

The detonation of liquid explosives by gentle impact. The effect of minute gas spaces

By F. P. BOWDEN, M. F. R. MULCAHY, R. G. VINES AND A. YOFFE, *Tribophysics Section, Council for Scientific and Industrial Research, University of Melbourne*

(Communicated by Sir David Rivett, F.R.S. and Sir Robert Robertson, F.R.S.—
Received 12 January—Read 9 May 1946)

An experimental study has been made of the physical conditions which occur during the impact of solids on liquid explosives. It is shown that the high impact sensitivity of liquid or gelatinous explosives is due to the entrapping of minute gas spaces during the impact. These tiny gas bubbles (the mass of bubble may be about 10^{-10} g. and its volume at atmospheric pressure about 10^{-7} c.c.) are heated by adiabatic compression and initiate the explosion. Bubbles of this size are, of course, difficult to detect, and they are readily entrapped under many conditions of laboratory experiment and practical operation. Because of the effect of the entrapped gas spaces the sensitivity of liquid explosives is profoundly affected by the shape of the impacting surfaces or by the distribution of the explosive. If, for example, one of the surfaces contains a small pin-hole or cavity, nitroglycerine may be exploded when the potential energy of the fall hammer is as low as 20 g.cm. If the liquid explosive is initially distributed on the anvil in the form of droplets or as parallel strips which coalesce during the impact and entrap gas, the sensitivity is also very high. Even when a continuous film of the explosive is struck between flat surfaces small amounts of gas may be entrapped and may initiate the explosion. If precautions are taken to prevent the entrapping of gas, nitroglycerine is comparatively insensitive to initiation by impact between curved or flat surfaces, and impact energies of the order of 10^5 – 10^6 g.cm. may be necessary to cause explosion. The effect of the gas is mainly a physical one (adiabatic heating), but the chemical nature (oxidizing property) of the gas is also important.

INTRODUCTION

The detonation of solid explosives by mechanical impact has been investigated fairly extensively, but there is still some doubt as to the mechanism, or mechanisms, by which the mechanical energy of the blow initiates the explosive reaction. Liquid explosives may also be detonated by a mechanical blow, but the experimental study of this has not been so extensive, and again, the mechanism of initiation is not fully understood. The study of explosives in the liquid state possesses some advantages since the explosive is homogeneous, and factors such as crystal size, crystalline form, and density of packing, which lead to wide variation in the sensitivity of solid explosives, do not occur. Nevertheless, the impact sensitivity results which are given by various workers for a liquid explosive, such as nitroglycerine, do differ widely. A usual method of measuring sensitivity is to place a film of the explosive on a flat anvil and strike it with a flat-faced weight—in some cases a flat-ended cylinder or disk is allowed to rest on the film, or is suspended above it, and struck by the hammer. The sensitivity may then be expressed in terms of the potential energy of the hammer necessary to give detonation. Berthmann (1941) gives the sensitivity of nitroglycerine on steel surfaces as 14,000 g.cm. Will (1906) gives it as 4000 g.cm. Other values quoted in the literature range from higher than 14,000 down to 500 g.cm. Much of this early work has been undertaken to get

some standard test for sensitivity which would serve as a practical guide to safety in manufacture or operation.

An attempt has been made to investigate in more detail the physical conditions which occur during impact and to determine the factors which are responsible for initiation. Since both the physical and chemical changes which occur during the impact are very rapid, it is necessary to use electrical and optical methods which will record transient phenomena lasting for only a few microseconds. Measurements have been made of the period of contact between the impacting surfaces, of the time during collision at which initiation is observed, and of the rate and mode of propagation of the explosion from the point of initiation through the liquid film.

A factor which was found to be of great importance was the shape of the anvil or striker or the geometrical arrangement of the explosive itself (Bowden, Eirich, Ferguson & Yoffe 1943 *a*; Bowden, Eirich, Mulcahy, Vines & Yoffe 1943 *b*). It has been shown, for example, that if one of the surfaces contains a small pin-hole or cavity, initiation occurs with very gentle impact. Explosions occur with nitroglycerine when the impact energy is as low as 20 g.cm. If the nitroglycerine is distributed as droplets or parallel strips on the anvil and struck with a flat surface, or if a gas bubble is introduced into a continuous film of the liquid, it is again found that a gentle impact will cause detonation. The same effect is observed with other liquid or gelatinous explosives. It will be shown in this paper that the high sensitivity of liquid explosives is due to the entrapping of minute gas spaces in the explosive.

