45; 1900.

† Mem. poudr. salp., XIII, 228; 1905. Lheure-Burkard, Z. ges. Schiess Sprengstoffw., 2, 228, 249, 308, 427, 446; 1907.

pulse, electric contacts which were opened by the vibration of a metallic membrane as soon as it was struck by a concussion of the air. The first point for the breaking of the current was in the body of the explosive itself, and consisted of a small copper wire embedded in it. In consideration of the destructive effect of the concussion the next registering apparatus was constructed as simply as possible. A thin sheet of metal, fastened to a wooden stake by means of a weak string, pressed against a metal screw fastened to the same stake. As soon as the metal sheet began to vibrate in consequence of an explosive impulse the current was broken between the metal sheet and the screw. More delicate apparatus (Fig. 31) was chosen for the greater distances. A small steel ball *K*, fastened to the insulated spring *F*,

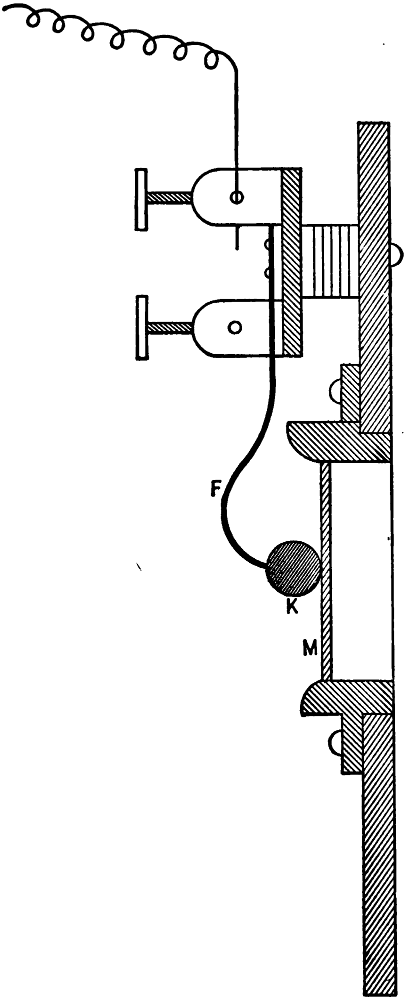

FIG. 31.—Apparatus for Indicating Air Concussions.

pressed lightly against a sheet-iron plate *M*. In the condition of rest the current flows through membrane, ball and spring, but under the influence of the concussion the ball swings slightly back, breaking the contact between ball and membrane. The velocity of the explosion impulse at a given distance was found to be dependent not only upon the quantity of explosive used but also upon the nature of the explosive.

TABLE 43. DEPENDENCE OF THE VELOCITY OF THE EXPLOSION IMPULSE UPON THE NATURE OF THE EXPLOSIVE.

Explosive.	Quantity, kilograms.	Distance from the explosion, meters.	Average velocity of explosive impact, meters.
Picric acid	100	0–20	638
		20–40	379
		40–60	357
Cheddite	150	0–20	590
		20–40	413
		40–60	360
Black powder	300	0–20	530
		20–40	380
		40–60	360

2. INTENSITY OF THE EXPLOSION IMPULSE.

147. The military problem of placing submarine mines at such a distance apart that the eventual explosion of one should not endanger the others gave the first occasion for experiments in regard to the intensity of the explosive impulse. H. L. Abbot* measured the concussion propagated under water in the following manner: An explosive charge was placed at the center of an iron ring which was held in a horizontal position in deep water by means of a swimming buoy. Six

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* Gen. H. L. Abbot, Experiments and Investigations to Develop a System of Submarine Mines, Washington, Government Printing Office; 1881. See also P. Chalon, Explosifs modernes, 246; 1886.

Noble compression gauges (section 105), with lead compression disks, were fastened at regular distances apart on the periphery. The diameter of the iron ring varied in the several series of experiments between $2\frac{1}{2}$, $3\frac{1}{2}$, $4\frac{1}{2}$ and $5\frac{1}{2}$ meters. The compression of the lead disks showed that the explosion impulse is propagated in all directions with equal intensity and that the intensity is approximately in inverse proportion to the square of the distance from the explosion center. The magnitude of the force exerted was not in direct proportion to the quantity of the explosive used, but was much less. Its increase, when the original charge was doubled, was not as much again, but only about one-fourth of the original magnitude. If we denote the weight of the explosive substances by P and the distance from the explosion center by d, the energy E transmitted by the concussion is

$$E = m \cdot \frac{\sqrt{P}}{d^2},$$

in which m is a constant dependent upon the kind and conditions of the explosive used.* This formula, however, is applicable only to an incompressible medium, and water is not entirely incompressible, even at considerable depths, especially under pressures of several thousand atmospheres † such as obtain in explosions. In fact the intensities determined by H. L. Abbot can hardly be expressed in a simple constant proportional to the distance and mass of the explosive used.

148. R. Blochmann ‡ used the apparatus, designed by

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* J. P. Cundhill and J. H. Thomson, Dict. Exp., XIX; 1895.

† M. Jacob, Compt. rend., **138**, 1259; 1904.

‡ R. Blochmann, Mar. Rund., **9**, 197; 1898. See also C. E. Bichel, Mar. Rund., **16**, 1345; 1905. R. Threlfall, Phil. Mag., (5), **21**, 185; 1886.

E. Mallard and H. le Chatelier, with which to measure the intensity of the explosion impulse. The apparatus consisted of a spring manometer in connection with a rotating drum, so that the time consumed by the phenomena accompanying the explosion could be measured. The explosion impulse, propagated through the water, was received by pistons of definite diameter which acted upon previously tested springs, the shortening of which was registered. The diagrams obtained with this apparatus (Fig. 32) are marked by a series of characteristic pressure maximum, the first two of which are of especial interest. The first pressure maximum, *A*, is due to an impulse progressing with the velocity of sound and may be regarded as the actual explosion impulse. We have here, evidently, the phenomenon described above (section 137) for air, with the difference that in this case it occurred in water. The second, apparently greater, pressure maximum, *B*, is due to a dynamic cause which is propagated much more slowly (with a velocity of only a few meters), such as would be given by the actual movement of water masses. R. Blochmann attempted also to derive from the diagrams traced by the dynamometer the absolute amount of work done, but did not succeed in obtaining a satisfactory agreement with the theoretical.

FIG. 32. Blochmann's Diagram showing Action of Subaqueous Explosions.

149. Still less can the relations existing in the case of explosions in elastic media be expressed numerically when the air as well as the ground takes up and propagates the explosion impulse, which, as a rule, is the case. The following experiment has been carried out at Cummersdorf (section 145), in order to obtain a better understanding of the very complex mechanical forces observed in accidental explosions of large quantities of explosives.

A number of posts, buried in the earth, were grouped radially around the explosion center and specially constructed spring attachments for the measurement of the force were affixed to these posts. As a control on this experimental method, delicately balanced balls were used, which were propelled forward from their position of rest by the concussion. In addition, panes of glass were fastened firmly to the posts in such a manner as to be broken by the concussion.

150. L. Thomas* describes similar experiments which were undertaken with the purpose of determining whether the shipment of large quantities of dynamite at a distance of 12 kilometers from Antwerp would constitute a danger to that city. A number of plates, 50 in all, some of which were movable and some firmly fixed, were set up in an open field in all directions about the explosion center and at distances of from 5 to 1000 meters. In addition to this two wooden huts were built within the supposed limit of the explosion impulse (concussion), roofed with tiles and provided with glass windows. The charges of explosive used consisted of 25, 50, 150 and 1000 kilograms of gelatin dynamite in the usual packing boxes, each of which

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* Mem. poudr. salp., XIII, 161; 1905. See also Lheure-Burkard, Z. ges. Schiess Sprengstoffw., **2**, 228, 249, 308, 427, 446; 1907.

contained 25 kilograms of the explosive in the form of wrapped sticks. They were exploded, one after the other, lying free on the ground The destructive effects extended to 17.5, 40, 55 and 125 meters from the explosion center, respectively, corresponding to the increasing amounts of explosive employed. Outside of this a small neutral zone was observed, beyond which the force of the explosion was directed towards the center, the plates were thrown down towards the origin of the explosion, the window frames were forced outwards and most of the glass was thrown outwards.

151. It is evident that a more definite knowledge of the complicated mechanism of the explosive impulse cannot be gained so long as we are confined to the crude apparatus previously in use. Yet the French Commission,* from the above-mentioned experiment (section 146), has succeeded in discovering a significant physical law governing the dependence of the explosion impulse, or concussion exerted at a distance from the explosion, upon the quantity of explosive detonated. It appears that, in so far as the destructive effects of the explosion impulse is concerned, the force of the explosion acts as if the energy of the exploding substance were concentrated in the air on the surfaces of concentric spherical figures whose centers lie at the center of the explosion. If, as above (section 147), we denote by d the distance from the explosion within which the force of the concussion is still felt, by P the weight of the explosive employed, and by m a constant dependent upon the kind and condition of the explosive, we have, from the above-mentioned experimental results,

$$d = m\sqrt{P}.$$

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* Mem. poudr. salp., XIII, 161; 1905. See also Lheure-Burkard, Z. ges. Schiess Sprengstoffw., **2**, 228, 249, 308, 427, 446; 1907.

The limits at which the impulse is felt were shown to be approximately proportional to the square roots of the quantities of explosive employed. With an increasing charge the danger zone soon becomes practically independent of the charge. A comparison of the distances at which the explosive impulse is felt, calculated by this method, with the actual danger zone observed in accidental explosions, shows a sufficient agreement to prove the correctness of this method for practical purposes.

TABLE 44. DANGER ZONES IN GREAT EXPLOSIONS.

Accidental explosions.		Explosive.		Danger zone.	
Place.	Year.	Quantity, kilograms.	Kind.	Observed meters.	Calculated meters.
Corvilain.....	1889	5,500	Black powder	340, great damage	500
Vigna-Pia....	1891	260,000	Black powder	1500, great damage 6000, slight damage	3600
Santander....	1893	30,000	Dynamite	600, great damage	1700
Keeken......	1895	20,000	Dynamite	1200–2200, according to the direction	1400
Johannesburg.	1896	50,000	Explosive gelatin	1800, great damage	2500
Lagoubran....	1899	100,000 100,000	Black powder Smokeless powder	4500, slight damage 3200, great damage 7000, slight damage	2200
Avigliana.....	1900	10,000	Explosive gelatin	1300	1200

152. If the concussion strikes a second explosive with sufficient energy this will itself be brought to explosion. The distance at which detonation is caused by this kind of influence has been shown by numerous experiments to be primarily a function of the quantity of the first charge, which determines both the velocity and the intensity of the resulting impulse.* According to the experiments of F. Mauerhofer,† M. Coville ‡ and others,

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* Charles E. Munroe, The Determination of the Relative Sensitiveness of Explosive Substances through Explosion by Influence, J. Am. Chem. Soc., **15**, 10; 1893.

† F. Mauerhofer, Osterr. Berg. Hütt. Supplement, 19; 1882.

‡ M. Berthelot, Force mat. exp., I, 118; 1883.

who, however, used only small quantities of explosives, there exists a direct relation between these two figures in which, moreover, the character of the medium may be taken into account by the addition of a corresponding factor. In the case of great quantities of explosives the distance at which detonation may be transmitted steadily increases, but not in proportion to the quantity of the primary explosive.* Thus, a primary charge of 10 grams of guhr dynamite will just detonate a second charge at a distance of 4.5 meters, while a distance of 20 meters would be expected if the distance increased proportionally to the charge.

153. A. Kette† proposed to determine this zone of influence for explosives by exploding one of two explosive bodies of like shape and weight, placed near but not in contact with each other.‡ The numerical factor desired is then calculated from the varying distance at which the detonation is transmitted to the second body. In a preliminary experiment two cartridges of a known explosive are used and the distance at which one is detonated by the other determined. Then in a second experiment the distance is determined at which detonation is transmitted from the normal explosive to the explosive to be tested, and finally the test is made in the inverse order to determine the distance at which the detonation is transmitted from the explosive to be tested to the known normal explosive. The explosive to be detonated, *n* (Fig. 33), is provided with fuse *z* and fastened on a board to which the explosive to be tested, *n'*, is also fixed. The distance between the two bodies is measured before the explosion and the experiment is

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* P. Chalon, Exp. mod., 266; 1889.

† D. R.-P. A. Nr. 22,698 of Feb. 12, 1902.

‡ Charles E. Munroe, J. Am. Chem. Soc., **25**, 10; 1893.

repeated until the maximum distance at which the detonation is just transmitted from *n* to *n′* is discovered.

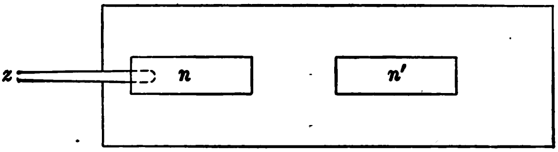

FIG. 33. Measurement of the Capacity of Explosives to Detonate by Influence.

154. It is yet doubtful whether any relation exists between the chemical composition of an explosive and its ability to transmit its detonation to another body of the same kind. At any rate such a relationship, though suspected, has not been proved. With many explosives (e.g., picric acid) this specific ability to transmit detonation at a distance is very slight. It should be mentioned in this connection that closely related explosives such as explosive gelatin, guhr dynamite, 80 per cent, and 65 per cent gelatin dynamite show an almost arbitrary variation in respect to the distance at which detonation is transmitted under identical conditions.

The susceptibility of a secondary charge to detonation by the shock from the explosion of a primary charge is probably not confined to solid and liquid explosive substances. It is believed that many fire-damp explosions, surprising for their wide extension, are to be explained by the susceptibility of fire damp to such influences.

Air, being a very elastic medium, deadens the effect of the explosion impulse upon another explosive to an especially great extent, and it is, on this account, of practical importance to make as small as possible the space which separates two cartridges which are to be detonated by influence. If there be a considerable air space between the two cartridges, even though the second one is detonated, there is a probability that the initial impulse transmitted from the first is so modified in strength that the explosive reaction does not occur with that velocity necessary to produce good results. A dynamite cartridge, for instance, which had been detonated by a detonator blew a hole in the ground 30 centimeters in diameter, while a second cartridge similar to the first, detonated by influence, caused a hole of only 22 centimeters. As the distance between the two cartridges was increased a gradual diminution in the quantity of earth thrown out by the second was readily recognized. If two dynamite cartridges are hung in the air so that they just touch, the detonation is not usually transmitted, partly because the quantity of air between the two is usually sufficient to lower the intensity of the concussion below the point necessary to cause detonation. In the same way substances which contain air, especially loose sand, etc., are able to weaken the explosive force, and the protection offered by walls of earth in the vicinity of an explosion is due principally to this weakening effect.

155. Two intense explosion impulses, which meet each other from opposite directions, can so compress the air at the point of meeting that it glows. The compression necessary for this phenomenon is comparatively small, and may easily occur between two cartridges detonated near each other. The increase of temperature caused by the sudden compression of a gas, especially the air, is determined by the equation*

$$\frac{T}{T'} = \left(\frac{p}{p'}\right)\frac{k-1}{k},$$

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* R. Clausius, Mech. Wärmetheorie, 65; 1887. See also P. Vieille, Compt. rend., **130**, 238; 1900.

in which T' and p' represent the initial temperature and pressure, e.g., 273 degrees absolute (= 0° C.) and 1 atmosphere, and k the ratio between the two specific heats under constant pressure and constant volume. It only requires, then, a compression of about 200 atmospheres to heat the air momentarily from 0° C. to 1000° C. A. Siersch* first noticed this phenomenon when detonating simultaneously two suspended cartridges, and Ph. Hess† deserves the credit of calling attention to its significance in blasting in mines containing fire damp.

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* A. Siersch, Oesterr. Berg. Hütten., 4; 1896.

† Ph. Hess, Mitt. Art. Geniew., **31**, 26; 1900.

CHAPTER VII.

THE FLAME OF AN EXPLOSION.

156. The formation of a more or less extensive flame is not a necessary accompaniment of explosive reactions; yet it is to be considered as an almost constant result of the high temperature of the gases of an explosion. Sufficient occasion has been given for a closer study of this phenomenon since the theory has gained credence that the degree of safety of an explosive towards fire damp in blasting work is determined principally by the character of the flame accompanying its explosion, and that the danger observed in the use of black powder, dynamite and many other explosives is due to this cause.

According to its outward appearance the flame accompanying explosive reactions shows differences in intensity, illuminating power, size and duration, and it seems that these variations are dependent upon the conditions under which the explosion occurs as well as upon the chemical and physical character of the explosive system.*

157. The first attempts to obtain an idea of the size of the flame accompanying an explosion under varying conditions consisted in laying very combustible substances, such as black powder or dry nitrocellulose, in a circle around the explosive to be tested.† This experiment showed that often ignition did not occur where apparently all conditions necessary to an ignition were fulfilled.

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* F. Heise, Spreng. Zünd. Spreng., 64; 1904.

† A. Siersch, Oesterr. Zeitschr. Berg-Hüttenwes., **44,** 41; 1896.

158. A. Siersch,* who first expressed the view that the size of the flame gives an immediate measure of the safety of an explosive toward fire damp, obtained most valuable experimental material by photographing the explosion's flame. The experiments were conducted on a dark night and the cartridge suspended in the air at a measured distance in front of an opened lens was exploded. It was clearly established from the photographs that the various types of explosives are characterized by definite light phenomena. As a rule the size of the flame was directly proportional to the heat of explosion. Explosives having very high specific heats (Table 4), such as explosive gelatin (92 per cent nitroglycerin), guhr dynamite (75 per cent), and gelatin dynamite (65 per cent), produced large pictures on the sensitive plate. Explosives with comparatively low specific heats, such as dynamites of low nitroglycerin contents and carbonite, and, more especially, the ammonium nitrate explosives, produced a much smaller flame. In some cases the flame appeared to be entirely absent. Besides the character of the explosives the experimental conditions also affected the photographs. Quite naturally the size of the flame on the sensitive plate was dependent upon the quantity of explosive employed, and this is in accordance with the experience that the safety of an explosive in practical use decreases with an increasing charge (section 161).

159. Every combustible gaseous mixture requires a certain length of time to react explosively, though this may be very short (section 31). It is easy, therefore, to understand, as regards the safety of an explosive in the presence of fire damp, that the longer the duration

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* A. Siersch., *loc. cit.* See also Wilkoszewski, Z. ges. Schiess Sprengstoffw., **2**, 141; 1907.

of the hot explosion flame the more certainly will the fire damp in the mine be ignited. E. Mallard and H. le Chatelier* discovered that in order for a mixture of methane and air to be exploded by a flame of a certain temperature this temperature must be maintained for a sufficient length of time (section 37). It had indeed been long suspected that the cause of the low degree of safety of black powder (which has a comparatively small heat of explosion) was the relatively long duration of the explosion flame.

160. C. E. Bichel † repeated and extended the experiments of Siersch from this point of view. A steel mortar of about the same bore as that used in practical work was placed in an upright position and a measuring stick was set up just back of it. As a rule 100 grams of the explosive to be tested were loaded in the mortar and the charge fired electrically. The flame was photographed at night, a quartz lens and a rapidly revolving sensitive film being used in order to register the chemically active rays as completely as possible. An opaque film with a perpendicular slit was inserted between the lens and the cylinder holding the sensitive film. When this cylinder remained at rest the length of the picture corresponded to the length of the flame and the width of the picture to the width of the slit in the opaque film. When the cylinder was revolved rapidly, the picture increased in width, and this increase, as calculated from the measured velocity of revolution, gave the duration of the flame in thousandths of a second. Just as there is a relation between the size of the flame and the safety of an explosive, there exists

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* See also H. le Chatelier, Grisou, 47.

† C. E. Bichel, Zeitschr. Berg-Hütten-Salinwes., **50,** 669; 1902. Also Methoden und Apparate der Sprengstoff-A. G. Carbonit zur Prüfung von Sprengstoffen, 1907, by the same writer.

also undoubtedly a relation between the duration of the flame and the safety of the explosive. If this relation was not expressed in the above-described photograph as definitely as might be desired it was probably due to the fact that the photograph registered every luminous phenomenon, even though it might not be sufficient to cause ignition, and did not register non-luminous phenomena which might possibly be better able to cause the ignition of fire damp.*

161. It remains to be noticed that besides size and duration of the flame of explosion there are other characteristics of an explosive which influence its safety in the presence of fire damp. Among these characteristics may be mentioned for instance the kind of processes to which the explosive has been subjected in its manufacture. The finer and more intimately mixed the separate components and the more homogeneous the finished product, the higher will be the degree of safety of an explosive. Even safe explosive mixtures may become unsafe if not sufficiently well mixed.† It has already been mentioned that the theoretical connection between the various phenomena here discussed is not yet entirely understood. Empirical investigations are still being carried on by a method devised by H. Winkhaus,‡ which has been adopted in the experimental

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* The explosion's flame when generated in a glass vessel shows the bright spectrum lines of sodium and calcium; when generated in an iron vessel, those of iron. G. D. Liveing and J. Dewar (Proc. Roy. Soc., **36**, 471; 1884), as well as H. Dixon (Phil. Trans., **200**, 315; 1903), have shown the probability that the luminosity of the oxyhydrogen flame is caused principally by vaporized particles from the walls of the vessel.

† F. Heise, Spreng. Zünd. Spreng., 87; 1904. For method used by U. S. Bureau of Mines, see Bull. 15, Investigations of Explosives used in Mines, **95**; 1912.

‡ H. Winkhaus, Glückauf, 1895 and 1896. See also H. Beyling, Glückauf, 435; 1903. W. Eschweiler, Prüfung von Sprengstoffen auf Schlagwettersicherheit, B. Kon. angew. Chem., II, 303; 1903.

mine stations in Germany, Austria, the United States and England. According to this method the safety of an explosive is judged according to the weight of the maximum charge which can be fired from a mortar into a gaseous mixture of definite composition, e.g., benzene and air,* without causing it to ignite. The experiments show that with an increasing quantity of one and the same explosive all those phenomena which favor the ignition of the gaseous mixture, among which is the duration of the flame, become more pronounced. At a certain maximum charge the safety of all explosives yet devised ceases. This fact becomes all the more significant in view of an erroneous conclusion drawn by E. Mallard and H. le Chatelier from a series of experiments on the irregular conduct of mixtures of methane and air as regards their velocity of ignition (section 37), that certain explosives do not ignite fire damp.† Figs. 34 to 36 show a longitudinal section, cross section and side view of an apparatus in use at the experimental mine station in Gelsenkirchen. In principle this consists of a gallery *A* which is open at one end and closed at the other end by a strong wall of masonry *K*. Two steel mortars *m* and *m′*, having an outer diameter of about 50 centimeters and a bore 55 millimeters wide and 46 centimeters deep, are placed in this masonry in an oblique position. The fan *l* and the ventilator in the tube *f* allow the gallery to be filled with an atmosphere of any desired character. The gallery is supplied with observation windows *g*. The method of testing, above described in brief, has proved so successful that not a single case has become known in which a previously tested explosive, which showed a high de-

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* O. Guttmann, Ber. Kon. angew. Chem., II, 319; 1903.

† P. Duhem, Thermodynamique et Chemie, 474; 1902.

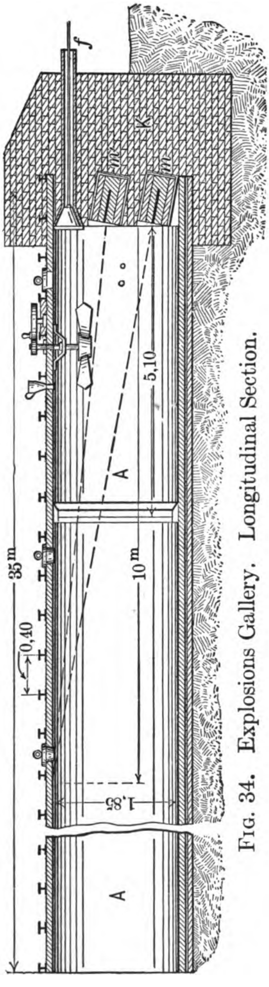

FIG. 34. Explosions Gallery. Longitudinal Section.

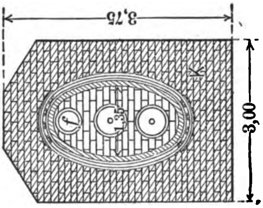

FIG. 35. Explosions Gallery. Cross Section.

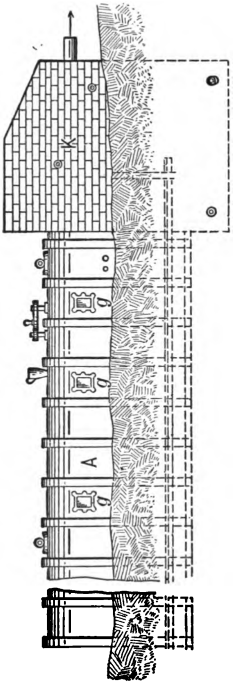

FIG. 36. Explosions Gallery. Exterior View.

gree of safety in the tests of the past few years, has caused fire-damp or coal-dust explosions in mines.*

162. According to C. E. Bichel † the length of the explosion's flame plays an important part also in the

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* H. Beyling, Glückauf, 1142; 1907.

† C. E. Bichel, Glückauf, 1040; 1904.

transmission of the detonation from one charge of an explosive to another placed but a short distance away. This was concluded from the following experimental data. These maximum distances for the transmission of detonation were obtained from 65 per cent gelatin dynamite lying free on the ground.

TABLE 45. DISTANCES AT WHICH DETONATION OCCURRED FOR GELATIN DYNAMITE.

Weight of charge, kilograms.	Intervening distance, meters.
1	0.90
5	1.45
10	1.80
25	2.25
50	2.50
100	2.75
200	5.25

When, however, the charge was sunk in the earth its power to transmit the detonation was lessened, while, in general, an increase in this power is to be expected since the transmission of the concussion waves (section 152) takes place through the earth which is a much better conductor than the air. Yet, detonation by influence cannot in every case be referred to the effect of the explosion's flame. The fact of the transmission of a detonation from one body to another through a considerable layer of water, for instance, where the influence of the explosion's flame must be very slight on account of its rapid cooling, is opposed to this theory,* and cannot be understood if it be not by a disturbance of equilibrium.

163. On the other hand in the case of the so-called double explosions in coal mines, characterized by a

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* A. Siersch, *loc. cit.*

transmission of the explosion between two separated collections of fire damp or coal dust, the length of the flame of the first explosion seems to play a most important part.* In many cases where the explosion was a very extended one, as in the explosion in the Courrières mine on March 10, 1906, ignition might have been caused by flying coal dust, or perhaps the explosion impulse was transmitted through the intervening rock bed.

The fearful explosion just mentioned, which sacrificed the lives of 1100 men and is the most frightful catastrophe in the history of mining, occurred at 7 o'clock in the morning in the mines belonging to the Courrières Company.† The mine, which covered an area of over 5000 hectares, is a part of the coal fields in the Calais district, which is about 55 kilometers in length. The company had 14 shafts, all of which, with the exception of one which was being sunk, were in connection during the day. The explosion extended through five of these shafts. On the 6th or 7th of March, a fire was discovered in a flue in the vicinity of shaft 3, and this was cut off from the rest of the mine by dams until the 10th of March. It seems that little danger was apprehended from this fire because the mines of the Calais district were usually free from fire damp. Early on the 10th of March, the morning shift of 1400 men entered four of the shafts, and at 7 o'clock the workmen were surprised by a terrific explosion. The accident became known from the volumes of smoke and dust which issued from the shafts, accompanied by a loud roar. Rescue work, which was immediately begun, and which was assisted later by a troop of Westphalian

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* A. Hasslacher, H. ber. P. S. Kom., 125; 1887.

† Glückauf, No. 12, 13; 1907.

miners equipped with good oxygen apparatus, was very difficult on account of cave-ins and mine fires. The system of ventilation had to be changed twice in order that, on the one hand, the miners still living should not be deprived of air, and on the other hand, that no fresh air should be supplied to the fire which followed the explosion. Only 300 of the workmen who had been caught in the mine were saved, while 1100 were killed.

It seems established that the cause of the explosion was not due to the ignition of fire damp. The mine was so free from fire damp that the work was carried on in many places with open lights. Not a trace of fire damp could be detected after the explosion, even in the room in which the ventilation had not yet been reëstablished. On the other hand it seems certain that the terrific explosion was caused by the ignition of dry coal dust. Nor was this ignition caused by the fire which had been burning for several days, as was at first supposed, but very probably by a blown-out blasting charge. In order to find out the cause and the center of the explosion, the direction taken by the explosives was determined, as usual, by the evidence of the paths along which the explosive force was exerted. During the examination a bore hole was discovered in the northwest part of the mine, which was probably the center of the explosion, for the severely burned bodies found near this, as well as the charred coal dust, indicated a very strong local heating. It could not be learned what charge had been used here. According to the testimony of experts it was probably from 400 to 500 grams of the explosive, "Favier 1," consisting of 88 parts of ammonium nitrate and 12 parts of dinitronaphthalene. The bore hole seems to have been only lightly tamped and an ignition of the coal dust was consequently very probable.

It was especially disastrous in this catastrophe that the numerous mines were connected in a system. The main purpose of this arrangement was evidently to simplify the ventilation and hauling. In this case, however, it facilitated the transmission of the explosion flame from one mine to the other, so that there resulted a more extended coal-dust explosion than had ever been experienced.

164. The gases of smokeless powder are usually rich in carbon monoxide, hydrogen and methane. If these products become mixed with air while they are still in the barrel of the gun they may produce combustible mixtures which under unfavorable conditions may give rise to dangerous secondary explosions.

The accident which occurred on April 13, 1904, on the U. S. S. "Missouri," and which cost the lives of 32 men, was ascribed to such an "after flame" or "flare back."* The ship was engaged in target practice off the coast of Florida when suddenly a dull report was heard proceeding from the 12-inch after turret and magazine. This was accompanied by flames and burning particles which rose to a great height. The ship was in danger of being destroyed by the explosion. The turret, which was filled with flames, was connected by an open chute with the handling room which contained 455 kilograms of loose powder in bags, and the fierce flames soon reached a number of copper containers in the steerage magazine holding about 1000 kilograms of smokeless powder. Since all the officers and men, who were in the turret at the time of the

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* Army and Navy Register of June 4, 1904. Mar. Rund., 15, 737; 1904.

accident, were killed, the cause of the explosion could not be definitely ascertained. It was thought probable that some unburned gases remained in the chamber of the gun and that these became mixed with air and later ignited by some glowing particles from the previously fired powder bags. It had been noticed before the accident that, when the breech was opened soon after a heavy charge was fired, flames and hot gases struck back and singed the hair and clothing of the gunners. This was particularly noticeable when shots were fired against a strong wind.

165. Shots from guns, especially of large caliber, are often accompanied by a flame from the muzzle. This, as well as the "after flame," is due to a secondary ignition of the combustible components of the explosion's gases when they become mixed with the outer air in the proper proportions and are heated to a sufficiently high temperature to be ignited.* Powders which have high heats of explosion seem especially liable to produce this flame. Moreover, small irregularities or differences in the manufacture of a type of powder, which cannot be detected in the finished powder with certainty, may also be influential in causing the flame. According to W. Heydenreich,† this flame may be modified or entirely prevented by a proper manufacture of the powder grains and choice of loading charge. The addition of certain substances‡ to the powder, such, for instance, as sodium bicarbonate, di-cyandiamide $C_2H_4N_4$, soap, etc., has also been proposed for this purpose. M. Dautriche§ prevents the formation of the

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* E. Bergmann, Z. Elektrochem., **12**, 568; 1906.

† W. Heydenreich, Kriegstechnische Zeitschr., **4**, 305;. 1901. H. Berlin, Handbuch der Waffen lehre, 8; 1904.

‡ D. R. P. No. 195,486. A. Frank, Chem. Ztg., 939; 1907.

§ M. Dautriche, Chem. Ztg., 335; 1908. See also French patent No. 385,769 of L. Villa. Ann. Rept., H. M. I. Exp., 91; 1907.

flame in a similar manner. The method is based on the observation that a cloud of fine dust composed of any potassium or sodium salt impedes the combustion of gas or dust mixtures. It is claimed that he eliminates the flame entirely by loading in front of the powder bags an additional charge composed of such salts (section 51).

PART II.

CHAPTER VIII.

CHARACTERISTICS OF PARTICULAR EXPLOSIVES.

1. Physical Changes in Explosives.

166. It is evident from the foregoing that explosions are essentially simple reactions the many outward manifestations of which are to be ascribed to the conditions under which the explosion occurs and to the varying character of the explosive system under consideration. Only in so far as definite relationships can be established between these latter and the explosion itself, can the physico-chemical characteristics of the explosive substance enter into consideration. There are, however, definite properties of the technically important explosives which undoubtedly influence the explosive reaction and, under certain conditions, become very significant, especially where it is desired to obtain a definite effect from a given explosive. A delicate test for the constancy of these properties is in fact a technically important necessity.

The conditions, or the changes in the conditions, of explosive systems are often very difficult to determine with accuracy, partly on account of the small variations which may become significant, or of the heterogeneity of the substance, and partly on account of the insufficiency of our methods of investigation.

167. The volumetric density is one such factor of varying, undeterminable magnitude, but nevertheless of great practical significance. Heterogeneous explosives of the type of black powder, which are composed of several components that can be easily separated and that in themselves are not explosive, require a certain, previously determined density. This is necessary not only in order to secure a constant composition which cannot be altered by the shaking and jostling unavoidable in transportation, but also in order to obtain the greatest ballistic and practical effectiveness. Also in the case of gelatinized explosives for propellants, such as explosive gelatin, differences or variations in density, caused by evaporation of the gelatinizing liquid, or expulsion of air from the pores, are manifested by a varying velocity of combustion or detonation and a correspondingly irregular effectiveness. In the case of less sensitive mixtures of the type of ammonium nitrate explosives, which are compressed from a pulverized condition during the process of manufacture, there exists a limiting density below which the explosive is detonated with the usual detonating agencies, but above which detonation cannot be effected, at least under practical conditions (section 73).

168. The tendency of many explosive substances to absorb moisture from the atmosphere is also of practical significance. This property limits the use of several substances which would otherwise be very valuable as components of explosive mixtures, as for instance sodium and ammonium nitrates. These substances are always rejected for ballistic purposes on this account. For this reason also the amide powder, consisting of ammonium nitrate 38 per cent, potassium nitrate 40 per cent and charcoal 22 per cent,— an explosive of excellent

efficiency, — had to be withdrawn from the market because it was found impossible to manufacture it in such form as to exclude air.* For blasting purposes a slight variation in the degree of efficiency is allowable so long as the explosive retains its ability to be detonated easily. This may become uncertain, however, through the absorption of small quantities of moisture. Cartridges consisting of ammonium nitrate 95.5 per cent and trinitronaphthalene 4.5 per cent (*grisounite couche Favier*), which in a dry condition, are readily detonated by 0.5 gram of mercury fulminate and explode with all effect, lose this power when they have taken up 3 to 4 per cent moisture, and are then not even brought to explosion by a 2 gram detonator.† Moist detonators also lose their power to induce detonation (section 89).

169. Plasticity in continued cold weather is also necessary for many explosive mixtures. Nitroglycerin, however, freezes easily and thaws very slowly when the temperature is raised. This characteristic is met with in varying degrees in nearly all nitroglycerin explosives (guhr dynamite, gelatin dynamite, etc.), and is the source of much inconvenience and even danger, since frozen nitroglycerin in a bore hole is very difficult to detonate, and may become dangerous as an unexploded charge or a "blown-out" shot.

Nitroglycerin in compositions has also the disadvantage of liquefying at moderately high temperatures in moist air and consequently exudes and evaporates from explosive substances when they are exposed to continually varying temperatures and a moist atmosphere at the same time. A ballistite in cubes of 1 millimeter which had been exposed in the open air

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* A. Noble, Art. Exp., 424; 1906.

† Mem. poudr. salp., XII, 7; 1903–04.

within the temperature limits of 20° to 40° C., while the moisture ranged between 30 to 100 per cent, lost nearly 12 per cent of nitroglycerin by evaporation in the course of half a year.* Such a loss in the most essential component of a powder must naturally produce a considerable variation in the charge necessary to produce a given ballistic effect.

170. The power of nitrocellulose to collect static electricity is not only troublesome but has frequently been the cause of accidents due to a discharge of electricity in the form of sparks. An unusual occurrence which took place in the powder factory of the Nobel's Explosives Company in Ardeer, on Dec. 14, 1901, was due to the electrification of gelatinized powder when rubbed.† A workman engaged in winding up strings of cordite allowed the strands to run through his hand. The floor of the room was covered with lead, and the workman wore shoes with rubber soles. As he started to dip his fingers in a dish of acetone to free them of the fragments of cordite a spark sprang from his fingers to the acetone and ignited it. The workman was apparently charged with static electricity from rubbing the cordite. In fact, the experience was afterwards repeated as an experiment and was always successful so long as the workman was insulated. It could not be accomplished, however, after a copper nail had been driven in the rubber sole of his shoe. The nail acted as a conductor and carried off the electricity through the lead floor.

171. Regarding explosive substances as unstable substances which undergo slow decomposition (section 3) their degree of stability becomes of prime importance.

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* B. Wehrhahn, Chem. Ztg., 705; 1896. R. Wille, Plasto., 79; 1898.

† Ann. Rept., H. M. I. Exp., 210; 1901.

It is true that most of the explosives at present in use possess sufficient chemical stability for all practical purposes. Stability as a rule coincides with the highest degree of purity. No difficulty is experienced in assuring the chemical stability of the crystallizable compounds used in many explosives, such, for example, as the inorganic nitrates, nitro-compounds, chlorates, etc. Even nitroglycerin, although its ability to crystallize has not yet found wide use in its manufacture, can also be easily purified, tested for purity and kept in a stable condition. On the other hand, it was doubted for a long time that nitrocellulose could be obtained in a chemically pure state. Since then its chemical characteristics have become better understood, but it still presents greater difficulties for providing it with a reliable means for maintaining its stability than any other explosive manufactured on a technical scale. This is due mainly to the complicated structure of the plant fibers from which it is made.

2. Igniters, Fuses and Detonators.*

172 The oldest form of igniter is the straw fuse, or quick match, consisting of a hollow straw or small brass tube filled with pulverized black powder. A short, sulphured string fastened to one end was ignited and burned sufficiently long to permit the workmen to get

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* Literature: K. Zickler, Die elektrische Minenzündung, 1888. P. Chalon, Tirage des mines, 1888. A. v. Renesee, Die Elektrische Minenzündung, 1891. C. Haeussermann, Sprengstoffe u. Zündwaren, 1894. W. Maurice, Electric blasting, 1899. W. Denker, Elektrische Zündung in Steinbruchen, 1903. H. Rasch, Zündung durch verdichteten Sauerstoff, 1904. F. Heise, Spreng. Zünd. Spreng., 1904. R. Knoll, Das Knallquecksilber, 1908. H. Hoefer, Beitrage zur Spreng oder Minentheorie, 1880. A. Hasslacher, H. ber. Kom., 1887. Mem. poudres salp., Paris. Mitt. Geniew., Wien. Z. ges. Schiess Sprengstoff., München. v. Schwartz, Handb. Feuer, Exp., 1907.

to a safe place before the charge was fired. This method of igniting a charge has remained confined to the use of black powder in blasting.

173. The fuse, invented by Bickford in the year 1831, is more widely used, and may be used in wet bore holes. This consists of a hempen string, with a core of slow-burning powder, which is tarred or covered with gutta percha. The use of this kind of fuse increased in proportion as explosives came into use whose detonation was accomplished by means of the explosion of detonators, consisting of capsules filled with mercury fulminate, placed within the charge. Good fuse burns at from 50 to 100* centimeters per minute. For a more rapid transmission of the detonation from one point to several charges quick fuse has been used. This consists of three strands of ordinary powder fuse wrapped together and burns with a velocity of 150 meters per second. In place of black powder as a filling for fuses, nitrocellulose,† dynamite,‡ fulminating mercury§ and trinitrotoluene have each been used, and the velocity with which these fuses burn has reached as high as 7000 meters per second. For certain purposes it has been attempted to ignite the fuse without the use of open fire. With this in view, C. Roth‖ devised the following contrivance: A small cartridge case (or copper container) is fastened to one end of the fuse, and in this is put a raw cotton filling saturated with potassium chlorate and sugar, and a small, thin glass bulb filled

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* C. E. Munroe and C. Hall, A Primer on Explosives for Coal Miners, Bull. 17, U. S. Bureau of Mines, p. 34; 1911.

† Mem. poudr. salp., II, 36, 100; 1884–89.

‡ A. Nobel, D. R.-P. No. 45,712 of 1888.

§ Ph. Hess, Mitt. Art. Geniew., **38**, 115; 1907. W. Wachtel, Z. ges. Schiess Sprengstoffw., **2**, 71; 1907.

‖ C. Roth, D. R.-P. No. 43,117 of 1887.

with concentrated sulphuric acid. As soon as this little bulb is crushed and the acid comes in contact with the chlorate mixture the cotton is ignited and this ignites the black powder of the fuse. Priming caps (Amorces) have been used in a similar manner for lighting benzene mine lamps. These ignite first a mixture of benzene and air.

174. Cartridges supplied with detonators are fired whenever possible by electrical means. On account of its many advantages, this method of firing has become indispensable, especially for coal mines. Electric firing insures that the charge fires at a desired moment after the workmen have reached places of safety. Another important advantage is its comparative safety towards fire damp. Moreover, electric firing is the only method of firing which makes it possible to shoot a large number of charges at the same time — if we except the detonating fuses, filled with fulminating mercury or other similar substance, which are very seldom used. Many engineering feats, such as the cleaving of huge blocks of stone or the throwing down of entire stone walls at the same instant, can be accomplished only by the simultaneous discharge of all the shots. The sole objection to this method is its inconvenience. An electric current must be at hand, connections must be

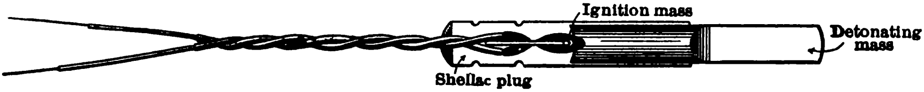

FIG. 37. Electric Detonator, Cross Section.

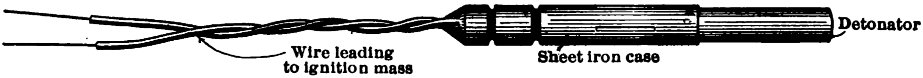

FIG. 38. Electric Detonator, Exterior View.

made and especially prepared detonators must be used. The arrangement of such an eléctric detonator is shown in Figs. 37 and 38. A fine platinum wire connecting the two poles is heated to incandescence by the current and causes the ignition of the priming charge which immediately surrounds it. This brings the detonator to explosion.

Mercury Fulminate.

175. The chief ingredient in detonators and percussion caps is mercury fulminate, whose use as an explosive is confined almost entirely to this purpose. Mercury fulminate, $Hg(CNO)_2$, was discovered by Howard in the year 1799. Its ability to explode gunpowder gave rise, about the year 1815, to its employment as a filler for percussion caps. This powerful explosive substance was recognized through Liebig's work on fulminic acid in 1822 as the mercury salt of a chemical compound,* which also combines with silver (silver fulminate), sodium, etc., producing salt-like compounds (fulminates), all of which are characterized by great sensitiveness towards a blow, friction and heat.

The technical preparation of mercury fulminate is accomplished by dissolving in a large balloon flask 1 part of mercury in 13 parts of nitric acid (specific gravity 1.36), and pouring this solution into another balloon flask which contains 8 parts of alcohol. The reaction begins after a short time, and is first made apparent by a slight evolution of gas. The liquid soon begins to boil, and, accompanied by violent frothing,

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* R. Scholl, Entwicklungsgeschicktlicher und kritisch experimenteller Vergleich der Theorieen uber die Natur der sogenannten Knallsaure und ihrer Derivate, 1893. L. Wöhler und K. Theodorovits, Ber., **38**, 1345, 1351; 1905.

gives off, at first, colorless gaseous by-products, such as carbon dioxide, ethyl nitrite, etc., followed by red vapors of nitrogen oxides. The reaction lasts a quarter of an hour and then the mercury fulminate separates in small, white to gray colored needles. The contents of the flask are then poured into a filter and washed with water until the filtrate no longer colors litmus red. The wet salt is then freed from most of its moisture, either in the free air or in a moderately warm, sometimes evacuated, bath. The yield is about 130 parts of mercury fulminate to 100 parts mercury.

Mercury fulminate possesses a sweet, metallic taste and is very poisonous, like all mercury salts. It is soluble in hot water, concentrated nitric acid and potassium cyanide, and can be regained from its solution by recrystallization in a pure condition. Boiling water completely decomposes it as do also hot acids and alkalies. The high specific gravity (4.43) of the compound is especially noteworthy, it being the highest among all the explosive compounds. This circumstance is often cited as of especial significance in view of its characteristic ability as a detonating agent. Its adaptability for this purpose is further intensified by the ease with which it is detonated either by moderate heating, by blow or by gentle friction. On this account mercury fulminate is not adapted either for blasting or for ballistic purposes, the more especially because in its energy content and the volume of gas developed it is far behind other explosives. In the technique of explosives it is used simply as a firing agent, in percussion caps and as the principal ingredient of detonators.

176. The composition used in percussion caps varies according to the nature and size of the powder charge to be fired. As a rule it is composed of mixtures of

mercury fulminate, potassium chlorate and antimony sulphide, to which glass is sometimes added to make it more sensitive.

Detonators are cylindrical copper shells closed at one end and having an inner diameter of from 5 to 8 millimeters corresponding to the usual diameter of the fuses. The charge of the detonator consists usually of a mixture of mercury fulminate and potassium chlorate which is compressed to a density of 2.8 by a pressure of about 250 kilograms per square centimeter. They are in ten different sizes according to the sensitiveness of the explosive to be detonated, and are numbered from 1 to 10. The charge and the size numbers are shown in the following table:

TABLE 46. DESIGNATIONS OF DETONATORS.

Designation No.	1	2	3	4	5	6	7	8	9	10
Charge in grams	0.3	0.4	0.54	0.65	0.8	1.0	1.5	2.0	2.5	3.0

Detonators are necessary to bring about the proper detonation of almost all explosives. No. 3 is usually sufficient for gelatin dynamite. Nos. 5 and 6 are used for explosive gelatin and carbonite. Nos. 8 to 10 are required for ammonium nitrate explosives. The detonators must, of course, be of regular composition, possess normal initial power and be properly introduced into the cartridge. If these conditions are not fulfilled, the explosion of the charge may take place only in part or not at all.

Recently the greater part of the mercury fulminate has been replaced in detonators by picric acid, trinitrotoluene, or tetranitromethylaniline, and the strong initial effect is thereby considerably increased. In this way 0.5 gram of mercury fulminate has been made to detonate a charge which required 3.0 grams of mercury fulminate in the old caps. Even this strengthened initial impulse, however, is not sufficient to detonate moist, compressed guncotton, such as is used for mines and torpedo charges. In such cases either an intermediate priming charge of dry guncotton is used, as suggested by E. O. Brown, or advantage is taken of the fact that pulverized trinitro-compounds of the aromatic series, such as those mentioned above, are able to transmit the explosion from the detonator to the wet guncotton.*

177. Mercury fulminate retains its explosive properties on being cooled even to the temperature of liquid air. It has also been compressed under great pressures without losing its detonating power if brought to explosion by suitable means, such as by electric sparks or an incandescent wire. In order to determine to what extent the Trauzl lead block test (section 89) is influenced by the density of loading (compression) of the mercury fulminate in the detonators employed,

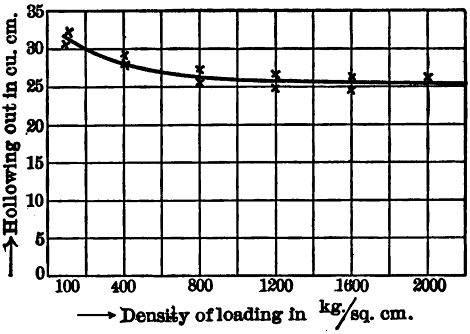

FIG. 39. Diagram of the Hollowing Out of a Lead Block showing the Dependence on Density of Loading (for Mercuric Fulminate).