The size of the gas spaces and the quantity of gas necessary to cause the explosion is very small indeed. A single tiny bubble (the volume at atmospheric pressure may be of the order of 10^{-11} c.c.) is sufficient to initiate the explosion. These minute bubbles are heated by adiabatic compression during impact and form a small nucleus of hot gas which initiates the reaction. The explosion then propagates from this hot nucleus. Unless precautions are taken to prevent the inclusion of such small gas bubbles they readily occur under many conditions of laboratory experiment and practical operation.

This paper is concerned primarily with the impact sensitivity of liquid and gelatinous explosives with different geometrical arrangements of the striker or explosive, and with the part played by adiabatic heating of small entrapped gas bubbles in initiating the reaction. The electrical and photographic study of the time at which initiation occurs and of the propagation of the explosion from the point of initiation is described in the second paper. A third paper deals with the initiation of a liquid explosive by friction.

IMPACT TESTS ON THIN CONTINUOUS FILMS OF NITROGLYCERINE

Experiments have been carried out on the sensitivity of thin continuous films of nitroglycerine to impact between flat surfaces. The nitroglycerine was spread as a film about 2 cm. in diameter and about 3×10^{-3} cm. thick on a lapped, grease-free, brass anvil (see figure 1(*a*)). This value was chosen since it was found that when

the film thickness was greater or smaller than 3×10^{-3} cm. the sensitivity decreased appreciably. The film was struck with a flat brass striker 2.5 cm. in diameter held in a pendulum type of fall hammer similar to figure 2 and to those described in

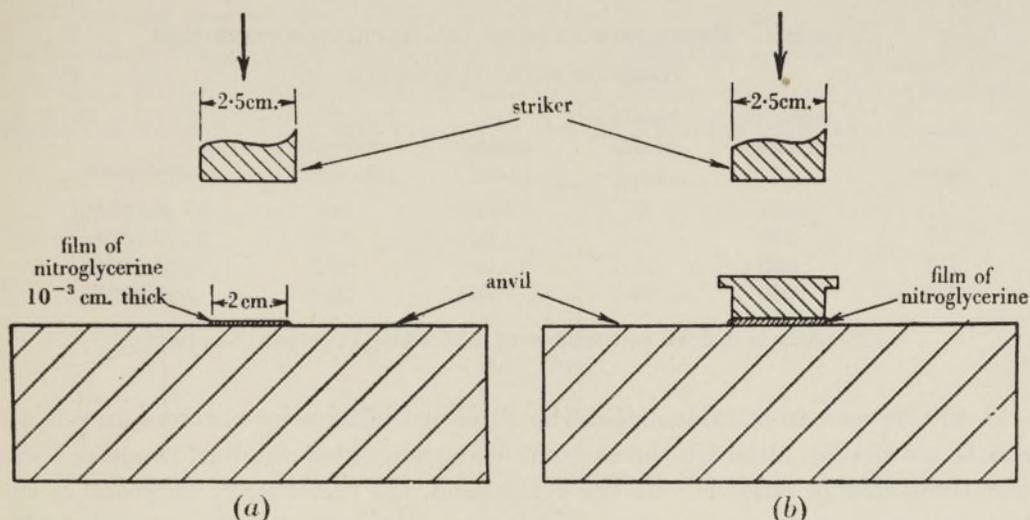


FIGURE 1. (a), nitroglycerine spread as thin film on brass anvil, and struck directly by flat pendulum fall hammer. (b), striker rests on thin film of nitroglycerine on brass anvil and is struck by subsidiary striker held in the hammer. The film may be formed with or without entrapped air spaces.

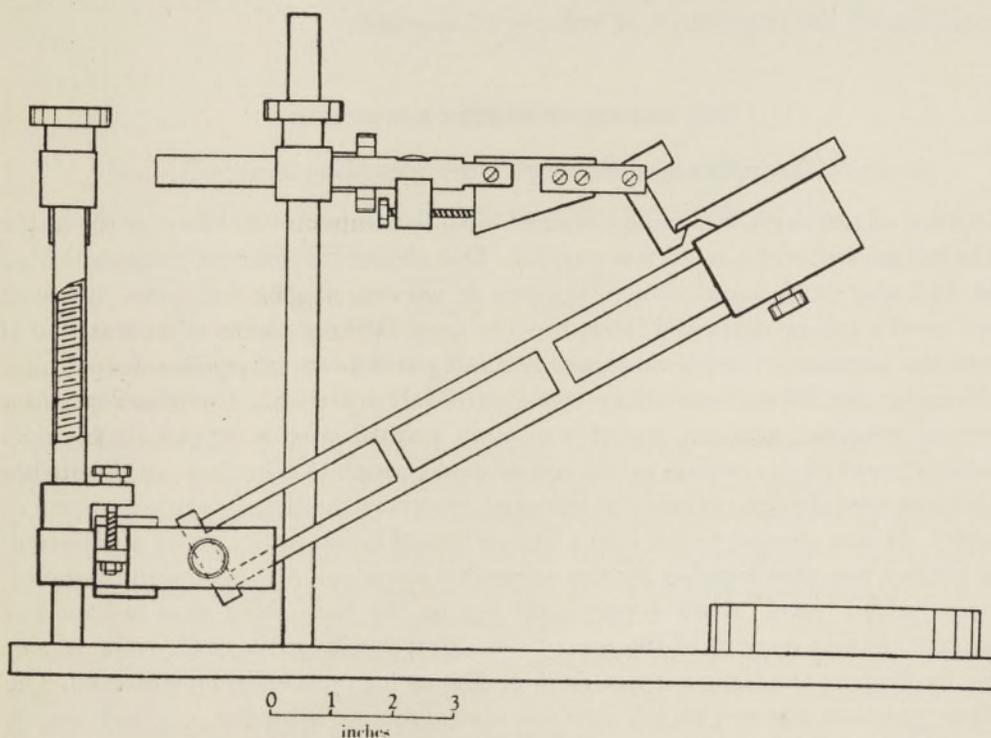


FIGURE 2. Pendulum hammer apparatus.

earlier papers (Bowden *et al.* 1943*a, b*). The striker was levelled on the anvil before each fall. The results obtained for different energies and velocities of impact are given in table 1.

TABLE 1. EXPLOSION EFFICIENCY OF THIN CONTINUOUS FILMS OF NITROGLYCERINE

series	mass of striker (g.)	height of fall (cm.)	energy (g.cm.)	velocity (cm.sec. ⁻¹)	efficiency*
I	1,030	58	60,000	340	30/46 (65%)
II	290	48	14,000	310	20/35 (57%)
III	850	21	18,000	200	14/54 (26%)
IV	380	20	7,600	200	2/20 (10%)

* Efficiency is defined as (number of explosions)/(number of impacts).

It will be seen from table 1 that the explosion efficiencies obtained in series I and II are similar, although the energies of impact which obtained in series I was four times that in series II. On the other hand, the velocities of approach of the hammer were about the same in both cases. This indicates that the explosion efficiency is determined more by the velocity of approach than by the energy involved. Furthermore, when in series II and III similar energies of impact were used, a high efficiency was observed with the greater height of fall, again demonstrating the importance of velocity of approach.

THE EFFECT OF MINUTE GAS SPACES

The influence of the shape of the impacting surfaces

In view of the variable results obtained with flat impacts the effect of the shape of the striker and of the anvil was studied. Flat strikers of different diameters were used and also curved and conical strikers of varying shapes and sizes. Some of these results will be discussed later, but the most striking observation was that if either the hammer or anvil contained a small pin-hole or cavity less than 1 mm. in diameter the impact sensitivity was enormously increased. The effect was first observed with flat surfaces, but it was more marked with a curved striker containing a small cavity with a raised rim of metal round it. The form of the striker which was used for the majority of the experiments with nitroglycerine is shown in figure 3. It was allowed to fall into a film or lens of liquid explosive on a flat anvil. The striker was first levelled by the adjusting screws on the pendulum hammer. It was judged 'level' when a very light tap on the bare anvil gave a faint but complete circular imprint of the cavity rim. After levelling, the cavity was usually filled by dipping the striker into a drop or film of nitroglycerine on the anvil. The striker was then allowed to fall into the nitroglycerine from the required height. Some typical results with brass surfaces are shown in table 2.