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* D. R. P. A., No. 25,477 of 1907.

L. Wöhler and O. Matter* measured the chamber produced by 2 grams of mercury fulminate loaded in No. 8 copper capsules, and compressed with pressures of from 100 to 2000 kilograms per square centimeter, i.e., with from 30.1 to 602 kilograms to each capsule of 0.301 square centimeter area of cross section. The diagram (Fig. 39) showing the dependence of the cavity hollowed out in the lead block upon the density of loading indicates for mercury fulminate a slight decrease with increasing density up to pressures of about 800 kilograms per square centimeter. Above this, up to 2000 kilograms per square centimeter, corresponding to an increase in density from 2.98 to 3.35, the influence of the pressure upon the size of the explosion chamber produced in the lead block is not recognizable.

178. As long as mercury fulminate was the only known priming substance for general use† its exceptional property was supposed to be connected on the one hand with its high specific gravity, which allowed a high density of loading and a correspondingly high maximum pressure, and on the other hand with its relatively great velocity of detonation.‡ Recent experiments, particularly those by L. Wöhler and O. Matter, have shattered this theory. It might be supposed that a sudden development of explosive energy is a more important characteristic for the initial explosive than a high velocity of propagation of detonation. There are, however, explosives having much greater detonation velocities than that found for mercury fulminate e.g., nitromannite, which have no efficiency

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* L. Wöhler and O. Matter, Z. ges. Schiess Sprengstoffw., **2**, 245; 1907.

† See, for instance, J. Führer, D. R. P. A., No. 15,476.

‡ C. E. Bichel, Glückauf, **41**, 1195; 1905.

as initial detonators.* It was then discovered that silver hydronitride, the silver salt of hydronitric acid (HN_3), although its density is not greater than that of mercury fulminate, is yet far more powerful as a primer than the latter. L. Wöhler and O. Matter† extended their investigation on detonators to sulphur nitride, N_4S_4, diazobenzene nitrate, sodium fulminate, basic mercury nitromethane, trimercuraldehyde chlorate and trimercuraldehyde perchlorate (Table 47). The two last-named substances and silver hydronitride proved, like mercury fulminate, to be initial detonators which are capable of general application. The other substances named did not possess this power. The initial effect of these highly sensitive compounds upon nitro bodies, such as trinitrotoluolene, which are relatively difficult to detonate, was determined by exploding cartridges filled with the explosive and detonator on lead plates. The minimum quantity of mercury fulminate necessary to detonate picric acid was 0.25 gram, and even this varied with the experimental conditions and more especially with the area of the contact surface between detonator and explosive. The minimum charge of silver hydronitride was only one-twelfth as much (0.02 gram). Some of the results of these experiments are set forth in Table 47.

179. The great sensitiveness of these detonating substances to initial impulses of all kinds necessitates a very careful handling of them, especially in transportation. The German railroad transportation bill of Oct. 26, 1899, paragraph B, gives the following rules for packing detonators for transportation:

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* A. Sobrero, Compt. rend., **25**, 121; 1847.

† L. Wöhler and O. Matter, Z. ges. Schiess Sprengstoffw., **2**, 181, 203, 244, 265; 1907. See also D. R. P., No. 196,824 of March 2, 1907.

TABLE 47. SUMMARY OF THE PROPERTIES OF SEVERAL INITIATING AND RELATED SUBSTANCES.

No.	Primer, etc.	Chamber made by 2 grams in lead block, cubic centimeters.	Action of 1 gram on lead plate.	Minimum charge detonating picric acid, gram.	Heat developed by explosion of 1 kilogram, calories.	Specific gravity.	Temperature at which it puffs off,* °C.	Literature.
1	Diazobenzene nitrate.	43.1	Moderate	......	690	1.37	90	M. Berthelot and P. Vieille, Mem., I, 99; 1882–83.
2	Sulphur nitride, N_4S_4.	39.2	Moderate	......	700	2.22	190	M. Berthelot and P. Vieille, Mem., II, 10; 1884–89. R. Schenck, Lieb. Ann., **290**, 176; 1896.
3	Mercury fulminate.	25.6	Good	0.25	410	4.43	195	M. Berthelot and P. Vieille, Mem., II, 3; 1884–89.
4	Silver hydronitride.	22.6	Good	0.0237	...	....	290	Th. Curtius, Ber., **23**, 3023; 1890: **24**, 3341; 1891.
5	Trimercuraldehyde perchlorate.	18.3	Good	0.1	...	....	...	K. A. Hoffmann, Ber., **38**, 1999; 1905.
6	Trimercuraldehyde chlorate.	15.3	Good	0.4	...	....	130	
7	Sodium fulminate.	14.9	Slight	......	...	1.92	150	L. Wöhler, Ber., **38**, 1353; 1905.
8	Basic mercury nitromethane.	7.5	Slight	......	...	....	160	J. U. Nef, Lieb. Ann., **280**, 278; 1894.

* For the method used for determining this temperature see L. Wöhler and O. Matter, Z. ges. Schiess Sprengstoffw., **2**, 204; 1907.

1. Detonators must be packed in rows, with the mouth upwards, in strong metal containers holding not more than 100 each, and in such a manner that all motion or jostling of the detonators is impossible even on shaking. The empty spaces in the separate detonators and between them is to be filled with dry sawdust or similar substances free from sand or grit. The bottom of the box and the underside of the cover must be covered with felt or cloth, and the inner walls with pasteboard in such a manner that all actual contact between the detonators and the walls of the container is impossible.

2. Each box, so filled, is to be glued down with a strong strip of paper that holds the top so firmly pressed down against the contents of the box that, on shaking, no noise of loose detonators can be heard. These boxes are to be wrapped in packages of five and bound firmly together with a wrapper of strong packing paper or put in a box together. The packages are then to be packed together in a strong wooden box whose walls are at least 22 millimeters thick, or in a strong metal box, in such a way that space between the separate boxes or between these and the walls is avoided so far as possible. Spaces in the box which might allow jostling of the packages are to be filled with dry paper, straw, hay, tow or fine shavings. The top of the box, if of metal, is then to be soldered on; if of wood it must be fastened with brass or tinned wooden screws. The space between the box and the outer casing must be at least 30 millimeters and must be filled with sawdust, straw, hay or fine shavings.

3. This box, the top of which must press down firmly on the contents so that no shaking or jostling can occur, is then placed with the top up in a strongly built wooden case the walls of which must be at least

25 millimeters thick and the top of which is to be screwed on with brass or tinned wooden screws. The space between box and case must be at least 3 millimeters and must be filled with sawdust, straw, tow or fine shavings.

4. The separate boxes must not contain more than 20 kilograms of explosive. Boxes whose total weight exceeds 25 kilograms must be provided with handles to facilitate handling.

180. The following occurrences show how easily explosions of deteriorating material may occur if handled carelessly.

The well-known paper caps (Amorces) are regarded, singly, as quite harmless. They may be quite dangerous, however, if a considerable number of them are exploded at one time. On May 14, 1878, an explosion of paper caps, which killed 14 persons and wounded 16 others, occurred in a toy store in Paris. In some unexplained manner several caps caught fire. In spite of the fact that these caps were quickly grasped in an effort to extinguish the fire, it spread to the neighboring boxes and the explosion of the whole stock of from 6 million to 8 million caps, making a total weight of 64 kilograms, immediately followed. The force of the explosion was so great that, among other things, a foundation stone one cubic meter in size was thrown to a distance of 52 meters.*

Two girl employees of an explosive factory in Westquarter were engaged in carrying a box containing detonating caps and priming composition for same from the magazine into the workroom. They set the box on the ground and began to dance together. One of the girls stumbled and turned over the box of explosives,

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* M. Berthelot, Force mat. exp., I, 82; 1883.

which caused the explosion of the whole load, and both girls were blown to pieces.*

In a factory for the manufacture of electric primers, a primer was being tested for its electrical resistance with the help of a suitable electric measuring instrument. In these tests the end of a primer, armed with a detonator, was stuck in an iron protecting box. On drawing such a detonator out of the box it exploded and the workman lost an eye because of the flying fragments of copper.†

On May 31, 1906, a box containing about 1900 detonating caps exploded in the freight sheds of the Belgian revenue station, Welkenraedt, situated only 150 meters from the border. Three persons who were present in the shed at the time of the explosion were completely blown to pieces. The official in charge in a neighboring room was thrown through a window without being injured. In a very short time the whole building was in flames. The sound of the explosion was heard throughout a radius of several miles. A freight car standing about 20 steps in front of the shed and loaded with 5000 kilograms of powder and 20 cases of dynamite had fortunately been removed just in time. The cause of the explosion is not known. It is presumed that the box was broken open for the tariff examination.‡

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* J. Phillips, The Handling of Dangerous Goods, 249; 1896.

† Chem. Ztg., No. 45, 1906.

‡ Ibid.

CHAPTER IX.

PROPELLANTS.*

181. Propellants, in distinction from blasting explosives, may be defined as explosives with regulated velocities of combustion. A sharp distinction between the two kinds of explosives cannot be drawn, and so long as black powder was the sole propellant and blasting explosive, there was no necessity to make any distinction between the two kinds. Every explosive system could also be used as a propellant if it were possible to regulate the velocity of its combustion at will. This, however, is by no means the case. Furthermore, in considering the applicability of an explosive for use as a propellant it must be judged not only from a ballistic standpoint, but also with a view to its safety in use, its stability and its ease of handling, all of which

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* Literature: J. Upman and E. v. Meyer, Das Schiesspulver, 1874. O. Guttmann, Industrie der Explosivestoffe, 1895. F. Böckmann, Die explosiven Stoffe, 1895. R. Escales, Das Schwartzpulver, 1904. A. Pouteaux, La poudre sans fumée et les poudres anciennes, 1893. J. A. Longridge, Smokeless Powder and Its Influence on Gun Construction, 1890. J. Castner, Das Schiesspulver, 1892. S. J. v. Romocki, Die rauchschwachen Pulver, 1896. R. Wille, Plasto., 1898. W. Heydenreich, Lehre vom Schuss, 1908. J. B. Bernadou, Smokeless Powder, 1901. A. Noble, Art. Exp., 1906. Brinck, Inn. Ball., 1906. M. Jähns, Geschicte der Kriegswissenschaften, 1889–1891. S. J. v. Romocki, Gesch. Exp., 1895–96. v. Löbells, Jahresberichte uber die Veränderungen und Fortschritte im Militärwesen. Sporting Guns and Gunpowders, 1897. Mem. poudr. salp., Paris. Mitt. Art. Geniew., Wien. Arms and Explosives, London. Kriegstechnische Zeitschrift, Berlin. Z. ges. Schiess Sprengstoffw., München. O. Guttmann, Monumenta Pulveris Pyrii, 1906.

are of equal importance. On account of these requirements a choice of propellants, so far as chemically different explosive systems are concerned, is yet limited to an undesirable degree. Attempts to regulate the velocity of explosion by preparing the explosive in various shapes or forms give greater prospect of success. Even black powder has been pressed into plates or prisms pierced by a number of holes. The forms of flattened grains, strips, rolls, plates, cubes, strings and tubes have been chosen for smokeless powder. These are made in various dimensions according to the calibers of the guns or the desired ballistic effects.

1. *Black powder.*

182. Black powder was gradually developed from the "Greek fire" and was known before anyone thought of using it in firearms. It was originally composed of more or less intimate mixtures of potassium nitrate with charcoal, resin, native paraffin, petroleum containing earth and similar combustible substances, and was used partly for fireworks and partly for the production of fire and smoke for military purposes.* The first employment of such mixtures as propellants was probably in the latter half of the 13th century. For six hundred years black powder remained the sole chemical propellant, until finally in the last ten years of the 19th century it was replaced by the gelatinized smokeless powders. At present black powder is used to a very limited extent for ballistic purposes, mostly in the form of sporting powders.

The oldest composition of black powder from potassium nitrate, charcoal and sulphur has undergone very

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* S. J. v. Romocki, Geschichte der Sprengstoffchemie, etc., 13; 1895.

few changes in the course of time. The old German military powder contained 74 per cent potassium nitrate, 16 per cent wood charcoal and 10 per cent sulphur. The military powder of other countries had a similar composition.* For sporting powders the per cent of potassium nitrate is usually somewhat higher than this. Various attempts have been made to substitute the various components of black powder by other substances having similar properties. Thus, potassium nitrate has been replaced by sodium nitrate, barium nitrate and even ammonium nitrate, in spite of its deliquescence in moist air. Wood charcoal has also been replaced by wood dust, starch, etc.

The serviceableness and effectiveness of black powder depends not only upon its composition, but to just as great a degree upon the careful pulverization and intimate mixture of its components and the density and uniformity of the powder grains.

The pulverization and mixing of the components take place principally in cylindrical iron or wooden drums with the help of bronze balls. In this way they are mixed as rapidly and as safely as possible. The sulphur and potassium nitrate are often pulverized together because the sulphur by itself balls up. When the various constituents are pulverized they are mixed in the desired proportions in drums of thick sole leather by means of hardwood balls. The loose powder so obtained is not yet a usable gunpowder and is only applicable for use in fireworks. As a rule, it is immediately moistened with from 10 to 20 per cent of water and mixed in incorporating mills. Since explosions frequently occur during this process, due to the sliding

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* An extensive survey is found in v. Jüptner, Exp. Stoff. Verbren., 57–58; 1906.

motion of the heavy wheels upon the bed, Gruson conceived the idea of hanging the wheels from above so that they would never touch the bed. The powder mass is then run through a machine consisting of pairs of fluted bronze rollers lying one above the other, after which it is sifted and formed into cakes under high pressure in specially constructed presses. These cakes are broken up and the pieces broken into approximately uniformly sized grains by being passed through bronze rollers fluted longitudinally and transversely. The grained powder is glazed in oaken drums, in which process the sharp, easily breakable corners of the grains are broken off and all pores closed up. The polished powder is then dried, freed from dust and separated by sieves into grains of various sizes.

It is only within the last few years that any further step in the preparation of black powder has been taken, and this has been called forth by the desire for greater ballistic effects from big guns, especially against armorclad vessels. By pressing the powder grains into plates, prisms, cubes and other regular shapes* not only has its velocity of explosion in guns been regulated, but it has been considerably decreased. A great improvement was achieved in this direction by J. N. Heidemann and M. v. Duttenhofer, and, since 1882, has been adopted by all great nations as a propellant for heavy artillery.

Black powder presents a slate-gray color and a dull polish. Small-arms powders have a specific gravity of 1.5 to 1.6; pressed powders from 1.7 to 1.9. All kinds of black powder are sensitive to moist air. When stirred with water they lose their composition because the potassium nitrate is dissolved out. Sparks or flame ignite loose powder very easily, and it puffs off,

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* General Rodman, U. S. A., Properties for Cannon, and Qualities of Cannon Powder, Boston, Mass., 1861.

producing a thick white smoke. When struck by lightning it almost invariably explodes violently.

On the night of June 30, 1898, a violent storm raged in Belgium accompanied by many electrical discharges, one of which struck the black powder factory in Clermont-sur-Meuse. An explosion followed immediately. Three buildings with their contents of about 865 kilograms of black powder in various stages of preparation were destroyed by the lightning discharge and the accompanying detonation. There was no loss of lives. In view of the location of the factory in a deep valley surrounded by high trees, where a stroke of lightning had never been observed, it was not provided with lightning rods. On examination it was found that the lightning had first struck a very tall acacia tree and stripped it entirely of its bark. It then sprang to the belt gearing only a few meters distant and traversed its entire length, sending secondary discharges into the various factory buildings. This is the only explanation of the fact that three separate buildings blew up at the same instant, for only one detonation was heard. After this accident the supposition of the protection offered by the high trees was abandoned and lightning rods were put on all dangerous buildings.*

Blows or friction, especially of iron upon iron, cause the explosion of black powder very easily.

Among the gaseous products of the explosion of black powder are found principally carbon dioxide, carbon monoxide and nitrogen. The solid residue, which appears as smoke and constitutes nearly three-fifths of the whole weight of powder, consists mainly of potassium carbonate, potassium sulphate and potassium sulphide.

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* Mem. poudr. salp., X, 59; 1899–1900.

The transportation of black powder is governed by strict laws. Loose grain powder is packed first in thick drill bags, and these are again packed in strong boxes or casks sealed with heavy paper. Pulverized powder which contains much dust comes in leathern bags. Prismatic powder is usually transported in boxes in which the prisms are packed closely together separated by sheets of felt.

2. *Smokeless powder.*

183. The greatest impetus to the movement (so closely connected with the history of civilization) of substituting smokeless powder for black powder as a propellant came from the advanced technique of small firearms. It was recognized that a decrease in the gun caliber would afford a number of ballistic and tactical advantages, so long as the loss in the weight of the projectile, as a consequence of its decreased diameter, was balanced by the increased initial velocity imparted to it. As far as black powder was concerned its limit of efficiency in this direction had been reached by the middle of the eighteenth century. About that time, men began anew to sample and test the large number of explosive substances then known, to see if any of them might furnish a suitable or more efficient substitute for the old black powder. The characteristics of the organic nitrates and nitro bodies that caused them to burn without smoke and without residue made these substances a favorite field of investigation. Such investigators as v. Lenk, Abel, Otto and others had made unsuccessful attempts (section 96) to use nitrocellulose as a propellant. They had tried numerous means of compressing the loose fibers of the nitrated cotton, such as

twisting, pressing, etc.,* in order to bring it to a less bulky form, and at the same time to regulate its high velocity of combustion in the firearm. In the meantime, however, since the year 1869, the celluloid industry had developed and had furnished the information that it was possible to considerably decrease the high velocity of combustion and the explosive properties of nitrocellulose by treating it with a proper solvent. On this principle Reid, together with Johnson,† in 1882, prepared in Stowmarket a partly gelatinized nitrocellulose powder for sporting purposes. In 1884, M. v. Duttenhofer‡ prepared in Rottweil a fully gelatinized grain powder from nitrated cellulose for military purposes. In 1886, P. Vieille (section 67) produced the first gelatinized flake powder made from guncotton. In 1889, A. Nobel§ succeeded in employing nitroglycerin also for propellant purposes by using it as the solvent for nitrocellulose.

Almost all smokeless powders consist mainly of nitrocellulose in a more or less completely gelatinized condition. An analysis of flake powder gave 97.5 per cent nitrocellulose, 0.5 per cent calcium carbonate, 0.5 per cent acetone and 1.5 per cent of moisture. Smokeless sporting powders usually contain, besides nitrocellulose, considerable quantities of certain foreign substances, such as barium nitrate, ammonium bichromate, etc., which facilitate the process of combustion without increasing too much the gas pressure in the firearm. Nitroglycerin-containing powders have nitroglycerin and nitrocellulose as the principal ingredients.

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* H. Rohne, Z. ges. Schiess Sprengstoffw., **2**, 124; 1907.

† D. R. P., No. 18,950. C. E. Munroe, The Development of Smokeless Powder, J. Am. Chem. Soc., **18**, 821; 1896.

‡ English Pat. No. 17,167 of 1887.

§ D. R. P., No. 51,471.

Both explosive substances are most intimately combined in the gelatinized condition (section 213). Ballistite, a smokeless gunpowder, contains two parts of nitroglycerin to three of nitrocellulose. Cordite, an English military powder, is composed of 65 per cent of nitrocellulose, 30 per cent of nitroglycerin and 5 per cent of vaseline. Both these types of powders originally contained much larger quantities of nitroglycerin, but this was decreased when it was found that the high nitrogen content was injurious to the piece (section 120). A third class of smokeless powders contains, besides nitrocellulose, nitrated aromatic hydrocarbons. To this class belongs plastomenite, composed of 68 per cent nitrocellulose, 13 per cent trinitrotoluene, 6 per cent dinitrotoluene and 13 per cent barium nitrate.

Finely ground nitrocellulose is the starting point in the preparation of flake powder. This is first freed from moisture either by drying at high temperature or by the use of alcohol which drives out the water from the nitrocellulose fibers. The nitrocellulose, still moist with alcohol, is then kneaded in kneading machines of the same kind as is used in bread bakeries. It is mixed with the solvent in this machine in the proportion of about 1 : 1 and thoroughly kneaded for several hours. The mass is then run through rollers which transform it into thin homogeneous and transparent sheets. These sheets leave the rollers in a leathery condition and can easily be cut into strips in a cutting machine, and these strips further cut into square leaflets or flakes. Many factories do away with the unhandy rolling of the kneaded mass by running it into a press machine, the mouth of which is so formed that the sheets come out as strips of the proper width, and these are immediately cut into squares by another machine. During all these processes the nitrocellulose is constantly losing the solvent, but not to such an extent as to render a final drying operation at a higher temperature unnecessary, for the last 2 to 3 per cent of alcohol or acetone are removed with great difficulty,* on account of the fact that the vapor tension of these substances becomes smaller in the gelatinized mass with decreasing concentration. The freshly prepared powder shows rough edges, does not run freely and is not usable on account of its electric properties. These objectionable features are overcome by revolving the powder for some time with graphite in polishing drums, after which it comes out smooth, polished and fit for use.

Gelatinized powders which contain nitroglycerin are prepared in a somewhat different manner, particularly in those cases where no particular solvent for the nitrocellulose is employed. Ballistite is prepared according to the method of Lundholm and Sayers, by pouring into warm water a special kind of nitrocellulose, along with the necessary quantity of nitroglycerin and stirring the resulting emulsion until the two components gelatinize. As soon as this takes place the greater part of the water is pressed out and the crumbly mass is forced through heated rollers until a homogeneous and transparent sheet of leathery consistency is obtained. This is finally cut into squares (flakes) or cubes, which are usually covered with a thin coating of graphite. In the preparation of cordite, a solvent, usually acetone, must be added to the mixture of nitrocellulose and nitroglycerin, because the highly nitrated cellulose used in cordite will not gelatinize with nitroglycerin

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* K. Exler, Z. ges. Schiess Sprengstoffw., **1**, 379; 1906. See also A. Müller, All. Chem. Kol., 111; 1907. W. Ostwald, Lehrb. Allg. Chem., II, (3), 217; 1906.

alone. The kneaded mass is pressed in hydraulic presses and forced out through nozzles in a continuous cord. This is finally cut in lengths corresponding to the length of the powder chamber in the cartridges to be loaded. Perforated powders are made by a method similar to that employed in making cordite, with the difference that the mouthpiece of the press consists of hollow cones into which the pins which produce the perforations project.

Various methods of preparation are used in the manufacture of smokeless sporting powders. In this connection especial interest attaches to the completely gelatinized grained sporting powder prepared by Wolff & Co., at Walsrode. Nitrocellulose is treated in kneading machines with glacial acetic acid until complete gelatinization takes place; warm water is then added and water vapor conducted into the mass, while the kneading machine is still in operation. By this process the stiff gelatin falls into fine grains. These are treated with boiling water until the solvent is completely driven out and finally dried.

The various smokeless powders agree in their characteristics only in so far that they all contain nitrocellulose as the chief ingredient. Otherwise they present widely different characteristics. In general appearance, size, color, smell and density, there is a striking dissimilarity. Flake powder for weapons appears as small squares from 1 to 2 millimeters on each side, and from 0.2 to 0.4 millimeter thick, of a brown or silver-gray color, horny consistency and with a specific gravity of from 1.5 to 1.6. Cordite for guns, on the other hand, resembles light brown cords of 1 millimeter diameter, and from 40 to 50 millimeters in length, that are so soft they can be cut with the finger nail. Among the perforated powders designed for heavy guns such forms as inch-thick rods 1½ meters in length, which resemble hard rubber canes more than they conform to the usual conception of a powder grain, are found. The grained sporting powders have a grain diameter of from 0.5 to 1 millimeter, and may frequently be pulverized between the fingers. Examined under the microscope the fibrous structure of the nitrocellulose may be recognized, in a more or less gelatinized condition, according to the method of preparation.

The fully gelatinized powders,* consisting only of nitrocellulose, are unharmed by water and may even be boiled in water without suffering permanent injury. Powders containing nitroglycerin, on the other hand, are easily affected by water, the nitroglycerin gradually exuding through the moistened surfaces. The fully gelatinized powders burn with a vivid flame, without explosion, on being ignited in the open air. Even when struck by lightning they only burn, while black powder nearly always explodes.

On June 5, 1900, shortly after 5 o'clock P.M., lightning struck a powder magazine in the old firing grounds at Jüterbog. The magazine contained about 18,000 kilograms of smokeless powder and a number of metal cartridges filled with the same.† The magazine, which was built of brick and surrounded by a wall of earth, burned about three hours before the powder contents took fire. Immediately a high column of flame arose and the crackling reports of the burning metal cartridges could be heard a long distance. No actual

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* C. E. Munroe, Development in the Explosive Art in the United States during the Last Five Years. VI. Int. Cong. Applied Chemistry, **2**, 670; 1907.

† Ann. Rept., H. M. I. Exp., 45; 1900.

explosion or concussion of the ground was observed. The catastrophe did no damage to buildings in the vicinity. Even the closed wooden door of the surrounding wall was uninjured.

Violent blows or friction can bring the powder mass to explosion, even when it is fully gelatinized. On Dec. 15, 1902, 14 boxes of raw cordite mass, weighing about 450 kilograms, exploded in the factory of Curtis and Harvey at Lower Hope Point, Kent. The building in which the explosion occurred was devoted to that single process in which the raw cordite mass, consisting of dry guncotton and nitroglycerin, was pressed through narrow meshed sieves. It is possible that the explosion occurred during this operation, induced perhaps by an electric spark. It is more probable, however, that the heavy boxes, the corners of which were covered with bronze, were struck sharply together. In this way some of the spilled mass might have been subjected to such a glancing blow as to have produced the explosion. Since the building and contents were completely destroyed and the two workmen in it were killed it was not possible to determine the cause of the explosion.*

With powders containing no nitroglycerin the explosion is usually confined to the part actually struck and is not transmitted. In this respect smokeless powders are much safer than black powder.

The products of the explosion of gelatinized powders are usually gases or vapors. They consist principally of carbon dioxide, water vapor, nitrogen and carbon monoxide, and contain small quantities of methane and free hydrogen. While 1 kilogram of black powder produces by explosion not more than 280 liters of gas,

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* Ann. Rept., H. M. I. Exp., 1902.

this quantity of smokeless powder produces as much as 900 liters (Table 28). At the same time the heat developed, which expands the gases, is more considerable with smokeless powder and reaches 1300 heat units, while black powder produces not more than half that amount (Table 4).

184. To summarize, smokeless powder offers the following advantages over black powder:

1. Two or three times the efficiency, corresponding to the much greater heat of explosion and the greater actual volume of gases developed.
2. Abolition of the troublesome smoke development in consequence of the absence of solid products in the explosion chamber, a circumstance which first made the full utilization of magazine guns and rapid fire-cannon possible.
3. The possibility of much more completely conforming the powder, in size and form, to any particular gun.
4. Greater uniformity in effects in consequence of greater homogeneity in the body of the powder.
5. Greater stability towards wet and damp weather, since the components of the powder are very little changed, if at all, by water.
6. Freedom from dust even after long transportation.
7. Less danger in the preparation of the usually moist flexible powder mass.

The following disadvantages of smokeless powder as against black powder are to be considered:

1. The two or three times greater price for the same weight of powder.
2. The greater wear on the gun barrel in consequence of the greater velocity of the projectile. For the same effect smokeless powder is not more objectionable in this respect than black powder.

3. Variations in temperature and atmospheric moisture affect the velocity of the combustion of smokeless powder to a much greater degree than they do that of black powder.

4. Less power of resisting high temperatures. Nitrocellulose and nitroglycerin, the principal ingredients of smokeless powder, are comparatively easily decomposable chemical substances.

Progress in the development of powder always incites a corresponding progress in the manufacture of firearms. In this connection the following summary of the development of German firearms (Table 48) is of interest.*

TABLE 48. BALLISTIC COMPARISON BETWEEN BLACK POWDER AND SMOKELESS POWDER.

	Black powder.				Smokeless powder.	
Year.	1740	1841	1870	1884	1888	1905
Diameter of barrel....................mm.	20.1	15.4	15.4	11.0	7.9	7.9
Weight of projectile.......................g.	30	31	21.5	25	14.7	10.1
Powder charge............................g.	14.5	4.8	4.8	5.0	2.6	3.2
Velocity of projectile v_{25}..................m.	100–200	280	340	430	620	860
Kinetic energy of the projectile at the muzzle, mkg.	30–50	140	140	250	310	400
Space traversed for 1.7 elevation..........m.	100	200	250	350	550	700
Aimed shots per minute............number.	4	5	8	12	20–25	20–25
Greatest distance aimed................m.	300	560	1200	1600	2000	2000
Distance traversed by projectile.........m.	1000–1500	2000	2500	3000	4000	4000

Up to the year 1888, black powder was used as the charge in guns. Since that date smokeless powders have been used. The most notable effect of this change is the great increase in the rapidity of firing, by which from 20 to 25 shots have been fired per minute. It is also conspicuous that the change in the propellant has produced a flattening of the trajectory of the projectile,

* Cf. H. Rohne, Z. ges. Schiess Sprengstoffw., I, 187; 1906.

a fact due to the increased initial velocity of the projectile accompanying a corresponding decrease in its weight.

In spite of this latter fact the kinetic energy of the projectile at the muzzle of the gun is not decreased, but on the contrary has been greatly increased since the time of Frederick the Great. In the year 1884, 5 grams of black powder produced a kinetic energy of 250 kilograms at the muzzle; that is 1 gram of powder performed a work of 50 kilograms. With the introduction of smokeless powder the work done by 1 gram of powder rose to 112 kilograms and in the year 1905 reached 123 kilograms.

185. A summary of the characteristics and compositions of the most important propellants is shown in Table 49.

TABLE 49. CHARACTERISTICS AND COMPOSITIONS OF IMPORTANT PROPELLANTS.

Kind.	Characteristics.	Designation.	Composition.
Sporting powders.	Easily ignitable grains or thin, loose flakes, sometimes only gelatinized on the surface.	Hirschmarke	78% KNO_3, 12% C, 10% S.
		Schultze pulver	24% guncotton, 24% collodion cotton, 13% cellulose, 33% KNO_3, 4% paraffin, 2% moisture.
		E. C.	26% guncotton, 28% collodion cotton, 4% cellulose, 38% KNO_3, 2% camphor, 2% volatiles.
		Walsrode	99% nitrocellulose, 1% acetic ether.
		Amberite	77% nitrocellulose, 10% paraffin, 11% $Ba(NO_3)_2$, 2% volatile.
		French powder J.	83% nitrocellulose, 17% ammonium bichromate.
		English sporting powder ballistite.	62% collodion cotton, 38% nitroglycerin.
Musket powders.	Coarse grains or completely gelatinized flakes, cubes, cords, etc.	Musket powder M./71.	76% KNO_3, 15% C, 9% S.
		French powder B.	68% guncotton, 29% collodion cotton, 2% vaseline, 1% volatiles.
		French powder B. N.	41% guncotton, 29% collodion cotton, 19% $Ba(NO_3)_2$, 8% KNO_3, 2% soda, 2% volatiles.
		Schwab	98% nitrocellulose, 2% volatiles.
		Ballistite	59% collodion cotton, 40% nitroglycerin, 1% diphenylamine.
		Cordite M. D.	65% guncotton, 30% nitroglycerin, 5% vaseline.
		Plastomenite	68% nitrocellulose, 6% dinitrotoluene, 13% trinitrotoluene, 13% $Ba(NO_3)_2$.
Great gun powders	Large grains or perforated prisms of very high density, and fully gelatinized strips, rods, cylinders, or tubes of considerable dimensions.	Brown prismatic powder.	78–80% KNO_3, 19–20% C, 0–3% S.
		Amide powder	40% KNO_3, 38% NH_4NO_3, 22% C.
		Fillite	59% collodion cotton, 40% nitroglycerin, 1% diphenylamine.
		Maxim-Schüpphaus.	85% guncotton, 10% nitroglycerin, 5% castor oil.
		R. R.	98% nitrocellulose, 2% volatiles.
		Pyro-collodion powder.	98% nitrocellulose, 2% volatiles.

CHAPTER X.

BLASTING EXPLOSIVES.*

186. Every explosive system might be termed a disruptive or blasting explosive so far as circumstances, such as cost of production, ease of handling, transporting and the like (section 11), allow it to be used on a technical scale. As regards their composition the disrupting explosives may be single chemical substances, like picric acid; or mixtures of several explosive components, like explosive gelatin; compositions of nitroglycerin and nitrocellulose; or intimate mixtures of

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* Literature: M. Berthelot, Force mat. exp., 1883. N. Hake and W. Macnab, Explosives and Their Power, 1892. L. Gody, Traité des matières explosives, 1907. O. Guttmann, Ind. Exp., 1895. O. Guttmann, Handbuch der Sprengarbeit, 1906. M. Eissler, The Modern High Explosives, 1893. M. Eissler, Handbook on Modern Explosives, 1897. H. Maudry, Explosive Präparate, 1895. P. Chalon, Exp. mod., 1902. G. Sanford, Nitro Explosives, 1896. A. W. Cronquist, Lehrbuch der brisanten Sprengmittel, 1886. Das Wesen und die Behandlung der brisanten Sprengstoffe, 1888. M. Dumas-Guilin, Manuel der dynamiteur, 1889. A. Perret, Les Explosifs, 1902. J. Daniel, Les explosifs industriels, 1893. R. Molina, Esplodenti e modo di fabbricarli, 1893. v. Jüptner, Exp. stoff. Verbren., 1906. A. C. Key, A Primer of Explosives, 1905. M. v. Förster, Schiesswolle in ihrer militarischen Verwendung, 1888. R. Escales, Die Schiessbaumwolle, 1906. R. Escales, Nitroglyzerin und Dynamit, 1908. Treatise on Service Explosives, 1907. Posts chemisch-technische Analyse, II, 909, 1908. H. Kast, Spreng- u. Zündstoffe. H. Schmerber, Recherches sur l'emploi des explosives, 1900. A. Macquet, Explosifs de sûreté, 1893. H. le Chatelier, Le grisou. A. Hasslacher, H. ber. P. S. Kom., 1887. C. E. Bichel, Untersuchungsmethoden für Sprengstoffe, 1902. W. Denker, Unfallverhütung bei Sprengarbeiten, 1907. Glückauf, Essen. Öesterr. Berg.-Hütten, Wien. Ann. mines, Paris. Ann. Rept. H. M. I. Exp., London. V. D. Majendie and J. H. Thomson, Guide-Book to the Explosives Act, 1906.

components in themselves not explosive, like black powder. There are also in use many explosives which cannot be classified under either of these heads, but are crosses or mixtures of two classes. Among disrupting explosives composed of mixtures of nonexplosive components, the powerful mixtures recommended by H. Sprengel* in London in 1873, and characterized by their safety in preparation and handling, deserve special mention. The ammonium nitrate mixtures are most important among these explosives on account of their safety in coal mines under conditions which prevent the use of other explosives, as, for instance, in the presence of fire damp.

1. *Nitroglycerin.*

187. Nitroglycerin is the product of the action of nitric acid and sulphuric acid on glycerin. The name nitroglycerin has become fixed by custom, although it does not properly describe the chemical nature of the substance since nitroglycerin is not a nitro compound but a nitric ester of glycerin. Glycerin being a triacid alcohol should form also mono- and disubstitution products. In fact both the mono- and dinitroglycerin have recently been prepared, starting either from glycerin itself or from trinitroglycerin.†

Nitroglycerin has been known since the year 1846. It was first obtained by A. Sobrero‡ in Turin, yet its use as an important technical explosive did not begin until about 20 years later. A. Nobel, in Stockholm,

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* H. Sprengel, Dingler's pol. J., **212**, 327; 1874.

† A. Mikolajzack, Glückauf, **40**, 629; 1904. F. Schreiber, Bergbau, 1904. F. Volpert, Z. ges. Schiess Sprengstoffw., I, 167; 1906. W. Will, Ber., **41**, 1107; 1908.

‡ A. Sobrero, Compt. rend., **24**, 246; 1847. Arms and Explosives, **16**, 5, 22; 1908.

first succeeded in finding in kieselguhr a suitable absorbent for this liquid, which is so dangerous and inconvenient to handle by itself, and, what is even more important in explosive technique, he discovered, in detonating caps, a safe method for detonating that mixture of it with kieselguhr which he called dynamite.

Glycerin which is to be used in the manufacture of nitroglycerin must be as free as possible from foreign substances, especially water. The acid mixture necessary for the nitration of 100 parts (by weight) of glycerin is usually composed of 270 parts of nitric acid (94 per cent monohydrate) and 450 parts of sulphuric acid (96 per cent monohydrate), and the yield in pure nitroglycerin is from 215 to 220 parts. The form of the nitrating vessel is of great importance in obtaining a proper nitration reaction. In the early days of the manufacture of nitroglycerin small earthenware pots were used, which were surrounded by cold water. At present, however, large closed lead vessels are employed, which are supplied with an inner cooling arrangement, or cooling worms with inlet and outlet tubes, and thermometers. The whole apparatus is, for safety, connected with large drowning tanks filled with water, into which the contents may be dumped if a sudden decomposition of the nitration mixture, which might lead to an explosion, should take place. The nitration is so conducted that the temperature of the acid mixture should never rise above 25° C. Since nitroglycerin is lighter than the acid mixture used in nitration, it rises to the top as fast as formed, and this characteristic is taken advantage of in separating it as fully as possible from the acid. The nitroglycerin, still impure and hence unstable, is run from the separator into lead-covered wooden tanks in which it is thoroughly washed with water and dilute soda solution. The nitroglycerin, thus purified from acids and lower nitrates of glycerin, must be filtered because it usually contains a quantity of slimy substances and other impurities carried over mechanically. The filter for this purpose is filled with dry salt which absorbs the last traces of water which may be present.*

188. Theoretically, 100 parts by weight of pure glycerin should yield 246 parts of nitroglycerin. In practice, however, even under the most favorable circumstances, so high a yield is not obtained. This is due partly to the fact that nitroglycerin is soluble to an appreciable extent in the ordinary nitrating acids and partly because the formation of nitroglycerin from glycerin and nitric acid is a reversible reaction. The yield in nitroglycerin is, therefore, a function of the equilibrium established between nitroglycerin, sulphuric acid, nitric acid and water. Besides trinitroglycerin, the most of which separates as an oil, though a not inconsiderable quantity remains dissolved in the acid, the acid mixture contains the lower nitrates of glycerin, dinitro- and mononitroglycerin, and perhaps also glyceryl esters of sulphuric acid. The quantity of trinitroglycerin that can be obtained in a pure state depends to quite a large extent upon the concentration of the various components after equilibrium has been established. From this standpoint, F. L. Nathan and W. Rintoul† have sought to ascertain the conditions for the most favorable mixture of the nitrating acids and preliminary thereto determined what influence the concentration of the acid components exercises upon

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* O. Guttmann, Ind. Exp., 394; 1895. F. L. Nathan and W. Rintoul, Soc. Chem. Ind., **27**, 293; 1908.

† F. L. Nathan and W. Rintoul, J. Soc. Chem. Ind., **27**, 193; 1908.

the solubility of pure trinitroglycerin in nitric acid, considering all conditions which decrease the yield of nitroglycerin as due to the solution of this substance. Definite quantities of nitrating acid were shaken with weighed quantities of trinitroglycerin at a constant temperature until saturated, and the nitroglycerin not dissolved was recovered and weighed. The influence of each component of the nitrating acid was determined by making a series of experiments in which two of the components were held in a constant ratio to each other and the third was varied. There was thus obtained three series of results:

1. Constant ratio $\frac{H_2O}{HNO_3} = 1:1$; Variable: H_2SO_4.
2. Constant ratio $\frac{H_2SO_4}{H_2O} = 5:8$; Variable: HNO_3.
3. Constant ratio $\frac{H_2SO_4}{HNO_3} = 10:4$; Variable: H_2O.

The results are shown graphically in Fig. 40. The solvent or destructive effects of the various acid mixtures show minima in certain places which correspond to maximum yields of trinitroglycerin. Other places on the curves are characterized by marked solvent or destructive effects on trinitroglycerin and should consequently be avoided in every stage of the nitrating process or if unavoidable should be rapidly passed over. A thorough study of these relations should be made from the standpoint of chemical kinetics and laws of equilibrium, but it would be quite complicated on account of the many stages and components.

189. Nitroglycerin is a colorless, odorless, oily liquid of 1.6 specific gravity. It has a burning, sweet taste and is poisonous. It is dissolved only slightly by water

(about 1 : 600), but easily in alcohol, ether, chloroform, etc.* It is volatile with steam and on this account is easily diffused through the moist atmosphere of a room, a fact which may be readily recognized by one working with nitroglycerin through the violent headache it causes.†

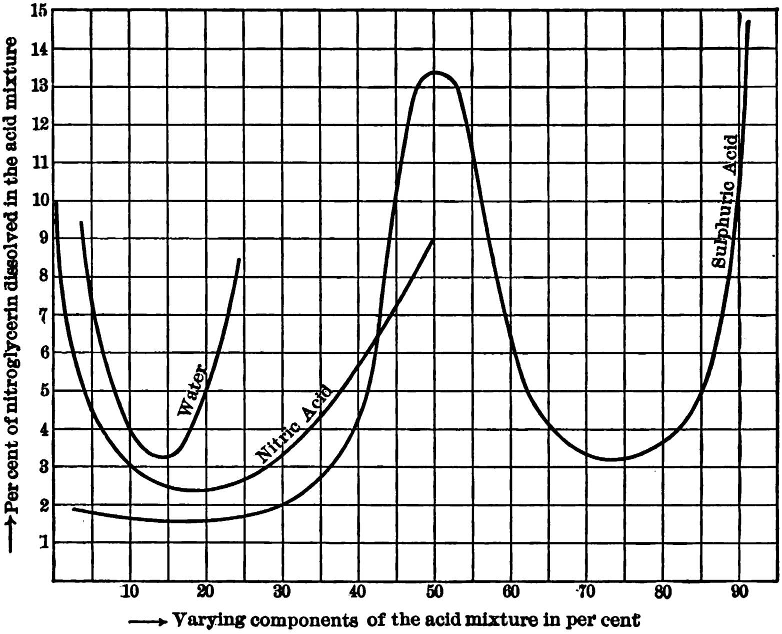

FIG. 40.

Nitroglycerin freezes at 13° C., and has, when frozen, the specific gravity of 1.735. It has been recognized recently that nitroglycerin has two crystalline modifications‡ and two freezing points. One modification

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* Arthur H. Elliott, On Nitroglycerin, School of Mines Quarterly, 4; 1882.

† See also B. Wehrhahn, Chem. Ztg., 705; 1896. Geo. C. Law, M. D., Glonoinism, Trans. Med. Soc., N. J., 1899.

‡ H. Kast, Z. ges. Schiess Sprengstoffw., 1, 225; 1906.

crystallized at 2° C. into thin rhombohedral leaflets which give to frozen nitroglycerin a soft pliancy. The other modification crystallized at 12.5° C. into hard, warty, prismatic needles. The latter is the modification usually observed in frozen nitroglycerin. This polymorphism of nitroglycerin appears also in guhr dynamite and explains in part the oft-noticed unequal resistance of dynamites of different origin against freezing.

190. The freezing of nitroglycerin constitutes an inconvenience and even danger in the technique of nitroglycerin explosives, since frozen nitroglycerin is detonated with difficulty in the borehole and consequently may become dangerous as an unexploded charge or a "blown-out" shot (section 122). Consequently, frozen nitroglycerin should be thawed out before using, although the thawing-out process takes time, is inconvenient, and requires special apparatus. A good method is to inclose the frozen explosive in water-tight metal boxes and set these in moderately warm water.* A specially designed thawing apparatus, the so-called thermophore,† is also in use. These apparatuses give off a moderate heat of about 50° C. for a long time. In principle they depend on the fact that warmed and melted sodium acetate crystallizes again very slowly and gives out heat while doing so. If frozen cartridges of dynamite, for instance, were dipped directly into warm water, some nitroglycerin would escape from the cartridge, assemble on the bottom of the vessel and thus probably give rise to an accidental explosion. It is dangerous to place dynamite in very

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* C. E. Munroe and C. Hall, A Primer on Explosives for Coal Mines, Bull. 423 U. S. Geological Survey, page 28, 1909.

† E. g., the apparatus described in D. R. P., Nos. 39,494 and 143,265.

warm places, in the immediate vicinity of stoves, steam pipes or an open fire. The careless thawing of frozen dynamite has already caused numerous accidents. These accidents occur most frequently in the first three months of the year, since nitroglycerin in storage does not freeze for some time after the beginning of cold weather, but when once frozen withstands higher temperatures for some time without returning to the plastic condition. Several instructive occurrences and accidents are briefly described.*

On March 21, 1879, several miners attempted, contrary to regulations, to thaw out frozen dynamite cartridges by dipping them in warm water. The water, containing some of the nitroglycerin which escaped from the dynamite, was afterwards poured under the grate of a stove. An explosion, which detonated by influence a number of cartridges lying about on the floor, followed and three people were seriously wounded.

On Nov. 26, 1890, a miner attempted in a similar manner to thaw out frozen dynamite cartridges by dipping them into a bucket filled with warm water. While thus engaged he thought of the proper manner of thawing such material in a specially designed warm-water apparatus, but used, to fill the apparatus, the water from this bucket which had already taken up some nitroglycerin. Some time later another workman, who was ignorant of this fact, took this same water out of the thawing apparatus, put it in a bucket and set it over the fire to heat. An explosion, which killed two men and wounded a third, followed.

The following accident occurred on March 27, 1895. Someone laid frozen dynamite cartridges on warm ashes

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* From the Ann. Rept. H. M. I. Exp.

to thaw, and left them in charge of another. The cartridges exploded suddenly and tore the man's head from his body. On Feb. 15, 1881, a miner attempted to thaw out dynamite cartridges by rubbing two cartridges together between his hands. The cartridges exploded and wounded him severely. Another workman was killed on April 9, 1886, in trying to thaw frozen dynamite over a candle. It has often happened that miners have set frozen dynamite cartridges on a hot stove in dishes, pans or similar vessels. Almost without exception, explosions have resulted from such careless handling.

Even a prescribed warm-water apparatus may cause an explosion by careless or ignorant handling. In a stone quarry in Bergisch-Gladbach, 20 dynamite cartridges, while being thawed out in an apparatus, took fire and burned, but fortunately no explosion occurred. The cause of the phenomenon was finally established. It seems that the inner metal vessel had not been sufficiently cleaned after having become smeared with nitroglycerin and that this latter in the course of time decomposed by continued warming and thus set fire to the cartridges.

191. To obviate the objections due to the tendency of nitroglycerin to freeze, various admixtures have been proposed which at least retard freezing either by lowering the freezing point, or by preventing crystallization through the formation of undercooled solutions, or by both these methods. Among such admixtures may be mentioned nitrobenzene,* dinitrotoluene and many other nitrated hydrocarbons which in quantities of from 5 to 10 per cent of the nitroglycerin present materially lower the freezing point; also isoamylnitrate,† methyl

* Belg. Pat. No. 171,291.

† D. R. P., No. 51,022.

and ethyl nitrates,* turpentine oil† and many others. Many practical considerations, among which may be mentioned especially the decrease in explosive energy as well as ability to be detonated (section 16), forbid the use of larger quantities of admixtures to produce a more considerable lowering of the freezing point.

Freezing of nitroglycerin is to a certain degree prevented by its careful gelatinization with suitable nitrocellulose, and for this reason well-gelatinized preparations such as nitroglycerin smokeless powders, which do not allow the nitroglycerin to escape, generally freeze with much greater difficulty than ungelatinized dynamites such as guhr dynamite and the like.