It will be seen that in the presence of a cavity an explosion efficiency of 100% may be obtained with a weight of 40 g. falling 10 cm. In fact, explosion of nitroglycerine may occur with a 40 g. striker falling 0.5 cm. (i.e. energy 20 g.cm.) corresponding to a velocity of approach of 30 cm.sec.⁻¹. When no cavity is present no explosions are obtained even with a 4 kg. hemispherical striker falling 150 cm., i.e. energy 6×10^5 g.cm. A similar increase in sensitivity was found for other liquid explosives when a cavity was present in the striker. This increase of sensitivity

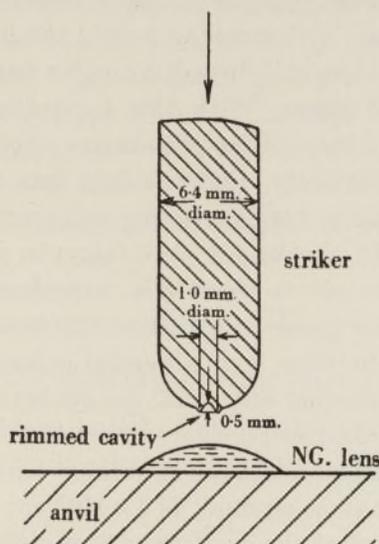


FIGURE 3

TABLE 2. EXPLOSION EFFICIENCY USING A CURVED BRASS STRIKER WITH A CAVITY AND RAISED RIM ON A BRASS ANVIL

mass of striker (g.)	height of fall (cm.)	energy (g.cm.)	velocity (cm.sec. ⁻¹)	efficiency
40	10	400	140	85/85 (100%)
40	5	200	99	33/41 (80%)
40	3	120	78	3/18 (17%)

is very remarkable: it is evident that liquid explosives may be detonated by the gentlest tap if the anvil or the hammer is of an appropriate shape. To what then is this extreme sensitivity due? One possible explanation is that it is due merely to a concentration of stress at the rim of the cavity. Since contact occurs only at the narrow rim of the cavity all the energy of the impact is concentrated in this small area. Experiments show, however, that this is not the cause. If the cavity is drilled right through the striker so that it is open at the top no initiation occurs, even with the heaviest impacts. Also it is found that when sharp-pointed strikers or curved strikers which give point contact are used no explosion occurs, even with impact energies of the order of 10^6 g.cm. With experiments of this type all

the energy of impact is concentrated into a small area and the stresses are sufficient to cause plastic deformation of brass and steel surfaces. Nevertheless, there is no explosion.

A second possibility is that, with the cavity, initiation is brought about by a tribochemical effect or viscous heating due to the very rapid flow of the liquid as it escapes through the narrowing gap between the rim of the cavity and the anvil. An apparatus for producing high rates of flow was constructed to test this hypothesis. It consisted of a small plunger fitting accurately into a cylindrical hole. When the plunger was struck with a falling weight the liquid explosive was forced out of the bottom of the cylinder and flowed through a narrow gap (thickness about 10^{-3} cm.) between parallel plates. With this apparatus it was possible to get detonation and to reproduce some of the phenomena obtained in the cavity impact. The experiments showed, however, that the flow was of secondary importance. The initiation was really due to the entrapping and compressing of very small gas spaces within the liquid. If precautions were taken to prevent the entrapping of gas no initiation was observed in these flow experiments. This indicated that initiation of the explosion by gentle impact was due to adiabatic compression and heating of entrapped gas bubbles, and a careful examination was made of the cavity experiments to see whether any small gas spaces could be detected there.

Observations under the microscope showed that with the normal experimental procedure a small amount of air is almost invariably entrapped within the cavity. The radius of this bubble may be as small as 5×10^{-3} cm., and it is usually present as a pocket of air in the roof of the cavity and is invisible to the eye. In fact, it may be very difficult to detect with a microscope, unless the cavity is searched with a fine probe and the bubble detached from the wall and brought out into the body of the liquid. It was found that if the air bubble is removed from the cavity the sensitivity to impact disappears. If the bubble is reintroduced the high impact sensitivity is again observed.

Table 3 gives comparative results for the explosion efficiency when air bubbles are deliberately either excluded or included.

TABLE 3

nature of impacting surface	Brinell hardness (kg./mm. ²)	mass of striker (g.)	height of fall (cm.)	energy (g.cm.)	efficiency	
					bubble present	bubble absent
brass	40-80	65	24	1550	15/16 (94%)	0/15 (0%)
steel	150-180	35	11	370	60/70 (85%)	0/60 (0%)
steel	150-180	200	35	7000	56/59 (95%)	0/30 (0%)

It will be seen that a bubble is necessary in order to obtain explosions with energies of impact ranging between 370 and 7000 g.cm.

Experiments were also performed in which the striker was filled with nitroglycerine (with or without a bubble) and lowered into a lens of nitroglycerine on the anvil. In this experiment the nitroglycerine had been previously degassed

under a vacuum pump and the inside of the cavity coated with a layer of shellac in order to reduce the possibility of formation of air bubbles on the metal surface. The striker was held in the lens about 0.75 mm. above the anvil surface by a guide and struck by a weight of 250 g. falling about 30 cm. so that the cavity was completely immersed during the whole of the experiment. The ratios of explosion to impact were:

Bubble in cavity 10/10. No bubble observed in cavity 1/20.

The efficiency of a bubble in causing initiation depends on its size and position in the cavity. Bubbles close to the roof of the cavity are more effective than those suspended near the opening. This, no doubt, is due to the smaller likelihood of a bubble near the roof escaping on impact. For impacts of 195 g. falling 35 cm. (7000 g.cm.), the lower limiting diameter of effective bubbles situated close to the roof of the cavity appears to be about 0.1 mm., i.e. a bubble of diameter less than 0.1 mm. did not initiate explosion at this impact energy. Very large bubbles are also ineffective.

THE PRESSURE AND TEMPERATURE DEVELOPED IN THE BUBBLE DURING IMPACT

The effect of initial gas pressure

The temperature rise in the bubble depends, of course, upon the compression ratio, and if the process is truly adiabatic and the gas ideal, is given by

$$T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}}$$

It is of interest to calculate the temperature rise in cases where the initial pressure p_1 and final pressure p_2 can be estimated, and also to investigate the effect which an alteration of the pressure ratio or of γ has on the incidence of explosion.

A rough experimental estimate of the minimum amount of compression of the bubble in the cavity necessary for initiation may be obtained from a consideration of the results obtained with impacts on anvils of varying hardness (Bowden *et al.* 1943*a*). It has been found that, whereas an initiation is readily effected with cavity brass strikers (Brinell hardness 60–80 kg./mm.²) falling on a lead anvil (hardness 4 kg./mm.²), no explosion has been observed when the anvil is of the softer indium (hardness 1 kg./mm.²), although the indium is plastically deformed by the impact.

The average kinetic flow pressure of indium has been determined and is of the order of 4 kg./mm.² for low-velocity impacts of the order of 50 cm.sec.⁻¹; the average kinetic flow pressure of lead under similar conditions is about 8 kg./mm.². The minimum pressure necessary for initiation which must be developed in the liquid and bubble during the impact must, therefore, lie between 4 and 8 kg./mm.².

If it is assumed that the pressure of the liquid inside the cavity does not exceed the kinetic flow pressure of the metal, an approximate estimate of the pressure may

be made. The maximum temperature rise for an adiabatic compression from atmospheric pressure to 4 kg./mm.² (400 atm.) is of the order of 1300° C. For a final pressure of 8 kg./mm.² (800 atm.) the temperature rise is about 2000° C. We have measured the ignition temperature of nitroglycerine when heated in bulk and find a value of 265–275° C, so that high temperatures may well cause initiation.

Since the initial mass of the gas bubble is about 10^{-9} g., the actual quantity of heat developed in the gas bubble for a temperature rise of 2000° C is about 4×10^{-7} cal.

*Cavity experiments in low-pressure atmospheres of air,
nitrogen, ether and carbon tetrachloride*

A series of experiments was carried out in a vacuum chamber which contained the pendulum fall hammer. This chamber could be evacuated down to moderately low pressures (10^{-2} cm. Hg) or filled with appropriate gases. The arm of the fall hammer could be released from an electromagnet and the experiment observed through a glass window.

In the cavity experiments and in many of the other impact experiments the initial volume of the small entrapped gas bubble is fixed by geometrical consideration. If, before the experiment, the initial gas pressure p_1 is lowered, the ratio of p_2/p_1 will be increased and the temperature rise may be greater. On the other hand, the mass of the entrapped gas and the amount of heat developed will be reduced. In the limit if the initial pressure is very low the mass of entrapped gas and the quantity of heat developed may be so small that it may no longer be capable of initiating the explosion.

The results of carrying out cavity impacts in air at different pressures are shown in table 4. Before use the nitroglycerine was degassed under the vacuum of a hyvac pump. Before each experiment the chamber (containing the nitroglycerine) was evacuated to less than 0.1 cm. and the air then admitted to the required pressure.