192. S. Nauckhoff ‡ has investigated the behavior of nitroglycerin at low temperatures and the means employed for lowering its freezing point. He first determined the velocity with which pure nitroglycerin freezes at various undercooled temperatures, using in the experiments a nitroglycerin whose freezing point was determined as +12.3° C. The results of his experiments are shown in Table 50.

TABLE 50. INFLUENCE OF UNDERCOOLING ON THE VELOCITY WITH WHICH NITROGLYCERIN CRYSTALLIZES.

Temperature, °C.	Undercooling, °C.	Crystallization velocity, millimeters per minute.
+5	7.3	0.145
±0	12.3	0.183
−4,9	17.2	0.267
−17	29.3	0.125

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* Engl. Pat. No. 4179 of 1875.

† Belg. Pat. No. 145,542.

‡ S. Nauckhoff, Z. angew. Chem., **18, 11; 1905.**

The experiments were carried out in U-tubes of 3.5 millimeters inside diameter, graduated in centimeters. The tube was set in a cooling mixture and the velocity with which the boundary line between solid and liquid advanced was determined. According to these experiments the velocity with which nitroglycerin freezes is very small, somewhat like that of glycerin itself, a fact which is in accordance with the high viscosity of these liquids, especially in the cold. The heat of crystallization was also measured in order to have at hand all the data for the calculation of the molecular lowering of the freezing point of nitroglycerin. This, however, proved to be comparatively small (24 calories), and the quantity of heat given off per unit of time by crystallization was so small, on account of the very low velocity of crystallization, that no reliable experimental determination of the molecular lowering of the freezing point could be made. Technical experience had, nevertheless, established the fact that any substance dissolved in nitroglycerin caused a lowering of the freezing point. This is directly proportional to the concentration and inversely to the molecular weight of the dissolved substance. If γ represents the lowering of the freezing point, m the concentration of the dissolved substance (in grams per 100 grams of nitroglycerin) and M its molecular weight, the experiments of S. Nauckhoff prove the following relation:

$$\gamma = 70.5 \frac{m}{M}.$$

Both the observed and calculated lowering of freezing point was very small for all substances actually soluble in nitroglycerin; for instance, 1.7 per cent nitrobenzene caused a lowering of only 0.7° C.

Technical workers have had better results in their attempts to use, instead of admixtures which lower the freezing point of nitroglycerin, such substances as lower the velocity of crystallization and induce a state of undercooled solution. Among the substances that retard the freezing of nitroglycerin by the formation of undercooled solutions, without impairing too much the explosive energy, may be mentioned chlor-dinitroglycerin,* and other mixed esters of glycerin such as acetyl-dinitro-glycerin; † also the nitrated polyglycerins such as tetranitroglycerin. It should be possible in this way to produce practically unfreezable dynamites.

193. Nitroglycerin is not easily ignited, and yet it is sensitive to sudden heating, as may readily be seen from the numerous accidents caused by careless thawing of frozen nitroglycerin explosives. Violent blows, friction and, in general, all kinds of rough handling may cause detonation.

The products of the complete explosion of nitroglycerin are carbon dioxide, water, nitrogen and some free oxygen. No poisonous gases are found, a fact that is of importance in its technical use. Nitroglycerin finds its chief use in the gelatinized nitroglycerin powders and in the various dynamites. Liquid nitroglycerin itself is not allowed in commerce. A. Nobel suggested that it be dissolved in methyl alcohol to make it transportable. G. M. Mowbray, with the same purpose in view, filled it into metal bottles and froze it. Hundreds of thousands of kilograms of nitroglycerin were transported in America in this latter fashion apparently with comparative safety.‡

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* Belg. Pat. No. 183,454. † Z. ges. Schiess Sprengstoffw., 2, 21; 1907.

‡ Nitroglycerin for use in oil wells is largely transported in the United States in the unfrozen condition (Translators).

2. *Nitrocellulose.*

194. Analogous to the formation of nitroglycerin from glycerin is that of nitrocellulose by the action of nitric and sulphuric acids on substances containing cellulose, such as cotton, flax, wood fibers, jute,* etc. The product of the nitration, however, is not a simple chemical compound in the same sense as nitroglycerin. It is rather a series of nitric acid esters of cellulose, the properties of the various members of which are by no means fully determined.† According to the concentration and composition of the acid nitrating mixture we find, predominating in the nitrated product, nitrocelluloses of low nitration, characterized by their solubility in ether-alcohol (collodion cotton, pyro-collodion), or nitrocelluloses of higher nitration most easily soluble in acetone and glacial acetic acid (guncottons).

C. F. Schönbein, in Basel, discovered nitrocellulose in the year 1846. He obtained guncotton by treating raw cotton with strong nitric and sulphuric acids.‡ In the same year, R. Böttcher discovered an explosive cotton while engaged in similar experiments in Frankfurt am Main, and these two men joined to make a practical utilization of the discovery. The possessors of the process, which was originally held secret, did not hesitate in recommending the new explosive preparation to the German Confederation as a propellant in every way superior to black powder. Among the members of the commission appointed by the German Confederation to examine the discovery was an Austrian

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* O. Mühlhäuser, Dingler's pol. J., **283,** 88, 137; 1892.

† J. M. Eder, Ber., **13,** 169; 1880. See also G. Wolfram, Dingler pol. J., **230,** 45, 148; 1878.

‡ See G. W. A. Kahlbaum, "C. F. Schönbein," **110,** II; 1901.

artillery officer named von Lenk. Von Lenk persistently continued his experiments with the new substance after it was found that, on account of its uncertain action and its chemical instability, it could not be used as a substitute for black powder. He turned his attention to a more careful purification of the cotton before nitration and a more thorough washing of the acid esters from the nitrated fibers. He attempted further to decrease and regulate the dangerously high velocity of combustion of the nitrocellulose by twisting the fibers and by similar mechanical means (section 183). Two violent explosions of von Lenk's guncotton in the years 1862 and 1865 brought to an end all further experiments in Austria. In the meantime the English government received information of the work of von Lenk, and F. Abel set to work in Woolwich to adapt nitrocellulose to ballistic requirements. Although at first he met with no more success than von Lenk, yet in 1865 he discovered that by pulping it in a pulping machine and afterwards compressing it under great pressure it could be used with safety in explosive technology.* E. O. Brown † added another important step in the practical use of nitrocellulose when he discovered that moist compressed guncotton may be detonated with the help of a small quantity of dry guncotton and a detonator (section 176). The dream of C. F. Schönbein and von Lenk to substitute nitrocellulose for black powder was, however, not realized until P. Vieille, in the year 1886, discovered, in the gelatinization of nitrocellulose, a method for the satisfactory regulation of its velocity of combustion (sections 67 and 183); and on the other hand, a satis-

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* Eng. Pat. No. 1102 of 1865.

† E. O. Brown, Mechanic's Magazine, 478; 1872.

factory method for the stabilization of nitrocellulose was discovered (section 207).

The manufacture of nitrocellulose on a large scale is troublesome and comparatively expensive, but in general is free from danger of explosion. It begins with the purification and mechanical loosening and picking apart of the raw cellulose. The refuse from cotton factories is usually preferred for nitration, especially when a highly nitrated guncotton is desired. The cotton is dried as completely as possible immediately before treatment with the acid mixture. The operation of nitration is most conveniently carried out in closed iron centrifuges, provided with an outlet for vapor and gases. On account of the large volume and great absorbent power of loose cotton about fifty parts by weight of acid mixture are required to one part of raw cotton. The cotton is immersed quickly beneath the surface of the acid in small quantities at a time and exposed for half an hour to the action of the nitrating bath. The acid is then allowed to flow off, after which that held by the nitrated fibers is driven off by the centrifuge.* This operation is sometimes accompanied by a sudden fuming off of the entire contents of the centrifuge especially on hot days. In a normal operation the nitrated cotton is swept out of the centrifuge in small quantities at a time by a strong stream of water and washed into large washing vats. Here the nitrocellulose is washed free from acid, a little soda being sometimes added to the wash water. Earlier† it was believed that the nitrated cotton only required a thorough washing out to be stable. Since it has been

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* See also G. Lunge, Z. ges. Schiess Sprengstoffw., **1**, 1; 1906.

† See M. Pelouze and M. Maurey, Ann. chim. phys., (4), **3**, 186; 1864. O. Guttmann, Dingler pol. J., **249**, 456, 509; 1883.

recognized, however, that the cause of the instability of nitrocellulose lies elsewhere and especially in the formation of foreign, partly nitrated substances which are also insoluble in water, but which at high temperatures decompose much more readily than nitrocellulose itself (section 208), the nitrated cotton is now treated for several hours with boiling water. The foreign compounds are decomposed by this treatment and washed out in the following washings. The purified nitrocellulose is then more stable.* If compressed guncotton is to be prepared for blasting purposes or for the manufacture of smokeless powder, the nitrated cotton is now pulped in pulping machines which reduce the nitrocellulose to a mass similar to paper pulp. By drying this pulp in centrifuges until it contains about 30 per cent water, a product is obtained which is easy to handle and safe for transportation. If it is finally desired to dry this, it is placed in heated drying chambers or the moisture is driven out by forcing alcohol through it. 100 parts by weight of raw cotton yield about 160 parts of guncotton, or 150 parts of the less highly nitrated collodion cotton. In nitrocellulose factories the spent acid is again made fit for use by the addition of a suitable quantity of fortifying acid which raises it to its original composition, and in this way the cost of production is materially lessened.

The fibrous nitrocellulose before pulping can scarcely be distinguished from the ordinary raw cotton in appearance and structure. In polarized light, however, it shows a faint orange or blue shimmer, according to its degree of nitration, while cotton shows all the prismatic colors in brilliant tints.† Nitrocellulose is electric

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* See also R. Robertson, J. Soc. Chem. Ind., **25**, 624; 1906.

† L. C. de Chardonnet, Compt. rend., **106**, 633; 1888: **145**, 115; 1907.

in dry air.* In moist air it absorbs some moisture and, strange to say, the amount absorbed is exactly in inverse ratio to its grade of nitration. Guncotton of 13 per cent nitrogen content absorbs 1 per cent less moisture than collodion cotton of 12 per cent nitrogen content (section 200). Moist nitrocellulose is readily attacked by molds and bacteria. The suspicion that its chemical stability can be endangered by them or that an explosion can be caused has, however, not yet been verified.

The specific gravity of nitrocellulose is 1.66,† being higher than that of the raw cotton (1.58), and even than that of nitroglycerin (1.60). The technically important nitration grades of cellulose have approximately the same specific gravity as shown in Table 51.

TABLE 51. SPECIFIC GRAVITY OF NITROCELLULOSES OF DIFFERENT NITROGEN CONTENTS.

Nitrogen contents, per cent.	Density.
11.10	1.653
12.30	1.654
13.20	1.659

Nitrocellulose is completely insoluble in hot and cold water, but dissolves readily in acetone, acetic ether, nitrobenzene or pyridine. It shows a characteristically different behavior towards a mixture of two parts of ether to one of alcohol according to the degree of nitration. The highly nitrated guncotton is insoluble, while the low nitrated collodion cotton is readily solu-

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* O. Guttmann, Dingler's pol. J., **270**, 222; 1888.

† B. Wehrhahn, Chem. Ztg., 1004; 1893. H. de Mosenthal, J. Chem. Soc., **26**, 445; 1907.

ble. At about −100° C., however, highly nitrated cellulose is gelatinized with ether-alcohol, and hence is presumably soluble.* A special kind of collodion cotton † is also soluble in nitroglycerin and forms with it a viscous to semi-solid gelatin which allows no nitroglycerin to escape.

If highly nitrated, well dried, long-fiber guncotton is ignited it burns extraordinarily rapidly with a yellow flame and, on this account, small quantities of guncotton can be burned on top of black powder without igniting it, or on the open hand without injuring it. The sudden heating or ignition of large quantities of nitrocellulose, the rubbing of this substance between two hard bodies or subjecting it to violent blows may cause it to detonate. The following accident shows how easily guncotton ignites.

On Feb. 16, 1903, there occurred a spontaneous ignition of very highly compressed, dried guncotton at the arsenal in Woolwich. A large block of almost completely dry guncotton was being carefully broken apart with a phosphor bronze chisel to find out if it were dry on the inside. In the course of this operation one of the broken-off pieces suddenly burst into flame, ignited presumably by the friction of the working tool. Six persons were in the room at the time. Only one of them escaped unhurt; four others, who could not leave the building so quickly, were burned so frightfully that two of them afterwards died; the sixth could not escape and was burned. About 240 kilograms of dry guncotton which was piled up in another part of the building was ignited.‡

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* See D. R. P., No. 127, 143.

† A. Nobel, Engl. Pat. No. 4179 of 1875.

‡ Ann. Rept. H. M. I. Exp., 50; 1903.

The oxygen present in chemical combination in nitrocellulose is not sufficient for complete combustion of the carbon and hydrogen present. The products of the explosion of nitrocellulose (section 126) consequently regularly contain, besides carbon dioxide, hydrogen and nitrogen, carbon monoxide and, under certain conditions, methane and hydrogen also, and, in cases of incomplete transformation, nitrogen dioxide and hydrocyanic acid.*

Besides its use as an explosive, nitrocellulose has found very extensive use in the industries, such as in the preparation of celluloid, photographic films, artificial silks, filter material for strong acids, etc., which are far removed from the field of explosive technique. For submarine mines and torpedo charges very highly compressed guncotton is preferred, which may be sawed, bored or turned like wood, without danger if a stream of water is allowed to drop slowly on the parts during the operation. Otherwise there would be danger of an ignition from the friction of the tool. Nitrocellulose is also a component of many explosive mixtures and forms the basis of the much-used smokeless powders.

The transportation of nitrocellulose takes place in wooden boxes lined with zinc, which allow no moisture to escape from the nitrocellulose which must contain at least 30 per cent of moisture and be compressed into a solid mass. Dry nitrocellulose in loose form is not suitable for transportation on account of its inclination to fall into fine dust as well as its great sensitiveness towards blows or shocks.

195. The relation between the grade of nitration of cellulose and the technically important characteristics of the nitrated product, such as solubility in ether-

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* L. v. Karolyi, Ann. Physik., **118**, 544; 1863.

alcohol, or acetone, inner friction (viscosity) of solution, hygroscopicity, decomposition by heat, light, etc., have frequently been the subject of extensive investigations.

As far as the solubility in ether-alcohol is concerned it has long been recognized that a high nitrogen content of over 13 per cent (guncotton) corresponds to the minimum solubility in ether-alcohol, as a rule, of less than 10 per cent; and that nitrocelluloses of between 10 and 12.5 per cent nitrogen ("collodion cotton") content almost always have a high solubility in ether-alcohol, while cellulose nitrates of less than 9 per cent nitrogen content are usually very slightly soluble in ether-alcohol and are characterized generally by divergent properties. On the other hand, the solubility of all grades of nitration of cellulose having a nitrogen content between 9 and 10.5 per cent, and especially those technically important products with a nitrogen content between 12.5 and 13.5 per cent (Fig. 41), seem at first glance entirely irregular. It appears from the works of P. Vieille,* M. Bruley † and more especially G. Lunge ‡ and his pupils, that the varying degrees of solubility of the last-named group of cellulose nitrates of approximately like nitrogen contents are mainly determined by the composition of the acid nitrating mixture, a mixed acid of a high water content favoring solubility while one of a high sulphuric acid content decreases it. Although the nitrogen contents of the finished product is only slightly affected by these two opposing influences its solubility is a much more delicate index to its character. There is as yet no expla-

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* P. Vieille, Mem. poudr. salp., II, 212; 1884–89.

† M. Bruley, Mem. poudr. salp., VIII, 111; 1895–96.

‡ G. Lunge and E. Weintraub, Z. angew. Chem., **12**, 441, 467; 1899. G. Lunge and J. Bebie, ditto, **14**, 483, 507, 537, 561; 1901. G. Lunge, ditto, **16**, 197; 1903: **19**, 2051; 1906.

nation from a chemico-physical standpoint for the peculiar form of the nitrogen solubility curve. It is not impossible that the key to the problem of the colloid nature of these solutions is dependent upon their previous treatment in the nitrating bath.* So far we have been dependent upon empirical rules,† for the preparation of a suitable acid mixture for the production of a nitrocellulose of given characteristics.

196. A. Saposchnikow‡ suggested a way by which he hoped to gain a closer insight into the relation which exists between the composition of the nitrating acid and the nitrogen contents of the nitrocellulose produced. The course of the nitrating reaction depends essentially upon the proportions of nitric acid, sulphuric acid, water and cellulose in the nitrating mixture. During the course of the nitrating reaction the mixture undergoes a chemical change, in that the proportions of H_2SO_4 and H_2O are increased while that of HNO_3 is decreased, and a physical change occurs in the specific gravity of the acid mixture, the vapor tension of the HNO_3 present at any given instant, the electric conductivity of the mixture and probably a number of other constants. The minimum of electric conductivity as well as the least change in the vapor tension of the HNO_3 during the nitration is established when the acid mixture has a composition of about 25 per cent HNO_3, 65 per cent H_2SO_4 and 10 per cent H_2O, and this corresponds to the proportions which, according to the

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* See Handb. phys. Chem., vol. 8: A. Müller, Allgem. Chem. d. Kolloide. To prevent any erroneous application of the chemistry of colloids to nitrocellulose see the remarks of A. Müller, Z. f. Chemie. u. Industr. d. Kolloide, **2**, 173; 1907.

† Kisniemsky, Mem. poudr. salp., X, 64; 1899–1900.

‡ A. Saposchnikow, Z. phys. Chem., **49**, 697; 1904: **51**, 609; 1905: **53**, 225; 1905. Z. Schiess Sprengstoffw., **1**, 543; 1906.

experiments of G. Lunge and J. Bebie,* are best suited for the production of nitrocellulose of highest nitrogen content.

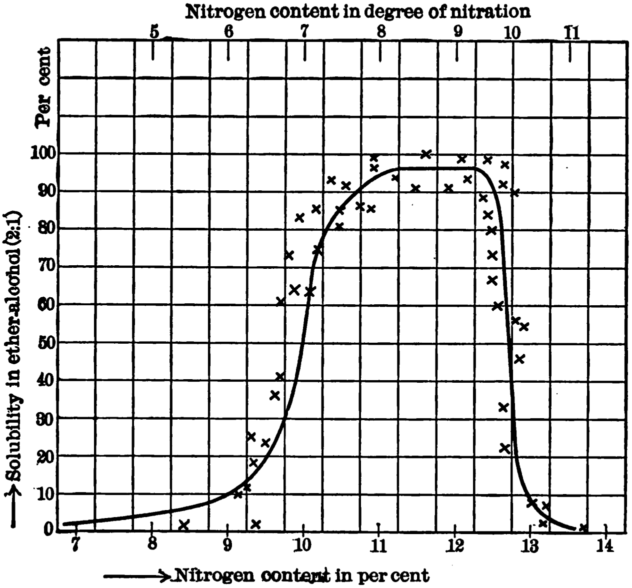

FIG. 41. Relation between the Nitrogen Content of Nitrocellulose and its Solubility in Ether-Alcohol.

197. Since the time of Ch. F. Schönbein it is believed that the principal part played by the sulphuric acid in the nitrating mixture is to maintain the concentration of the nitric acid monohydrate at the highest point, and thus increase its effectiveness during the nitration.† This view is strengthened by the fact, among other things, that the addition of even a small quantity of

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* G. Lunge and J. Bebie, Z. angew. Chem., **14,** 513; 1901. Opposed to this, see Guttmann, Chem. Zeitschr., **1,** 355; 1902. E. Berl and R. Klaye, Z. ges. Schiess Sprengstoffw., **2,** 381; 1907.

† J. S. v. Romocki, Gesch. Exp., 1896, I, 218; II, 125.

sulphuric acid raises the nitrating power of nitric acid upon cellulose considerably and allows a much weaker nitric acid to be used without decreasing the nitrogen content of the resulting cellulose nitrate. The highest grade of nitration hitherto obtained with the strongest nitric acid of nearly 100 per cent HNO_3 has a nitrogen content of 12.8 per cent. With the presence of strong sulphuric acid, however, nitrocellulose has been obtained with a nitrogen content of 13.5 per cent. It has further been shown that the sulphuric acid may be replaced, without any practical advantage however, by other substances having a strong attraction for water, as, for instance, phosphorus pentoxide.*

Later experiences† leave no doubt of the fact that other characteristics of nitrocellulose, such as solubility, viscosity, etc., are to be ascribed to the influence of the sulphuric acid and hence its action reaches much further than that of a mere concentration of the nitric acid monohydrate. It is known that sulphuric acid itself forms cellulose esters which, in the presence of nitric acid and water immediately decompose, the acid residue NO_3 taking the place of HSO_4. Such a reaction would not, as a rule, be detected in the nitrogen contents of the nitrated product, but might influence certain more sensitive characteristics, such as solubility, viscosity, etc. It is uncertain to what extent molecular changes (hydration, etc.) in the cellulose may take place in such a reaction. It is also possible that a mixed nitro-sulphuric acid ester of sufficient stability to exist

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* G. Lunge and E. Weintraub, Z. angew. Chem., 513; 1901. C. Hoitsema, ditto, 173; 1898. B. Rassow and W. v. Bongé, ditto, 732; 1908.

† See, among others, G. Lunge, Z. phys. Chem., **59**, 629; 1907. C. Kullgreen, Z. ges. Schiess Sprengstoffw., **3**, 146; 1908.

as such in the acid mixture and to withstand the effects of the succeeding washing with cold water may be the real starting point for the combined action of the two acids. If such be the case it should be possible to detect sulphuric acid esters by direct analysis of the products after they have been carefully freed from acids. In fact, under certain conditions,* nitrocelluloses have been produced containing up to 5 per cent of combined H_2SO_4. Under ordinary conditions of nitration these less stable sulphuric acid esters are either not formed at all or, if formed, are removed in the first processes of purification, which consist of boiling with water, extraction with alcohol or dilute acetone, etc.

If all previous knowledge in regard to the composition of the nitrating acid be collected and examined in connection with the solubility of the cellulose nitrates the fact presents itself that the function of the sulphuric acid is by no means sufficiently accurately characterized by its significance as an agent for the absorption of water. The controlling conditions have not yet been ascertained in a sufficiently satisfactory manner but an empirical idea of them may be gained if the nitrogen contents and the solubility of the nitrocelluloses be regarded as variables dependent upon the proportions of nitric acid, sulphuric acid and water in the nitrating acid.

198. Very little can be found in literature regarding the relations which exist between the conditions under which cellulose is nitrated and the inner friction (consistency, viscosity, etc.) of solutions of nitrocellulose in ether-alcohol, acetone, camphor, nitroglycerin, etc., notwithstanding the technical significance of such relations, since solutions of nitrocellulose are transition

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* C. F. Cross, E. J. Bevan and R. L. Jenks., Ber., **34**, 2496; 1901.

forms for its gelatinization and conversion into colloidal masses in the manufacture of celluloid, smokeless powder and the like.

According to G. Lunge* the viscosity of ether-alcohol solutions of collodion cotton is dependent upon the water contents of the nitrating acid. Judging from the limited amount of experimental data on the subject, G. Lunge expressed the opinion that, under otherwise similar conditions, especially constant temperature and duration of nitration, the viscosity rises with decreasing percentage of water in the nitrating mixture. This is shown in Table 52.

TABLE 52. INFLUENCE OF THE WATER CONTENTS OF THE NITRATING ACID UPON THE VISCOSITY OF NITROCELLULOSE.

Percentage of water in nitrating mixture.	Viscosity, seconds.
18.05	18.1
16.83	50.5
15.50	278

The influence of a high nitration temperature is shown not so much in an acceleration of the esterification process as in an increase of secondary reactions, which decrease the yield of nitrocellulose and presumably also reduce the size of the molecule. The same is true if the acid mixture be allowed to act for a longer time on the nitrocellulose or cellulose. It is probable that the relations discovered by G. Lunge apply not only to the collodion cotton used by him in his work, but equally well to all nitrated celluloses. E. Berl and

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* G. Lunge, Z. angew. Chem., **19**, 2056; 1906. See also M. Bruley, Mem. poudr. salp., VIII, 111; 1895–96. O. Guttmann, Schiess. und Sprengmittel, 102; 1900. W. Will, Ber., **37**, 288; 1904.