TABLE 4. EXPLOSION EFFICIENCY WITH CAVITY IMPACT
IN AIR AT DIFFERENT PRESSURES

Striker 205 g. falling 24 cm. initial air pressure p_1	Energy 4900 g.cm. explosion efficiency
76.0 cm. Hg, 1.00 atm.	31/32 (97%)
6.4 cm. Hg, 0.08 atm.	40/51 (78%)
2.0 cm. Hg, 0.03 atm.	5/23 (22%)
1.0 cm. Hg, 0.01 atm.	0/5 (~0%)
0.2 cm. Hg, 0.003 atm.	0/10 (~0%)

It will be seen that the gas bubble within the cavity may be still effective when the initial pressure p_1 is 2.0 cm. Hg. Again, the initial diameter of the bubble could be about 10^{-2} cm. so that its mass could be about 10^{-11} g. Assuming that the final pressure p_2 is about 600 atm., the theoretical maximum temperature rise would be

several thousand degrees. The actual quantity of heat developed within the bubble would, however, have fallen to about 10^{-7} cal. Apparently this small quantity of heat is still capable of initiating the explosion.

If the initial pressure is reduced to a low value ($p_1 = 10^{-3}$ atm.) explosion does not occur, presumably because the amount of entrapped gas and the quantity of heat developed is too small.

The experiments were repeated in atmospheres of ether and carbon tetrachloride vapours. For ether $\gamma = 1.08$ and for carbon tetrachloride $\gamma = 1.13$, so that for both these gases the adiabatic temperature rise of any entrapped bubbles would be greatly reduced. The results are given in table 5.

TABLE 5. CAVITY IMPACT IN GASES OF DIFFERENT γ

Striker 205 g. falling 24 cm. Energy of impact 2900 g.cm.

initial pressure of gas p_1 (cm. Hg)	atmosphere		explosion efficiency
6.4	air	$\gamma = 1.4$	40/51 (78%)
6.4	nitrogen	$\gamma = 1.4$	5/5 (~100%)
6.4	ether	$\gamma = 1.08$	0/8 (~0%)
6.4	carbon tetrachloride	$\gamma = 1.13$	0/6 (~0%)

It will be seen that, under these conditions of impact, the explosion efficiency is reduced from 78% to zero by the substitution of ether or carbon tetrachloride. The amount of ether which dissolves in nitroglycerine under 6.4 cm. Hg is almost certainly less than the Raoult's law value, i.e. 5% (wt.), and this consequently would have little desensitizing effect on the nitroglycerine (see later). The solubility of carbon tetrachloride in nitroglycerine would be expected to be even smaller than that of ether, since (as we have observed) nitroglycerine and carbon tetrachloride show only partial miscibility. For ether the theoretical temperature rise would be one-thirteenth and for carbon tetrachloride one-seventh that of air. This result, that gases of low γ reduce the sensitivity, is quite general and supports the view that it is the adiabatic heating of the entrapped gases which is responsible for the initiation.

THE INFLUENCE OF THE DISTRIBUTION OF THE EXPLOSIVE

An increase in the sensitivity of liquid explosives to flat impact may also be obtained by a suitable arrangement of the explosive on the anvil (Bowden *et al.* 1943*b*). If the explosive is distributed as a number of small droplets upon a flat surface or if bubbles of gas are introduced into a continuous thin film of the liquid, explosion may be obtained at relatively low energies of impact.

The size, number and distribution of the droplets are important. A single droplet or a few large drops will not explode even under high energies of impact. It is also found that very small droplets which are spaced widely apart are ineffective. The most effective arrangement consists of a number of small droplets (about 1 mm).

placed closely together. Experiments with a transparent striker show that with this arrangement small air pockets are normally entrapped between the impacting surfaces. Some typical results are given in table 6.

TABLE 6. THE SENSITIVITY OF NITROGLYCERINE TO FLAT IMPACT WHEN DISTRIBUTED AS A NUMBER OF DROPLETS OR WHEN AIR BUBBLES ABOUT 0.5 CM. DIAMETER ARE INTRODUCED INTO A THIN FILM

mass of striker (g.)	height of fall (cm.)	energy (g.cm.)	efficiency		
			droplet distribution	air bubbles in continuous film	continuous thin film
380	20	7600	—	7/7 (100%)	2/20 (10%)
180	20	3600	—	13/13 (100%)	0/7 (~0%)
180	15	2700	50/50 (100%)	—	—
180	10	1800	— (100%)	13/21 (62%)	—
40	15	600	3/25 (12%)	17/18 (94%)	0/20 (0%)

Explosions are readily obtainable with 40 g. falling 15 cm., while for continuous thin films the efficiency at this energy of impact is zero. Again it is suggested that the initiation of the explosion is due to the adiabatic compression of the gas spaces enclosed within the liquid film at the moment of impact.

The fact that a single drop (or a single strip) of explosive causes no increase in sensitivity provides strong support for the view that initiation is not due simply to liquid flow. Unless the geometrical arrangement is such that gas is entrapped during the impact, initiation does not occur at these impact energies.

Further work has shown that even if the amount of gas entrapped is exceedingly small it may still be sufficient to cause explosion. For example, a single bubble of air, having a diameter of 1 mm., in a very thin film of nitroglycerine, is capable of causing an explosion at an impact energy of 600 g.cm. (40 g. falling 15 cm.).

The effect of the gas spaces depends not only on the adiabatic compression; the chemical nature of the gas is also important (see later). For instance, the sensitivity of the explosive with oxidizing gases such as air, oxygen, nitrous oxide, is much greater than when inert gases such as nitrogen and carbon dioxide are used. This increase in sensitivity has been assumed to be the result of an initial reaction with the excess oxygen (possibly in the vapour phase) in which a large amount of energy is released and an explosion nucleus thereby created.

Further evidence that extremely small quantities of entrapped gas, either inert or oxidizing, are capable of producing explosion of liquid nitroglycerine on impact has been obtained from experiments with parallel strips of nitroglycerine.

The explosion of parallel strips of nitroglycerine

An increase in sensitivity even greater than that observed when air bubbles are introduced previous to the impact has been obtained when the nitroglycerine is simply distributed as two thin parallel strips on a flat anvil as shown in figure 4.

The strips were struck with a very flat brass striker about 1.5 cm. in diameter. Clean freshly lapped surfaces were used for each experiment. The results obtained under these conditions are shown in table 7 and compared with corresponding experiments in which the nitroglycerine was spread on the anvil as a continuous film.

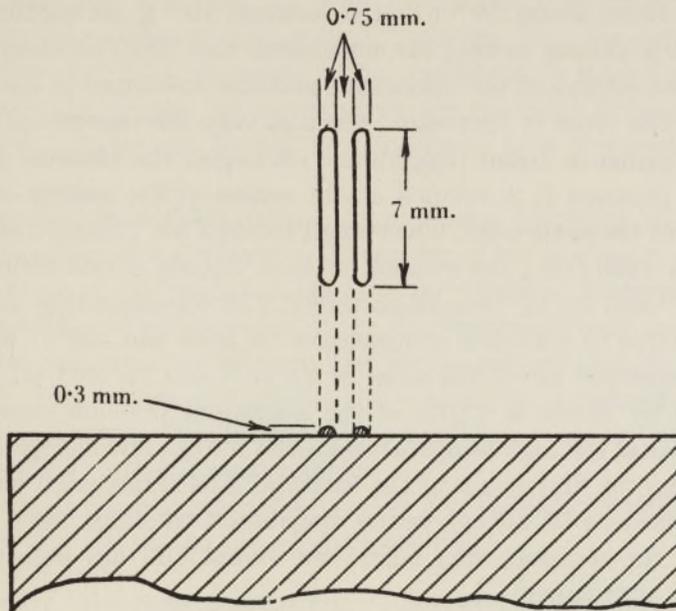


FIGURE 4. Nitroglycerine distributed as strips.

TABLE 7

mass of striker (g.)	height of fall (cm.)	energy (g.cm.)	efficiency	
			strips	continuous thin film
380	20	7600	—	2/20 (10%)
230	20	4600	22/25 (90%)	—
55	18	1000	23/39 (70%)	—
42	15	630	6/7 (80%)	0/20 (0%)
42	10	420	4/10 (40%)	—
41	8	330	4/10 (40%)	—
41	6	250	2/25 (10%)	—

Thus, as in the case of the experiments with droplets and bubbles, there is a marked increase in the sensitivity to flat-surface impact when the nitroglycerine is distributed as strips. With an impact energy of 7600 g.cm. the efficiency for continuous thin films is only 10 %, while with strips the efficiency is 90 % at 4600 g.cm. The lower limit of sensitivity with the strips appears to be 250 g.cm., which is not very different from that observed with cavity impacts (20 g.cm.).