R. Klaye,* who investigated the viscosity of highly nitrated celluloses in 2 per cent acetone solution, came to the conclusion that, in general, viscosity as shown in Table 53 is a function of the nitrogen contents.

TABLE 53. VISCOSITY OF NITROCELLULOSE AS A FUNCTION OF THE NITROGEN CONTENTS.

Nitrogen contents, per cent.	Viscosity.	
	Time required to discharge, seconds.	Calculated to solvent (acetone) = 1.
9.09	447	14
10.41	1,800	50
12.48	16,227	460
13.02	18,631	530
13.50	322,465	9500

The sudden increase in the viscosity of the solutions of nitrocelluloses whose nitrogen contents differ between 13 per cent and 13.5 per cent is remarkable. While the nitrocelluloses of highest nitration seem to contain a comparatively undecomposed cellulose molecule this is broken down if the cellulose is nitrated with a dilute acid mixture, and this splitting of the molecule is clearly indicated by the greatly lessened viscosity of the 2 per cent acetone solution. This molecular change is especially vigorous if the cellulose is first dissolved in sulphuric acid and then precipitated as nitroxyloidin,† by pouring the solution into nitric acid. The viscosity of this product is so small (37 seconds) that it can hardly be differentiated from that of acetone itself (35 seconds). Moreover, such relations may be very markedly influenced by the raw cellulose material according as this

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* E. Berl and R. Klaye, Z. ges. Schiess Sprengstoffw., **2**, 386; 1907. E. Berl and W. Smith, Ber., 1837; 1908.

† G. Lunge and E. Weintraub, Z. angew. Chem., **12**, 448; 1899.

is more or less strongly constituted. E. Berl and R. Klaye used for the above-mentioned experiments a pure cotton wool, washed free from oil with a 2 per cent caustic soda solution and then washed with hot distilled water until the wash water showed no alkaline reaction. In comparison with the raw cotton used in the manufacture of nitrocellulose which is cleaned and loosened up by mechanical means only, this material had already undergone various chemical changes before nitration.

199. The fact that nitrocellulose finds its largest use for ballistic purposes, where especial value is attached to an invariable, definite effect, has led to an investigation of its hygroscopic properties. According to C. Beadle,* the amount of moisture taken up by nitrocellulose when in a moist atmosphere is indirectly proportional to its nitrogen content and directly proportional to the number of unsaturated hydroxyl groups. This fact was deduced from the observation that the amount of moisture absorbed always stood in a certain relation to the yield of nitrocellulose from a given quantity of cellulose.

200. W. Will† has carried out these investigations on a broader scale and included in his experiments the most important grades of nitration of celluloses of various kinds. If the moist urecontent of the atmosphere was kept high (above 90 per cent saturation), but yet sufficiently below the limit at which slight unavoidable variations in temperature would cause a partial deposition of water on the nitrocellulose fibers,

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* C. Beadle, Chem. News, **70**, 247; 1894.

† W. Will, Mitt. Zentral wissen. techn. Unter., 1904, Vol. 4. The observed regularities did not apply to air completely saturated with moisture, as is stated in the article, but to a degree of saturation of about 90 to 95 per cent.

then there became apparent a number of remarkable regularities between the grade of nitration of the cellulose and the amount of moisture absorbed by it. Experiments were conducted with grades of nitrocellulose containing from 9 to 13.3 per cent nitrogen, the latter being the grade so largely used in technology, and in each case the substance was dried at 40 degrees to constant weight. In all these grades of nitrocellulose the sum of nitrogen contents and absorption of moisture in per cents gave an average of 14.6. This value was independent of the kind of cellulose which was nitrated, whether cotton, flax, hemp or jute, and also of the treatment to which the raw material or the finished product had been subjected, whether they had been treated with acids, bleaching materials or alkalis. The relation between the nitrogen contents of nitrocellulose and its hygroscopicity, which is expressed graphically by a straight line, proved to be true also for various temperatures (5°, 15°, 25° C.), (Fig. 42), but not for all possible degrees of saturation of the atmosphere.

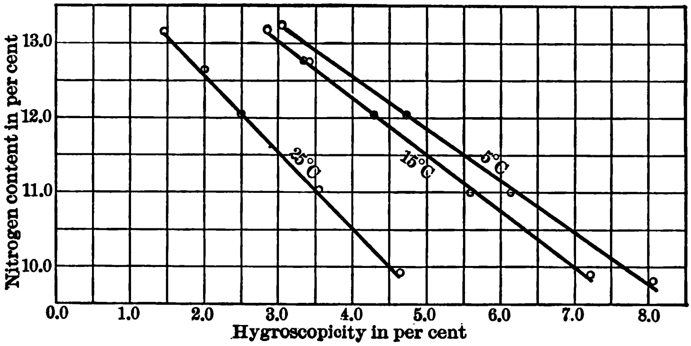

FIG. 42. Relation between the Nitrogen Content of Nitrocellulose and its Hygroscopicity at Various Temperatures.

The theory of absorption* does not seem to have been applied as yet to the hygroscopic properties of nitrocellulose, although such an experiment would be very interesting.

201. As has already been mentioned (section 171), nitrocellulose presents many problems regarding its chemical stability which have not yet been satisfactorily solved. Among the earliest systematic observations made on the stability of nitrocellulose are those of S. de Luca.† He found that the velocity of decomposition of an unstable guncotton increases with the moisture content of the air. A sample of such an unstable guncotton was divided into four parts, of which one part was kept in the dark, a second part was exposed to the reflected light of the laboratory, a third part, to the influence of direct sunlight, and the fourth part was heated on a water bath to about 50° C. In the velocity at which decomposition progressed, this last part was next to that exposed to the direct sunlight; then followed the part influenced by the reflected light, while the part kept in the dark decomposed most slowly. From this experiment heating was proved to be the strongest influence for bringing about a chemical decomposition in guncotton. Even a moderate temperature of 50° C., which may obtain in practice under unfavorable circumstances, was disastrous to the guncotton used, which, however, was undoubtedly very impure.

202. F. Abel ‡ thought he had sufficient ground for

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* See Handb. phys. Chem., Vol. 8. A. Müller, All. Chem. Koll., p. 111; 1907. W. Ostwald, Lehrb. All. Chem., II, (3), p. 217; 1906. Also Z. Chemie u. Industr. d. Kolloide, Vols. 1, 2 and 3.

† S. de Luca, Compt. rend., **53**, 300; 1861: **59**, 487; 1864.

‡ F. Abel, Phil. Trans., **156**, 269; 1886: Chem. News, **15**, 203; 1867. B. Pleus, Abel's Untersuchungen über Schiessbaumwolle, 1907.

the belief that the strong tendency of many nitrocelluloses to spontaneous decomposition, observed by S. de Luca and others, was due less to the nitrocellulose itself than to foreign, resinous by-products which are found in every guncotton, and which are present in pure cellulose and nitrated with it. These foreign substances could not be completely removed by the usual washings, nor even by a very careful and thorough purification process.*

F. Abel inclosed nitrocellulose in an evacuated, airtight glass balloon, which was connected with a barometer tube, and warmed it for months at a time to temperatures of 65° C. and more. The gases given off were measured and all changes in the appearance of the nitrocellulose noticed. It appeared that very pure nitrocellulose withstood to a remarkable degree the decomposing influence of long-continued heating, even at temperatures of almost 100° C. F. Abel believed further, that the lower nitration grades of cellulose (soluble guncotton, collodion cotton), if pure, show no greater inclination to change than the highest nitrated guncotton; and that accordingly the presence of these lower nitration grades of cellulose in such guncotton need not of themselves injure its chemical stability. The result of these studies of the behavior of nitrocellulose at higher temperatures was the so-called Abel test.†

It is based on the principle of the detection of the first traces of free oxides of nitrogen by means of starch-potassium-iodide test paper and has been adopted, especially in England, as an authoritative test for the chemical stability of explosives.

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* See also W. Will and F. Lenze, Ber., **31,** 68; 1898.

† O. Guttmann, Ind. Exp., 655; 1895. R. Escales, Die Schiessbaumwolle, 178; 1905. Ann. Rept., H. M. I. Exp., 189; 1906. Charles E. Munroe, Proc. U. S. Nav. Inst., **5,** 11; 1879.

203. On the other hand, P. Vieille* differed from F. Abel, and, from the gradually decreasing action of hydrochloric acid on nitrocelluloses of various nitrations as the nitrogen contents increased, he drew the conclusion that this behavior probably indicates unequal degrees of resistance and that consequently celluloses of low nitration are generally less stable than those of high nitration. P. Vieille was led to this conclusion by the observation that even cold hydrochloric acid acted readily on nitrocellulose of low nitration, and that nitrocelluloses of medium nitration (collodion cotton) required heating to be decomposed by an acid of the same concentration, while nitrocelluloses of 13 and more percent nitrogen (guncotton) must be boiled for a long time with acid to drive off all the nitrogen as nitrogen dioxide. This parallelism between the decomposing action of acids on the one hand and increased temperature on the other has not been confirmed by later experiments (section 208).

204. Ph. Hess † proposed that the heat liberated by the slow decomposition of explosives be used as a measure of their chemical stability. For this purpose equal quantities of the various explosives whose stabilities are to be compared are exposed under similar conditions to a temperature of 70° C. Thermometers are embedded in each sample in a similar manner and so arranged that they show the exact temperature of the explosive, while other thermometers control the temperature of the bath. By inclosing the sample in containers of material having a low specific heat conductivity, as, for instance, double glass walls with a filling of kieselguhr, the heat of decomposition is given off very

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* P. Vieille, Mem. poudr. salp., II, 224; 1884–89.

† Ph. Hess, Mitt. Art. Geniew., **14**, 92 (notes); 1883

regularly and very slowly, so that the observed temperatures t^1, t^2, t^3 . . . indicate the state of decomposition in each sample. If diagrams are drawn making the observed times the abscissas and the temperatures t^1, t^2, t^3 . . . the ordinates, the course of the decomposition is represented graphically and a comparison of the stability of various explosives is possible. Of course, such a comparison, which is based on rises of temperature, is practicable only when the heat of decomposition liberated is actually used up in the same measure in raising the temperature of the various samples, and is unreliable when the heat liberated is consumed with varying degrees in other ways, such for instance, as in vaporizing volatile components which must necessarily be the case in samples of powders containing different quantities of moisture or gelatinizing solvent.

205. O. Guttmann* attempted to find for guncotton and a number of smokeless powders relations between the temperature to which the explosive was heated and the time which elapse before the appearance of oxides of nitrogen. As an indicator, he used strips of paper moistened with a solution of diphenylamine sulphate. The test paper was hung in the test tube above the sample being heated and was colored blue-violet by the first trace of nitrogen oxides liberated. The intervals of time and temperature could be expressed as a geometrical series of the form $K + m$, $K + 2m$, $K + 4m$, $K + 8m$, $K + 16m$, in which K denotes a constant which expresses the retardation of the characteristic reaction in consequence of the poor heat conductivity and other factors. A high constant K denotes, according to O. Guttmann, that decomposition of the explosive sets in slowly under the influence of a definite

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* O. Guttmann, Z. angew. Chem., **10**, 233, 265; 1897.

temperature while a high progressions factor *m* denotes that the decomposition, once begun, progresses slowly.

206. C. Hoitsema* investigated the question whether the nitrogen evolved by the decomposition of nitrocellulose appears originally in other forms than as NO and N, such as N_2O_3 and NO_2, or whether the formation of these last-named compounds is due to the presence of impurities in the nitrocellulose. If these oxides of nitrogen really belong to more easily decomposable components, i.e., if they do not arise from a regular decomposition of the nitrocellulose molecule itself in its various stages, then they must appear earlier than the other gases, especially NO, and this last-named gas, although it appears in much larger quantities, should not be detected as early in the decomposition as N_2O_3 or NO_2. He found as an actual fact, that, under the same experimental conditions, the development of NO is first noticed at a higher temperature than that of other oxides of nitrogen.†

207. A deeper insight was obtained into the conditions upon which the chemical stability of nitrocellulose is dependent when it became practicable to study the course of an artificially induced decomposition of nitrocellulose in its various stages of manufacture, from the nitrating operation to the completion of the product, and to determine the relations which exist between its inclination to decompose and its state of purity. When systematically nitrated and purified nitrocelluloses were heated to high temperatures (e.g., 135° C.) and the velocity of their decomposition was determined, sometimes qualitatively and sometimes quantitatively,

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* C. Hoitsema, Z. phys. Chem., **27**, 567; 1898.

† See, on the other side, R. Robertson and S. Napper, J. Chem. Soc., London, **91**, 764; 1907.

it appeared that regular relations exist between the grade of purity of nitrocellulose and its stability at high temperatures.

It is well known that every esterification process is a reversible reaction in that the reacting components seek to establish an equilibrium (section 188). One of the most important proofs of the view that the process of nitration, as it proceeds between cellulose and the nitric-sulphuric acid mixture, is a reversible reaction is the fact, proved by E. Fromberg,* that nitrocellulose can be "renitrated." Instead of nitrating cellulose (cotton, etc.), as usual, the process of nitration may be conducted on collodion cotton, which has already been prepared, stabilized and pulped. The advantage to be gained by this process is that foreign bodies and impurities, which cling to even the best purified cellulose and influence the stability of the nitrated product, are removed. Moreover, the physical condition of such finely pulped nitrocellulose insures a thorough penetration and regular action of the nitric acid, and finally there is no liability of any local overheating, which frequently occurs in the usual nitration process, since this operation is attended by only slight rises of temperature. A test of nitrocelluloses so obtained by the qualitative stability test at 135° C.† proves that the stability of nitrocellulose at high temperatures is undoubtedly a function of the proportions of the components in the nitrating acid, i.e., nitric acid, sulphuric acid and water. A more rational method for the preparation of gun-cotton on a large scale is here indicated.

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* E. Fromberg, Bereitung und Anwendung der Schiessbaumwolle und des Kollodions, 18; 1860. See also J. M. Eder, Ber., **13**, 178; 1880.

† R. Escales, Schiessbaumwolle, 183; 1905.

208. Later quantitative investigations by W. Will* wherein the stability of nitrocellulose is judged from the quantity of nitrogen liberated at a temperature of 135° C. in a current of carbon dioxide (section 41), have proved the truth of this result. Raw cotton, such as is used in dynamite factories, was nitrated with mixtures of nitric and sulphuric acids of various concentrations. The samples of nitrocellulose so obtained were stabilized by boiling with water, tested by means of the stability test (section 41), and the following regularities were established.

(*a*) As regards their resistance to heating at high temperatures all nitrocelluloses may, by proper treatment, e.g., boiling with water, be brought to a kind of "limit condition" at which their velocity of decomposition, i.e., the relation between the loss in weight Δm and the time which has elapsed since the beginning of decomposition Δt, or the expression $\frac{\Delta m}{\Delta t}$, is a minimum. This is demonstrated in Fig. 43.

(*b*) This minimum of decomposition is a different but constant magnitude for the various nitrocelluloses, depending upon their nitrogen contents and the composition of the nitrating acid. It does not vary in proportion to the nitrogen contents but celluloses of the highest grades of nitration give off about double as much nitrogen as would be expected from a simple proportion (Fig. 44, Curves I and II).

(*c*) The amount of work (washing, etc.) necessary to arrive at this minimum of decomposition varies for the various nitrocelluloses and is dependent mainly upon

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* W. Will, Untersuchungen über die Stabilität von Nitrozellulose, Heft II; 1900: Heft III; 1902. O. W. Willcox, J. Am. Chem. Soc., **30,** 271; 1908. Zeitschr. angew. Chem., **21,** 1407; 1908. A. Saposchnikoff, Mem. poudr. salp., XIV, 42; 1908.

the water contents of the nitrating acid and the ratio of H_2SO_4 to HNO_3. It decreases with increasing per-

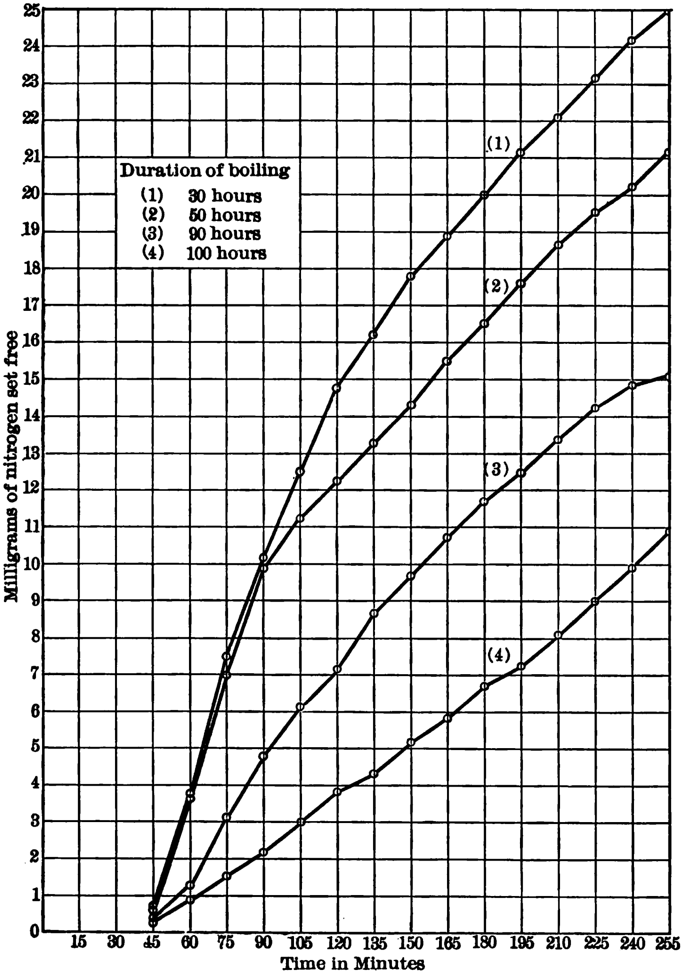

FIG. 43. Stabilization of Nitrocellulose by Boiling with Water.

centages of water and nitric acid. This explains why long, intensive boiling with water is usually necessary

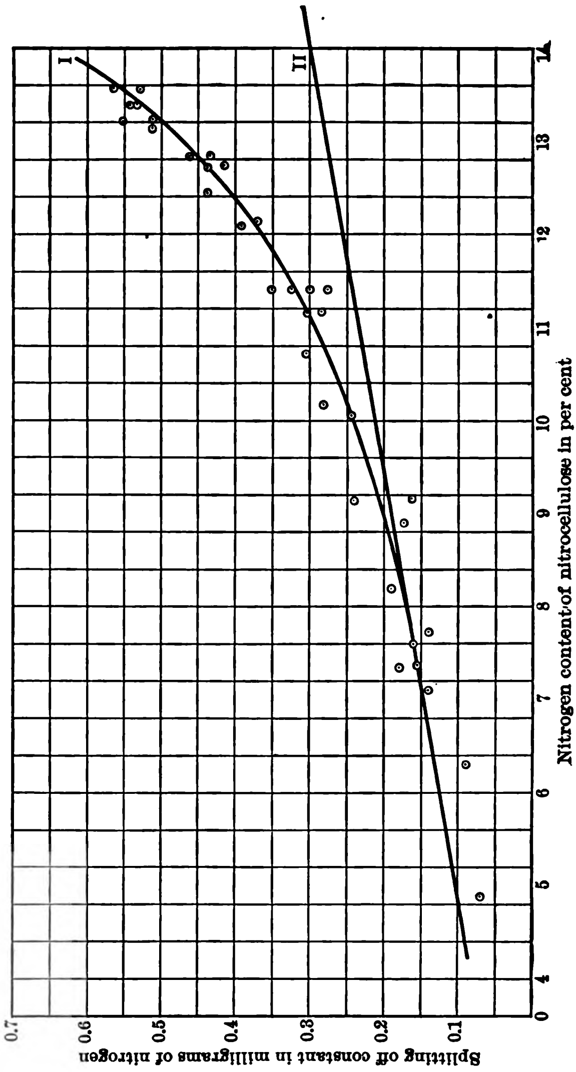

FIG. 44. Minimum Nitrogen split off by Various Nitrocelluloses.

to stabilize nitrocelluloses of high nitration while a much less time is sufficient for nitrocelluloses of medium nitration (though boiling is necessary), and often a mere wash with cold water is sufficient for those of low nitration.

(*d*) The temperature coefficient is the same for all nitrocelluloses in this minimum condition, and is about 1.9 to 2.0 for each 5 degrees increase between 130° and 160° C. It is seen from the foregoing, that, in spite of varying decomposition constants, all completely purified nitrocelluloses, of whatever grade of nitration, are of equal chemical stability.

209. The chemical stability of gelatinized nitrocellulose, strange to say, is often much lower than that of the ungelatinized.* Since the transformation of loose nitrocellulose into gelatinized nitrocellulose is essentially a process which does not disturb the chemical character of the nitrocellulose fibers but merely changes its physical condition for the purpose of lowering its velocity of combustion, increasing its cubical density, etc. (section 183), it does not readily appear why the chemical stability of a smokeless powder made from gelatinized nitrocellulose should not be the same as that of the nitrocellulose used in its manufacture. It is certain, however, that, in spite of painstaking purification of the raw material and careful preparation of the nitrocellulose, gelatinized powders often suffer decomposition in a comparatively short time.† The cause of this phenomenon is not yet explained. Reliable tests for the stability of a gelatinized powder prepared

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* See O. Silberrad and R. C. Farmer, Journ. Soc. Chem. Ind., **25,** 961; 1906. Z. ges. Schiess Sprengstoffw., **2,** 61; 1907.

† W. Will, Ber., **37,** 268; 1904. E. Bravetta, Z. ges. Schiess Sprengstoffw., **3,** 4, 72; 1908.

from a stable nitrocellulose are also wanting at present. In general, it may be said that stability tests which are founded upon the recognition and application of characteristic points in the course of a carefully conducted decomposition of the gelatinized powder are relatively more reliable than such tests as the Abel test (section 202), which depends upon the very first and often uncertain traces of an incipient decomposition. In this connection may be mentioned the new stability tests for gelatinized powders proposed by J. C. A. Simon Thomas,* R. Robertson,† A. Sy‡ and others.§ The difficulty, however, lies in determining what is to be regarded as a characteristic point in the course of the powder decomposition.

The explosion on the French battleship "Jena" on March 12, 1907, was due to a spontaneous ignition of the powder B caused by a decomposition of its nitrocellulose.|| The smokeless powder B used in the French navy is a nitrocellulose powder consisting in the main of 2 parts guncotton to 1 part collodion cotton, gelatinized with ether-alcohol. The ignition of the powder in a 10-centimeter cartridge magazine seems to have caused the explosion of the black-powder magazine and the ignition and detonation of the other magazines filled with powder B. The fire then spread to distant parts of the ship. The report of the senate commission ascribed the immediate cause of the catas-

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* J. C. A. Simon Thomas, Z. angew. Chem., **11,** 1027; 1898.

† R. Robertson, J. Soc. Chem. Ind., 819; 1902.

‡ A. Sy, J. Amer. Chem. Soc., 549; 1903.

§ Charles E. Munroe, The Development of Smokeless Powder, J. Am. Chem. Soc., **18,** 821–846; 1896. Also G. W. Patterson, Stability Tests of Smokeless Powder, Proc. VII Inter. Con. Appl. Chem., Section III B, 99–100; 1909.

|| Mar. Rund., **18,** 1166; 1907.

trophe to the fact that the magazine for the 10-centimeter cartridges, in which the powder B became ignited, was situated below a dynamo room in which the temperature was always very high, somewhere between 50° and 60° C. Since the refrigerating apparatus was not in use at the time the powder could have reached a high temperature. Moreover, 86 per cent of the contents of the magazine seem to have been an old powder whose chemical stability had been characterized in the last revision as doubtful.

3. *Nitrated aromatic compounds.*

210. Picric acid $C_6H_2(NO_2)_3OH$, which was discovered by Haussmann in the year 1788, was used as a natural dyestuff for silk and wool long before its important explosive properties were recognized. In the year 1873, H. Sprengel* called attention to the explosive property of picric acid and in 1886 E. Turpin † recommended the substance in a molten condition as a bursting charge for shells.

Picric acid is obtained by the nitration of carbolic acid. Equal quantities of carbolic acid and concentrated sulphuric acid are heated by steam to from 100° to 120° C. in iron vessels provided with a stirring apparatus. As soon as the mixture becomes easily soluble in cold water it is allowed to cool and twice the amount of water is added to it. The reaction product, phenol-sulphonic acid, is then poured into dilute nitric acid of about 60 per cent strength, contained in earthenware pots. At first the reaction proceeds very vigorously, accompanied by evolution of nitric-acid fumes.

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* H. Sprengel, J. Chem. Soc., London, **26**, 796; 1873. Dingler's pol. J., **212**, 332; 1874.

† E. Turpin, D. R. P., No. 38,734.

As soon as the reaction subsides the water surrounding the nitrating vessels is warmed by conducting steam into it. On cooling, the picric acid separates out in crystalline cakes. It is then separated from the mother liquor in centrifugal wringers, washed with warm water and recrystallized if necessary from hot water.

Picric acid crystallizes in bright yellow leaflets which are somewhat soluble in water and more easily soluble in benzene. It colors the human skin, as well as all animal tissues, an intense yellow. It has an extremely bitter taste and is poisonous. Picric acid melts at 122.5° C. without decomposing and this characteristic is taken advantage of in filling explosive bombs. Its specific gravity is comparatively high, being nearly 1.7. If ignited, picric acid burns slowly with a very smoky flame. It can be sublimed if heated carefully, while sudden heating may cause explosion. It is much less sensitive to shock, blow or friction than nitroglycerin or nitrocellulose. As an acid it combines with metals or basic compounds producing salts which, like lead picrate, are characterized by a high degree of sensitiveness (section 14), explode easily, and may act as an initial impulse for the picric acid itself, a characteristic which has sometimes led to accidental explosions of the acid.

The violent explosion of picric acid which occurred in Huddersfield on May 30, 1900, was undoubtedly caused by this initial effect of the picrates. A workman was repairing an iron steam pipe leading into the picric-acid drying room. 4600 kilograms of picric acid were contained in this and the two adjoining rooms, which were used for centrifuging and packing the explosive. While the workman was loosening the pipe from the wall with a chisel he noticed a spark leap suddenly from the pipe to the dry picric acid, which immediately ignited. The fire grew rapidly and, when, soon afterwards, the roof of the building fell in, a violent explosion occurred. The deep holes blown in the ground where the centrifugal packing rooms had been showed that a detonation had taken place there, while the picric acid in the drying house simply burned. There is no doubt that by the fall of the roof, metallic and earthy substances, especially lime from the mortar, brought into contact with the picric acid, reacted with it to form picrates whose explosion caused the detonation of the picric acid.* A. Dupré† investigated the initial effect of the picrates on picric acid. To determine this effect, he burned picric acid alone and then in mixtures or in contact with large quantities of iron, quicklime and chalk. Under the conditions of the experiments a simple combustion usually took place. Whenever combination between the picric acid and a base was established at a comparatively low temperature and then the temperature was suddenly raised, explosions of greater or less violence occurred in the whole mass.

On account of its pronounced acid character‡ picric acid, in the presence of moisture, decomposes nitroglycerin, nitrocellulose and even potassium nitrate, liberating nitric acid.§ On this account the explosive "Melinite," which was originally composed of picric acid and collodion cotton,|| was withdrawn after a short

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* Ann. Rept. H. M. I. Exp. 37; 1900.

† A. Dupré, Special Report No. 139, Appendix 2, to Ann. Rept. H. M. I. Exp. 23; 1900. Mem. poudr. salp., XI, part 2, 92.

‡ From the standpoint of electric conductivity picric acid is one of the strongest acids. W. Ostwald, Z. phys. Chem., **1**, 77; 1887.

§ M. Berthelot, Force mat. exp., II, 249; 1883.

|| E. Turpin, D. R. P., No. 38,734 of 1886.

time. Of the salts of picric acid, ammonium picrate has found application in ballistics. The products of the explosion of picric acid (section 128) correspond very closely to those of nitrocellulose.

As regards its chemical stability and the comparative infrequency of accidental explosions from it, picric acid, as a true nitro body, is far superior to the above-described nitric-acid esters, nitroglycerin and nitrocelluloses, while it is not inferior to them in explosive effect. Picric acid is used in explosive shells and, in the molten condition, in the filling for bombs. It forms the chief constituent of the French Melinite, the English Lyddite and the Japanese Schimose. The closely related cresylic acid is also used for similar purposes. Picric acid is transported in tight wooden boxes lined with paper. The presence of metals, especially lead, is forbidden.

211. Trinitrotoluene $C_6H_2CH_3(NO_2)_3$ is gaining steadily in importance among that class of explosives which indicate the gradual transition in technique from the sensitive explosive substances like nitroglycerin to the more resistant explosive substances like ammonium nitrate. It is already a component of many explosives and is also used alone, either pressed or fused, as charges for bombs.* The preparation of trinitrotoluene† is best carried on in three distinct steps. Toluene is first converted to the mononitrotoluene, which is then changed to dinitrotoluene by treatment with nitric acid and warming, and finally this is nitrated in sulphuric acid solution with strong nitric acid. One hundred parts of dinitrotoluene yield from 90 to 95 parts of trinitrotoluene, which is obtained as a mass of large

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* J. Rudeloff, Z. ges. Schiess Sprengstoffw., **2**, 4; 1907. R. Escales, ditto, **3**, 21; 1908.

† C. Häussermann, Z. angew. Chem., **4**, 508, 661; 1891.

radiating crystals melting at from 77° to 79° C. As obtained thus it is not entirely pure but sufficiently so to be used in technology.

Pure trinitrotoluene is at first of a light yellow color but it afterwards darkens to deep brown. It is only slightly soluble in water, better in alcohol, and dissolves with great rapidity in benzene with a lowering of temperature. Like picric acid, though not so pronounced, it colors the skin yellow. It is odorless and possesses no pronounced bitter taste. Pure trinitrotoluene melts at 81.5° C. with considerable increase of volume, but without decomposition. The specific gravity of trinitrotoluene, recrystallized from alcohol and dried, is 1.7, the same as picric acid. Unlike picric acid it does not form explosive salts with oxides of metals, a circumstance which greatly facilitates its application and handling.

On heating, trinitrotoluene ignites and burns rapidly with a very smoky flame. It has not been found to explode on heating in small quantities, but its near relation to picric acid indicates a similar behavior if large quantities are heated suddenly. It is only slightly sensitive to shock, blow or friction, but is brought to complete detonation by a detonator. On account of its comparative safety towards mechanical shocks its transportation by railroad is restricted by few conditions. In the products of its explosion trinitrotoluene resembles the nitrocelluloses of low nitration and picric acid.

4. *Guhr dynamite.*

212. Although nitroglycerin, under the designation "explosive oil," found ready application in explosive technology, yet its liquid condition was a serious hindrance to a more extended application on account of the inconvenience and danger attending its handling and transportation. In the year 1863, A. Nobel began to experiment with nitroglycerin with a view to the production of safe nitroglycerin cartridges by mixing it with such solid, porous substances, as black powder, charcoal, paper pulp, etc. By accident he discovered the excellent absorbent power of kieselguhr for nitroglycerin. In a shipment of nitroglycerin in metal cans, one of the cans sprang a leak and the nitroglycerin contents were completely absorbed by the kieselguhr in which the cans were packed. A. Nobel * named the mass prepared from nitroglycerin and kieselguhr "dynamite" and this designation has become general for all explosives composed of nitroglycerin and any absorbent material which prevents the nitroglycerin from dropping out.

Kieselguhr dynamite is prepared by mixing nitroglycerin and kieselguhr in the desired proportions. The most commonly used proportions are 3 parts nitroglycerin to 1 part kieselguhr, in the so-called 75 per cent guhr dynamite. The mass must be of the consistency of bread crumbs, after being repeatedly rubbed through wire sieves, which process insures a more complete homogeneity. The mass, so prepared, is put into presses and comes out in the form of cylinders which are cut into sticks, usually about 10 cubic centimeters in length by 19 millimeters in diameter, and which are immediately wrapped in paraffined or parchment paper.

Guhr dynamite is an odorless, yellow to brown, plastic mass of from 1.5 to 1.7 specific gravity. If ignited it burns with a rapid, luminous flame. In large quantities or under pressure the combustion may easily give rise

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* Engl. Pat. No. 1345 of 1867.

to an explosion, as the following accident shows. On Nov. 3, 1893, the Spanish steamer *Cabo Machichaco* arrived at the harbor of Santander with a cargo of about 2000 tons of iron, 1810 boxes of dynamite, many casks of petroleum, sacks of meal and other merchandise. Before the ship was docked a fire was discovered on board, and, despite the law to the contrary, it was brought closer in to shore. Thirty boxes of dynamite were quickly unloaded and carried to safety. A representative of the merchants replying to an inquiry, asserted that no more dynamite was on board. In the meantime, the fire increased rapidly in violence and a large number of spectators gathered on the dock to witness the unusual sight of a burning ship. About two and a half hours after the fire was discovered a fearful explosion occurred. Pieces of iron were thrown in all directions with such force that 510 persons were killed, and about one thousand more or less seriously injured, to say nothing of serious damage done to surrounding buildings.*

As regards sensitiveness towards shock and friction, guhr dynamite has little advantage over nitroglycerin itself and in other respects shares it properties. Among the latter may be mentioned its tendency to freeze, which, in a large measure, robs it of one of its greatest advantages, viz., its plasticity and flexibility in the bore hole, and, furthermore, makes its detonation uncertain. Moisture is injurious to guhr dynamite because it displaces the nitroglycerin and sets it free. It is, therefore, not suitable for wet bore holes. The importance of guhr dynamite has greatly decreased since the more powerful gelatinized dynamite (section 214) has

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* Ann. Rept., H. M. I. Exp., 55; 1893.

gained prominence in nearly all fields of explosive technology.

The transportation by rail of guhr dynamite, as well as that of all other explosives containing nitroglycerin, requires the observance of very strict regulations. The cartridges must be made into packages wrapped with strong paper. The packages are then to be packed tightly in strong wooden boxes or casks, containing at most 25 kilograms of dynamite in 10 packages. The joints of this container must be strengthened with iron hoops or bands and fit so closely that nothing can escape from the contents. The containers, whose gross weight must not exceed 35 kilograms, must be marked "Dynamite" and must bear a tag giving the contents and factory mark.

Legislation has been especially directed to guhr dynamite as a representative of all brisant substances. In the beginning of the year 1880, when dynamite attacks by anarchists were common in Belgium, England and Germany, the German government decided to put the dangerous handling of dynamite and similar explosives under police supervision and make its unlawful handling a criminal act. The result was the law of June 9, 1884, "gegen den verbrecherischen und gemeingefährlichen Gebrauch von Sprengstoffen." According to this law, whoever is engaged in the manufacture or sale of explosives must keep a register, in which may be seen the quantities of explosives manufactured, brought in from foreign countries, or in any other way obtained for the purposes of business, as well as the market in which they were bought and the length of time they are kept on hand. Whoever violates this law by preparing, importing, having for sale, selling or otherwise supplying to another, explosives without police authority; or whoever is found *in possession of such explosives without being able to prove the permission of the police* shall be punished by imprisonment for not less than three months nor more than two years.

5. *Explosive gelatin.*

213. In the course of experiments to find a more suitable absorbent for nitroglycerin than kieselguhr, A. Nobel* discovered, in 1875, that a certain kind of collodion cotton even in small quantities can transform liquid nitroglycerin to a gelatinized mass which is a much more powerful explosive than guhr dynamite, leaves no solid residue on explosion and yields no nitroglycerin in the presence of moisture. This preparation was the so-called "Explosive gelatin."

Explosive gelatin consists of from 90 to 93 per cent nitroglycerin and from 7 to 10 per cent of a special kind of collodion cotton. These are united by warming and stirring into a homogeneous, transparent and elastic gum. An idea of the nature of this preparation may be gained by dissolving 0.2 gram agar-agar in 7.8 grams glycerin on a water bath, stirring it well together and letting it cool. There is thus obtained a mass which may be drawn out to threads while warm, but is elastic when cold. In appearance this mass is quite similar to gelatin dynamite and the two components are probably united in the same way in both It is probably a kind of solution, as is indicated by the fact that the collodion cotton required must conform to very well-defined specifications.

Explosive gelatin is one of the most powerful of explosives and is, therefore, suited for shattering very

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* Engl. Pat. No. 41,791.

solid and tenacious material. It is much less sensitive to shock and friction than guhr dynamite; in fact, the addition of a few per cent of camphor produces almost complete loss of sensitiveness (section 16). The products of the explosion of explosive gelatin are carbon dioxide and water only. This explosive, however, like guhr dynamite, has been obliged to give way to the more modern gelatinized dynamites, especially in mining, because, on account of its elastic character, it does not completely fill the bore hole, and, moreover, it is too shattering in its action. The peculiar combination between nitroglycerin and nitrocellulose which characterizes explosive gelatin appears again in the newer gelatinized dynamites.

6. *Gelatin dynamite.*

214. Gelatin dynamite, in its various forms, is at present the most important of all the nitroglycerin explosives. It has gained this importance on account of the ease with which it is handled, the good results obtained by its use and its comparatively small cost. The composition of gelatin dynamite varies within wide limits, so that in consistency and plasticity it may be made to suit all purposes. One much-used gelatin dynamite has the following composition:

62.5 per cent nitroglycerin } gelatinized;
2.5 per cent collodion cotton }
25.5 per cent sodium nitrate;
8.7 per cent meal;
0.8 per cent soda.

Many gelatin dynamites contain potassium nitrate in place of sodium nitrate (English Gelignite). Ammonium nitrate is also sometimes employed as in the following ammon-explosive gelatin:

40–50 per cent gelatinized nitroglycerin;
46–55 per cent ammonium nitrate;
3.5–5 per cent meal;
0.5 per cent soda.

In the preparation of gelatin dynamite, nitroglycerin is first thoroughly mixed with the required quantity of collodion cotton in kneading machines. The other components, thoroughly mixed together, are then added and the kneading process is continued. The mass is then molded into sticks or cartridges in the same manner as guhr dynamite. Since gelatin dynamites absorb some moisture, especially those kinds which contain hygroscopic nitrates, it is immediately wrapped in water-tight paraffined paper.

7. *Blasting powder.*

215. According to O. Guttmann* the first record of the use of explosives in mines is found in the minutes of the Chemnitz Berggerichtsbuch of Feb. 8, 1627, according to which a Tyrolean, named Kaspar Weindl, on that day employed the first blasting charge in Ober-Biberstollen in Hungary. For two hundred years, black powder was the only explosive used for blasting. In more recent times nitroglycerin, guncotton and picric acid in quick succession have forced black powder into a subordinate position.

Blasting powder contains less nitrate and, in its place, more charcoal than black powder. Its composition is from 65 to 75 per cent potassium nitrate, from 10 to 15 per cent sulphur and from 15 to 20 per cent charcoal. For the sake of economy the cheaper sodium

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* O. Guttmann, Schiess- und Sprengmittel, 6; 1900.

salt[*] is also used in place of potassium nitrate, as in explosive saltpeter, petroclastite, bobbinite and similar modifications of blasting powder.

8. *Chlorate powder.*

216. As a further substitute for black powder, chlorate powders are sometimes used. These contain potassium chlorate in place of potassium nitrate, as in rackarock. These powders have received little attention on account of their greater sensitiveness towards shock and friction. In more recent times, however, the preparation of chlorates and perchlorates by electrical methods[†] has made these substances easy to obtain and it has been discovered that the addition of fatty oils to chlorate mixtures decreases their sensitiveness.

The explosives prepared by the method of Street[‡] consist principally of potassium chlorate intimately mixed with aromatic nitro compounds with the aid of vegetable or animal oils. The nitro bodies are first dissolved in the oil by warming it and while still warm the finely pulverized chlorate is mixed in until the mixture becomes cool. By this treatment every small chlorate particle becomes coated with a plastic covering which suffices to modify to a considerable degree the sensitiveness of the chlorate mixture towards mechanical, chemical and thermal influences. When finished this powder appears as a yellow pulverulent mass, and

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[*] This is almost exclusively used in blasting powder in the United States and particularly because it is a more efficient oxidizing agent (Trans.).

[†] See Handb. phys. Chem., Vol. I. F. Foerster, Elektrochemie wäss. Lösungen, 382; 1905.

[‡] D. R. P., No. 100,522 of 1897. Z. ges. Schiess Sprengstoffw., **1**, 125; 1906.

by slight pressure it can be compressed to tenacious, somewhat plastic cartridges. Explosives containing chlorate salts were formerly excluded from transportation, but they are now admitted under certain conditions.

9. *Safety explosives.*

217. The first attempts to eliminate accidents due to fire damp in mines were directed simply towards a thorough ventilation of the mine in order to remove all combustible gases. When, in 1816, H. Davy recommended, in place of the open miner's-lamps, the safety lamp, whose efficiency depends upon the principle that flame does not easily penetrate through a fine wire gauze, it was believed that all danger of accidents from fire damp was removed. The increasing use of explosives in mines, however, soon made it apparent that fire damp may also be ignited by the flame from an explosion and renewed attempts were made to meet this new source of danger. These attempts were directed towards increasing the safety of explosives to be used in mines. In the year 1876, an Englishman, J. Macnab, proposed the use, as stemming, of a cartridge filled with water, instead of the usual red-clay, to be used with charges of black powder to extinguish the flame of explosion. M. Settle perfected the form of the water cartridge by inclosing the real explosive cartridge in a larger water container, so that the pressure of the explosion is transmitted equally in all directions to the rock or coal through the water as the medium. Further experiments were directed towards eliminating the flame of explosion by the use of an extra cartridge filled with salts containing water of crystallization, such as crystallized soda. The idea was that the water of

crystallization would be driven from these salts by the heat of the explosion and so cool the flame. From the use of an extra cartridge containing salts having water of crystallization to the idea of incorporating such salts with the explosive itself in order to moderate the temperature of explosion was but a short step. The so-called "Wetter-dynamite," formed in this way, has been in use since 1887.*

Statistics prove that the number of fatal accidents due to the explosion of fire damp has steadily decreased in consequence of these precautionary measures.

TABLE 54. STATISTICS OF ACCIDENTS DUE TO FIRE DAMP.

(Number of deaths to each 10,000 miners due to explosions of fire damp in Belgium.)

Years.	No.
1831-40	9.65
1841-50	7.64
1851-60	4.28
1861-70	3.44
1871-80	4.87
1881-90	3.64
1891-1900	2.08
1901-1904	0.39

The following percentage of explosions of fire damp were due:

	To the safety lamp, percentage.	To the explosive, percentage.
1821-50	58	22
1851-80	52	37
1881-90	28	64

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* E. Müller, Engl. Pat. No. 12,424 of 1887.

While the larger number of the earlier explosions of fire damp was due to a careless use of safety lamps and the explosives themselves were not so frequent a cause of accidents, this relation has gradually been reversed. Since the year 1890, however, the relation has again changed in favor of the explosives, so that during the years 1891–1900, 1.63 of the 2.08 fatal accidents to each 10,000 miners were due to the lamps and only 0.45 to explosions caused by the mining operations.

218. At present the term safety explosives is used to designate solid or plastic explosive mixtures which possess a satisfactory degree of safety towards fire damp. They are frequently characterized also by great safety in handling, since they require a powerful initial impulse to bring about the explosive reaction. A more detailed description of safety explosives is most conveniently given by dividing the explosives into three groups corresponding to their various compositions, under the collective names: (*a*) Ammonite, (*b*) Carbonite, (*c*) Wetterdynamite. Of course there are transition types which do not belong strictly to any one group.

(*a*) *Ammonite.*

219. Ammonite, or more strictly speaking, ammonium-nitrate explosives consist mainly of explosives containing from 70 to 95 per cent of ammonium nitrate, besides combustible components, which are so-called carbon carriers, such as resin, meal, naphthalene. Other nitrates, such as sodium nitrate, or certain salts, such as potassium bichromate, which increase the safety of the mixture towards fire damp, are often found as components. The Köln-Rottweiler safety explosive, for instance, is a mixture of 93 per cent ammonium nitrate, 4.9 per cent linseed oil, 1.2 per cent sulphur and 0.9 per

cent barium nitrate. In the preparation of this explosive, the previously very finely pulverized components are first mixed by hand, then for a longer time in wooden drums and finally compressed in wheel mills or hydraulic presses. The cakes are then dried and broken up in graining machines. The grains are then passed through a fine-meshed sieve and packed in cartridge paper which is covered with tin foil to protect the cartridge from moisture.

Ammonites are comparatively insensitive to mechanical shock. Sparks or flames do not cause explosion so long as priming substances, especially detonators, or other explosives, are not in the vicinity. The hygroscopic character of ammonium-nitrate explosives is a disadvantage to this group. On this account these explosives must be especially well packed and must not stand too long in moist magazines, as they will absorb moisture and lose their explosive property.

These explosives possess in general a sufficiently high degree of safety. The transportation of ammonites is not subject to any restrictions. They are received by railroads as "goods in parcels."

(*b*) *Carbonite.*

220. The carbonites, under which term the ammonium carbonites and safety gelatin dynamites may also be classed, constitute a peculiar class of explosives which is characterized by its composition as well as by an exceptionally high degree of safety towards fire damp. Besides various nitrates and combustible components, they contain explosive substances, especially nitroglycerin. The "Kohlenkarbonite," as the oldest and safest of this class of explosives, deserves especial mention. This is a gray mass having the odor of bread dough and the composition 25 per cent nitroglycerin, 34 per cent potassium nitrate, 39.5 per cent meal, 1 per cent barium nitrate, 0.5 per cent soda.

In the preparation of this explosive, the potassium nitrate and meal are first mixed, after carefully drying and pulverizing each component. The following mixing is carried out in specially constructed mixers in which the dry powder is being mixed by revolving fans. When completed the mass is pressed into the form of cartridges.

The carbonites and the closely related safety explosives are distinguished from the ammonites by their sensitiveness to violent mechanical impulses and hence require relatively careful handling. They are also subject to freezing on account of the nitroglycerin they contain. On the other hand, they are characterized by a high degree of safety towards fire damp, which property has made them indispensable in mines containing combustible gases.

(c) *Wetterdynamite.*

221. Under the name "wetterdynamite" was understood originally only guhr dynamites to which were added salts containing water of crystallization, such as Glauber's salts, magnesium sulphate, ammonium oxalate, etc., with a view to making them available in mines containing fire damp. A wetterdynamite still used in England has the composition 31 to 34 per cent nitroglycerin, 11 to 14 per cent kieselguhr, 47 to 51 per cent magnesium sulphate, and 4 to 6 per cent of potassium nitrate. The safety as well as the explosive effect of this dynamite is hence comparatively low, and, in comparison with the above-mentioned classes of safety explosives, its use has steadily decreased. Nevertheless, it is well worth mentioning in view of the possible development of the idea that a part of the heat of explosion is transformed into a usable form of energy through the vaporization of water of crystallization.

10. *Hints on the handling, application and destruction of explosives.*

222. *Safety regulations in the manufacture of explosives.* To avert disasters as far as possible the manufacture and storing of explosives are conditioned on official permission which is given only after careful consideration of all conditions essential to safety. A most essential precaution is to separate the various factory buildings by a sufficient distance from each other as well as from inhabited houses, streets and roads (sections 149 to 151).

In Austro-Hungary the buildings of a factory for the manufacture of explosives are divided into various danger classes and the distance of isolation of a particular building depends upon the class to which it belongs. The first group includes buildings for the preparation of the raw materials; the second includes those buildings in which the explosive is prepared; the third, those in which the cartridges are made and packed; the fourth, the magazines for the finished powder; and the fifth, inhabited houses. The buildings of the first three groups must be at least 50 meters from each other and from any other building, and those of the last two groups at least 200 meters from each other and from any building of the other groups. Magazines with a capacity of 10,000 kilograms must be at least 200 meters from each other. All factory buildings which contain explosives must be at least 500 meters distant from any little-used public road or street and at least 1000 meters from frequently used roads, railroads, canals or inhabited houses. In Great Britain, the home of such regulations, the distances for various classes of buildings are still more strictly prescribed. Magazines with 10,000 kilograms' capacity must be 100 meters from public streets, 300 meters from a public railroad and 800 meters from a public building.

Further regulations for the safety of large quantities of explosives are directed towards the building material, construction and other architectural details of the buildings themselves.* These must be supplied with lightning rods, and, as a rule, should be constructed of a material which will fall to powder in case of an explosion instead of breaking into large pieces, since the latter would constitute a danger to houses in the neighborhood. Hard gypsum, gravel cement and sandstone fulfill such conditions. The magazines are usually surrounded by a wall of earth reaching somewhat higher than the ridge of the roof and about 0.5 meter thick at the top. Electric incandescent lamps are used almost without exception for illuminating purposes. Of course even this comparatively harmless method of lighting is not exempt from the usual regulations for illuminating apparatus.

A glance at the English statistics† shows that the safety regulations in force have been very effective. On the basis of the number of persons employed in "danger" buildings the number of accidents from explosions has steadily decreased (Fig. 45). Accidents resulting from the actual preparation of explosives are

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* See also O. Guttmann, Z. ges. Schiess Sprengstoffw., **3**, 266; 1908. J. Soc. Chem. Ind., **27**, 669; 1908. R. Feuchtinger, Spreng- und Zündmittel-mag., 1907. W. Waldmann, Mitt. Art. Geniew., 777; 1908.

† Ann. Rept. H. M. I. Exp., 10; 1905.

included in this calculation and it is noticeable that no deaths have resulted from this cause.

223. Definite statements as to the effect produced by a given explosive cannot as a rule be made. The course of the explosive reaction and, more especially, the velocity of the pressure development are dependent not only upon the chemical and physical character of the explosive itself, but to just as great an extent upon the character of the surrounding medium whose resistance is to be overcome. The work done by a given explosive may vary considerably according as it may be used for the destruction of elastic wood or tough iron, or for explosion in the unconfined condition in the open air or from a cartridge with considerable density of loading. Simply to give an idea of the relation between the amount of explosive used and the effect produced, it may be mentioned that the records of the construction of the St. Gothard tunnel in the year 1880 show that about 1 kilogram of explosive was used to each 1000 kilograms of rock blasted. The rock was a medium hard gneiss-granite. About 3.3 kilograms of guhr dynamite were required for each cubic meter of stone and only about 2.3 kilograms of the

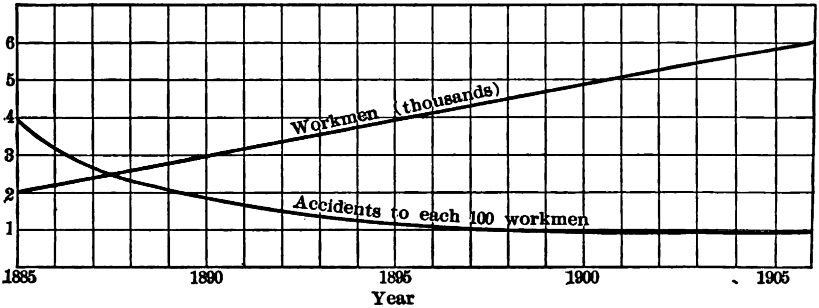

FIG. 45.

more powerful explosive gelatin. The actual utilization of the potential energy in an explosive is, as a rule, surprisingly small. It is calculated at about 15 to 20 per cent of the theoretical amount under the most favorable circumstances. Only under exceptionally favorable conditions, such as in the bursting of large closed masses of iron, like the so-called sow of melted iron in a blast furnace, can so much as one-third of its theoretical amount of energy be utilized. Propellants, likewise, give but slightly better results. For instance, the utilizable energy of a projectile at the mouth of a gun barrel is at most 35 per cent of the energy existent in the powder. The limit of the utilization of our materials for the purpose of application to mechanical work is about 32 per cent (in the Diesel motor).

The importance of explosives for technical purposes, the possibility to perform tasks with their help which would either be impossible with other means or at least would be performed only at enormous cost of time and money, cannot be better expressed than by giving a few examples of feats which have actually been accomplished with their aid. Cases similar to the following examples have become almost weekly occurrences on our globe.

There is a shoal in the East Sea between the Bornholm and Rugen Islands known as the "Adlergrund," which is formed by old glacial boulders lying on the bottom of the ocean. To deepen the shallowest places the Prussian government took up many of the stones by means of cranes from ships. Divers went down and fastened chains or grappling hooks on the stone blocks by which they were drawn up. To break up the heaviest boulders and thus facilitate the hoisting, charges of 10 kilograms of guncotton each were often detonated on the ocean floor at depths of from 4 to 6 meters. Each explosion broke up from two to four blocks of stone about 2 cubic meters in size and loosened them completely from their bed, so that they could easily be drawn up.*

One of the greatest triumphs of explosive technique was the shattering of Flood Rock, a large submarine rock near New York Harbor which seriously hindered navigation. The mass of rock to be removed covered an area of about 4½ hectares and had a cubical content of about 1.8 million cubic meters. In preparation the rock was undermined throughout. Two shafts were first sunk to the depths of about 20 meters and from these shafts horizontal passages were bored sometimes parallel and sometimes crossing each other at right angles. Some of these passages reached over 300 meters in length and the total length of all was about 6500 meters. 467 pillars, 25 square meters at the base, were left standing as supports for the huge mass of rock above, about 4 to 6 meters thick. Finally, on the 10th of October, 1885, these pillars were suddenly blown out, all at one time. The sea was lifted over a space 400 meters long and 250 meters broad, to heights as great as 60 meters. Although detonation was accomplished electrically, exploding all the mines at the same instant, three separate shocks were felt, corresponding to the three media, water, air and earth, in which the explosive waves were propagated with different velocities. 109,000 kilograms of rackarock and 34,000 kilograms of guhr dynamite were used. It should be mentioned that the direct initial impulse by means of detonators was in this case supplemented by the method of detona-

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* M. v. Förster, Komprimierte Schiesswolle, 24; 1886.

tion by influence for the purpose of limiting the number of electric wires as much as possible.*

During a severe winter, masses of ice averaging from 18 to 20 centimeters in thickness collected in the Rhone River just above Lyons. It became necessary to break up the ice field to allow free passage to the water and to prevent floods in case of a sudden thaw. A number of dynamite cartridges covered with clay were exploded on the surface of the ice but did not produce the desired effect. Trenches were then dug in the ice about 14 meters from the edge of the floe and measuring about 1 meter in length and 4 to 5 centimeters in depth. These were filled with about 210 grams of dynamite, which was covered with a layer of sand about 4 to 5 centimeters thick, and exploded. Immediately after the explosion cracks of from 40 to 50 meters long appeared in the ice. One of these was 220 meters long. But even this did not succeed in removing the ice jam. Holes of 8 to 10 centimeters in diameter were then bored in the ice and dynamite cartridges of from 17 to 30 grams in weight were sunk until about 70 centimeters below the surface of the ice. In this way, 50,000 square meters of ice were removed daily without difficulty.†

On March 29, 1885, the steamer "Leader," a vessel 86 meters long, 11 meters wide and 1100 tons register, stranded in the river Scheld just above the harbor of Antwerp. After fruitless efforts to extricate her, she broke in two. Although the wreck was not in the navigable channel it constituted a danger to navigation because it turned the course of the water and caused a deposit of sand in the channel itself. Hence, it became necessary to remove the wreck without delay. It was

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* P. Chalon, Exp. mod., 307; 1889.

† Ibid., 334; 1889.

broken up, a piece at a time, with charges of explosives, not exceeding 25 kilograms in weight out of consideration of the nearness of the city. A total of 2008 kilograms of gelatin dynamite was used, making the total cost of the work, including the wages of 45 days' work, about 9000 marks. In consequence of the continued blasting, at the spot where the ship sank, the bed of the river was lowered 9 to 10 meters.*

On Sept. 16, 1898, the steamer "Milwaukee," a great cattle transport of 7300 tons register, stranded during a fog on the rocks near Aberdeen. The ship carried water ballast and drew only 10 feet of water at the bow but 20 feet at the stern. Consequently, the bow projected considerably higher out of the water than the stern and the ship began to glide along the rocks. The bow was torn open by the rocks for a distance of 80 feet, while the stern was jammed fast between the rocks. This more valuable hind part of the ship with its boilers and machinery remained in good condition and it was decided to separate it from the forward part and save it if possible. The steamer, which was 470 feet long and 56 feet wide, was cut in half amidships by detonating a string of dynamite cartridges placed against the iron plates and stays. In all, 850 kilograms of dynamite were used in from 50 to 60 separate charges. After the explosion the forward part of the ship was left to the action of wind and wave, while the hind part was pulled off and landed safely in dock on Oct. 4, 1898. In this way about $200,000 out of a total value of $375,000 was saved.†

In 1876, a blast furnace in Schwechat had to be blown

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* P. Chalon, Exp. mod., 277; 1889.

† From the Book of High Explosives of the Nobel Explosives Co., p. 57.

open because a sow of iron of unusually large dimensions had formed in it. Its lower semicircular part was made of unusually tough iron, almost as hard as bessemer steel. This part was 4 meters in diameter and its walls were 0.65 meter thick. The upper cylindrical part of the furnace contained a mixture of iron, slag, stone and graphite and was 2.15 meters high by 2.45 meters in diameter. As this upper part was not valuable it was desired to remove it from the lower part as quickly as possible, so that the valuable material of this lower part could be regained for further use. In consideration of the blast furnace itself and the close proximity of other buildings and machinery it was decided to use repeated small charges of explosives. Nineteen holes, 25 centimeters deep, were bored in the iron mass, loaded with 55 grams gelatinized dynamite and fired in groups. The sow iron, broken from above, filled up the holes so that most of them had to be rebored. The same holes were loaded repeatedly, some as many as five times, with from 187 to 300 grams and detonated in groups until the iron mass was sufficiently broken up to be removed in pieces. The pieces of valuable iron had a total weight of 135,000 kilograms. In all, 32.5 kilograms explosive were employed at a total cost of only about 500 marks.*

11. *Destruction of explosives.*

224. Explosives require constant supervision, otherwise they constitute a danger, and for this reason it is expedient to destroy all factory waste, odds and ends of explosives, sweepings, etc., which contain explosive

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* Mahler and Eschenbacher, Die Sprengtechnik, 82; 1881.

† F. Heise, Spreng. Zund. Spreng., 126; 1904. Mem. poudr. salp., I, Part Two, p. 44; 1882–83. Ann. Rept. H. M. I. Exp.

substances. The method to be used must depend on the character of the explosive to be destroyed.

Black powder is best stirred with water, which dissolves out the saltpeter.

Smokeless powders should be strung out in a long, thin line and ignited at one end with a fuse or match. Nitrocellulose is destroyed in a similar way.

Water is not a suitable means by which to destroy dynamites of any kind, since it liberates the nitroglycerin, which, under certain conditions, may become very dangerous. Small quantities of dynamite may be destroyed by throwing it in a fire, a small piece at a time. Whole cartridges of dynamite are stripped of their paper wrapping, laid end to end and ignited at one end with a fuse. Since there is a possibility of an explosion in such cases the operator should withdraw to a safe distance. This method should be used only in still, dry air. Nitroglycerin itself is most easily destroyed by treating it with alcoholic caustic soda, which decomposes it. Explosives which contain ammonium nitrate and no nitroglycerin are thrown into water or burned piece by piece in a fire.

Detonators are best destroyed by exploding them with a fuse.

The elimination or destruction of mercury fulminate waste in igniter and detonator factories is sometimes attended with difficulties. The following accident is recorded in the yearly report of the Employers' Association for Chemical Industries for 1905 (Jahresbericht der Berufsgenossenschaft fur die Chemische Industrie). The waste detonators were thrown for months at a time into stoneware jars filled with sodium sulphide solution, with the idea that the mercury fulminate would be decomposed and rendered harmless. While the jar was being emptied into a drain, however, an explosion occurred which killed the workman who was emptying it. The directors' report of the Employers' Association for the year 1891 has already called attention to the danger of putting mercury fulminate in contact with alkaline substances, such as sodium sulphide, owing to the formation of explosive sodium compounds. The technical board of supervisors, because of such accidents, have investigated the question of the destruction of waste detonators and have come to the conclusion that the old method of boiling the fulminate salts with water is to be recommended. This decomposes the mercury fulminate, and the potassium chlorate can easily be separated from the mercury sulphide. The boiling must be continued for some time, because the decomposition of the compressed fulminate salt is naturally slower than the destruction of the waste matter from the manufacture of mercury fulminate. After sufficient boiling the caps must be burned separately in order to make certain of the complete destruction of all traces of explosive salts.

225. The most important explosives are classified according to their composition and characteristics in Tables 55 and 56.

TABLE 55. COMPOSITION AND CHARACTERISTICS OF IMPORTANT EXPLOSIVES (NOT INCLUDING "SAFETY EXPLOSIVES").

Class.	Characteristics.	Designation.	Composition.
Black powder....	Explosives which do not require a detonating cap.	Sprengpulver....	65–75% KNO_3, 10–15% sulphur, 15–20% charcoal.
		Sprengsaltpeter..	76% $NaNO_3$, 10% sulphur, 14% charcoal.
		Petroklastit.....	69% $NaNO_3$, 5% KNO_3, 10% sulphur, 15% (hard) coal tar, 1% potassium bichromate.
		Haloxylin.......	75% KNO_3, 15% sawdust, 8% wood charcoal, 2% potassium ferricyanide.
		Lithofracteur....	77% $Ba(NO_3)_2$, 2% KNO_3, 21% wood charcoal.
Guhr dynamite...	Explosives with nitroglycerin in an ungelatinized condition.	Dynamite I.....	75% nitroglycerin, 25% kieselguhr.
		Dynamite II....	18% nitroglycerin, 72% KNO_3, 10% wood charcoal.
		Rhexite.........	64–67% nitroglycerin, 18% $NaNO_3$, 11% decayed wood, 4–7% wood meal.
		Dynammon.....	45% nitroglycerin, 47.2% NH_4NO_3, 7.8 lignite.
....	....	Explosive gelatin.	90–93% nitroglycerin, 7–10% collodion cotton.
Gelatin dynamite.	Explosives with nitroglycerin in gelatinized condition, with an admixture.	Gelatin dynamite.	62.5% nitroglycerin, 2.5% collodion cotton, 25.5% $NaNO_3$, 8.75% meal, 0.75% soda.
		Gelignite........	54–63% nitroglycerin, 3–5% collodion cotton, 26–34% KNO_3, 6–9% wood meal, 0.5% chalk.
		Ammon-Sprenggelatin..	38–47% nitroglycerin, 2–3% collodion cotton, 46–55% NH_4NO_3, 3.5–5% dry meal, 0.5% soda.
....	Explosives with trinitrotoluol.	Donarite........	80% NH_4NO_3, 3.8% nitroglycerin, 0.2% collodion cotton, 12%trinitrotoluene, 4% meal.
		Permonite.......	42.5% NH_4NO_3, 32.5% potassium perchlorate, 10% trinitrotoluene, 10.5% starch meal, 3% wood meal, 1.5% moisture.
Ammonite.......	Ammonium nitrate explosives without addition of nitroglycerin.	Sekurite.........	37% NH_4NO_3, 34% KNO_3, 29% mono- and dinitrobenzene.
		Gestensroburite..	82.5% NH_4NO_3, 17.5% dinitrobenzene.
		Dynammon I....	88% NH_4NO_3, 12% lignite.
Ammonale.......	Ammonium nitrate explosives with addition of powdered aluminum.	Ammonal.......	72% NH_4NO_3, 23.5% powdered aluminum, 4.5% lignite.
		Anagon-explosive powder.	84.5% NH_4NO_3, 1.5% KNO_3. 8% wood charcoal, 5.5% powdered aluminum, 0.5% $Ba(NO_3)_2$.
Cheddite.........	Explosives with potassium chlorate.	Cheddite........	80% $KClO_3$, 10% nitronaphthaline, 20% dinitrotoluene, 8% castor oil.
		Selesia A........	75% $KClO_3$, 25% nitrated resin.
....	....	Oxyliquit.......	80% liquid air, 10% burnt cork, 10% paraffin.

TABLE 56. COMPOSITION AND CHARACTERISTICS OF IMPORTANT SAFETY EXPLOSIVES.

Class.	Characteristics.	Designation.	Composition.
Ammonite	Powerful explosives not sensitive to shock. Do not freeze. Hygroscopic. Comparatively safe.	Dahmenit A	91.3% NH_4NO_3, 6.5% naphthalene, 2.2% potassium bichromate.
		Roburit I	87.5% NH_4NO_3, 7% dinitrobenzene, 0.5% potassium permanganate, 5% ammonium sulphate.
		Westfalit	91% NH_4NO_3, 4% KNO_3, 5% resin.
		Antigrisou Favier II	80.9% NH_4NO_3, 11.7% dinitronaphthalene, 7.4% salammoniac.
Ammonkarbonite.	Explosives whose properties are intermediate between ammonites and carbonites.	Ammonkarbonite.	82% NH_4NO_3, 10% KNO_3, 3.8% nitroglycerin, 0.2% collodion cotton, 4% meal.
		Grisoutine B	88% NH_4NO_3, 11.75% nitroglycerin, 0.25% collodion cotton.
Karbonites and safety gelatin-dynamites.	Explosives of moderate power, stable, but freeze. Very safe.	Kohlenkarbonit	25% nitroglycerin, 34% KNO_3, 39.5% meal, 1% $Ba(NO_3)_2$, 0.5% soda.
		Phoenix I	30% nitroglycerin, 32% $NaNO_3$, 38% rye meal.
		Safety gelatin dynamite II.	29.6% nitroglycerin, 0.4% collodion cotton, 32% NH_4NO_3, 6% KNO_3, 10% soap, 17% rye meal, 3% liquid carbohydrates, 2% wood meal.
		Gelatin carbonite.	25.3% nitroglycerin, 0.7% collodion cotton, 6.9% (Leimglycerin) gelatin.
		Nobelite	25.6% salt, 41.5% NH_4NO_3, 28% nitroglycerin, 0.7% collodion cotton, 11% dextrine, 0.5% wood oil, 39.7% NH_4NO_3, 2.5% wood meal, 17.6% salt.
Wetter dynamite.	Explosives of comparatively low power. Freeze. Not sufficiently safe in fire-damp.	Wetter-dynamite	52% nitroglycerin, 13% kieselguhr, 35% crystal soda.
		Grisoutine D	40–45% nitroglycerin, 10–12% kieselguhr, 42–49% crystal magnesium sulphate, 1% soda.
		Grisoutite	42–46% nitroglycerin, 9–12% wood meal, 44–46% crystal magnesium sulphate.
		Nobel's Ardeer powder.	31–43% nitroglycerin, 11–14% kieselguhr, 4–6% KNO_3, 47–51% crystal magnesium sulphate.

A LIST OF REFERENCES REPEATEDLY CITED WITH THEIR CORRESPONDING ABBREVIATIONS.

ABBREVIATION.	TITLE.
All. Chem. Kol.	Allgemeine Chemie der Kolloide. A. Müller.
Ann.	Annalen der Chemie. Liebig.
Ann. chim. phys.	Annales de chimie et de physique.
Am. J. Sci.	American Journal of Science.
Ann. mines	Annales des mines.
Ann. Physik	Annalen der Physik. Poggendorf.
Ann. Phys. Chem.	Annalen der Physik und Chemie.
Ann. Rept. H. M. I. Exp.	Annual Report of H. M. Inspectors of Explosives.
Arms Exp.	Arms and Explosives.
Art. Exp.	Artillery and Explosives. Noble.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Kon. angew. Chem.	Berichte V internationaler Kongress für angewandte Chemie.
Bull. acad. Roy. Belg.	Bulletin academie Royale Belgique.
Bull. soc. chim.	Bulletin de la société chimique de France.
Chem. Dyn.	Studien zur chemischen Dynamik. Cohen.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News and Journal of Physical Science.
Chem. Stat. Dyn.	Chemical Statics and Dynamics. Mellor.
Chem. Zentr.	Chemisches Zentralblatt.
Chem. Ztg.	Chemiker-Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des séances de l'academie des sciences.
Dict. Exp.	Dictionary of Explosives. Cundill-Thomson.
Dict-aire exp.	Dictionnaire des explosifs. Désortiaux.
Dict. mat. exp.	Dictionnaire des matières explosives. Daniell.
Dingler pol. J.	Dingler's polytechnisches Journal.
Dynam. chim.	Etudes de dynamique chimique. van't Hoff.

Abbreviation.	Title.
Exp. mod.	Explosifs modernes. Chalon.
Exp.-stoff. Verbren.	Explosivstoffe und Verbrennungsmotoren. Jüptner.
Force mat. exp.	Sur la force des matières explosives.
Gas. Method	Gasometrische Methoden. Bunsen.
Gesch. Exp.	Geschichte der Explosivstoffe. Romocki.
Glückauf	Glückauf, Berg- und Hüttenmännische Zeitschrift.
Grisou	Le grisou.
Handb. Feuer. Exp.	Handbuch zur Erkennung, Beurteilung und Verhütung der Feuer- und Explosionsgefahr.
Handb. Phys. Chem.	Handbuch der angewandte physikalische Chemie.
H. ber. P. S. Kom.	Hauptbericht der Preussischen Schlagwetter-Kommission.
Ind. Exp.	Industrie der Explosivstoffe. Guttmann.
Inn. Ball.	Innere Ballistik. Brinck.
J. Am. Chem. Soc.	Journal of the American Chemical Society.
J. Chem. Soc.	Journal of the Chemical Society, London.
J. Gas. Wasser	Journal für Gasbeleuchtung und Wasserversorgung.
J. prak. Chem.	Journal für praktische Chemie.
J. russ. phys. chem. Ges.	Journal of the Russian Physical-Chemical Society.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Kriegtech. Z.	Kriegstechnische Zeitschrift.
Lehre Schuss.	Lehre vom Schuss. Heydenreich.
Lehrb. allg. Chem.	Lehrbuch der allgemeinen Chemie.
Mar. Rund.	Marine Rundschau.
Mat. exp.	Matières explosives. Gody.
Mech. chim.	Essai de mécanique chimique.
Mem. poudr. salp.	Mémorial des poudres et salpetres.
Mitt. Forsch. Ingen.	Mitteilungen über Forschungsarbeiten auf dem Gebiete des Ingenieurwesens.
Mitt. Art. Geniew.	Mitteilungen über Gegenstände des Artillerie- und Geniewesens.
Mitt. zentral. wissen.-tech. Unter.	Mitteilungen der Zentralstelle für wissenschaftlich-technische Untersuchung.
Oesterr. Berg-Hütten.	Oesterreichische Zeitschrift für Berg- und Hüttenwesen.

Abbreviation.	Title.
Phil. Mag.	Philosophical Magazine. London, Edinburgh and Dublin.
Phil. Trans.	Philosophical Transactions (London).
Plasto.	Plastomenit. Wille.
Polyt. Zent.	Polytechnisches Zentralblatt.
Proc. Chem. Soc.	Proceedings of the Chemical Society. London.
Proc. Roy. Soc.	Proceedings of the Royal Society of London.
Schiessbaumwolle	Die Schiessbaumwolle. Escales.
Spreng. Zünd. Spreng.	Sprengstoffe und Zündung der Sprengschüsse. Heise.
Theo. Chem.	Theoretische Chemie. Nernst.
Thermodyn. Gasreak.	Thermodynamik technischer Gasreaktionen. Haber.
Traite d'art.	Traité d'artillerie.
Vorles. theor. phys. chem.	Vorlesungen über theoretische und physikalische Chemie. van't Hoff.
Wied. Ann.	Annalen der Physik und Chemie. Wiedemann.
Z. Berg. Hütten. Salin.	Zeitschrift für Berg.-Hütten- und Salinenwesen.
Z. anorg. Chem.	Zeitschrift für anorganische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. ges. Scheiss. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. phys. Chem.	Zeitschrift für physikalische Chemie.

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