The presence of two or more strips is necessary to obtain the increase in sensitivity. When a single strip is used no increase is observed. This supports the view that initiation is not due to liquid flow but to the adiabatic compression of gas bubbles entrapped in the nitroglycerine during the impact.

In these experiments several extremely small bubbles may be entrapped, the volume of each being about 10^{-4} c.c. and its mass 10^{-7} g. At medium energies of impact (e.g. 400 g. falling 15 cm.) for continuous thin films between flat surfaces, Cherry (1945) has estimated the maximum pressure developed in the liquid during impact to be of the order of 1000 atm., while at very low energies of impact (40 g. falling 10 cm.) Eirich & Tabor (1945) have estimated the pressure to be 20 atm. The maximum pressure is developed at the centre of the striker. Assuming the pressures to be of the same order when small bubbles are present and that the gas is ideal even at 1000 atm., the volume of each bubble would decrease at these pressures to 10^{-7} and 3×10^{-6} c.c. respectively. The corresponding calculated temperature flashes due to adiabatic compression are 2000 and 400° C, and the quantities of heat developed are of the order of 3×10^{-5} and 7×10^{-6} cal. respectively. The calculation by Eirich & Tabor of the maximum pressure developed in the liquid indicates that the high temperatures, even for the low-energy impacts, may be reached during the first stages of the collision. This is in accord with the observation that explosions of nitroglycerine distributed as strips may occur at the initial phase of the collision, long before the liquid film has been squeezed out appreciably (see next paper).

Impact on parallel strips in atmospheres of air, nitrogen, hydrogen and ether

A series of experiments similar to those described earlier for cavity impacts was carried out with a flat striker on parallel strips of nitroglycerine. The vacuum box was evacuated to 10^{-1} cm. Hg and then filled with the appropriate gas. For the experiments with nitrogen and hydrogen the chamber was first flushed out three times with the gas and then filled to the required pressure. In the ether experiments the vapour was introduced by allowing a volume of the liquid to evaporate. It should be pointed out that in these particular experiments a small amount of air, about 10^{-1} cm. Hg, remained in the vessel. The results obtained are shown in table 8.

TABLE 8. COMPARISON OF EXPLOSION EFFICIENCY OBTAINED WITH STRIPS IN LOW-PRESSURE ATMOSPHERES OF AIR, NITROGEN, HYDROGEN AND ETHER

initial pressure of gas (cm. Hg)	Weight 230 g. Height 20 cm.			
	efficiency			
	air	nitrogen	hydrogen	ether
76	36/40 (90%)	14/16 (88%)	4/17 (24%)	—
10.0	27/32 (85%)	5/10 (50%)	12/27 (44%)	0/10 (0%)
3.5	22/26 (85%)	8/16 (50%)	—	3/20 (15%)

Again it will be seen that the explosion efficiency in ether ($\gamma = 1.08$) is less than in nitrogen, hydrogen and air at the same pressure. Assuming that the final pressure developed in the liquid (and the entrapped gas spaces) during the impacts is about 1000 atm., the maximum theoretical temperature resulting from the compression of ether at an initial pressure of 10 cm. Hg would be 270° C. When the initial pressure of ether is 3.5 cm. Hg the temperature could be 310° C. The corresponding estimated maximum temperature, resulting from the compression of air, nitrogen or hydrogen from the same initial pressures, could be about 8000 and 5000° C respectively. Since the figure given for the final pressure is uncertain, these simplified calculations should be considered as a comparative indication only.

It is also evident from table 8 that the explosion efficiency in a nitrogen and hydrogen atmosphere at a pressure of 10 cm. Hg is lower than in air at the same pressure. In view of the similar value of γ for nitrogen, hydrogen and air it is clear that the adiabatic compression of the gas represents only one of the factors operating in the initiation mechanism. The results suggest that, in addition to the physical effect of the gas in causing adiabatic heating, its chemical nature (oxidizing properties) is important. Similar behaviour has been found in experiments with nitroglycerine films containing gas bubbles.

Some additional experiments were carried out in air at a still lower pressure (10^{-2} cm. Hg), and the results are given in table 9.

TABLE 9. EXPLOSION EFFICIENCY OBTAINED WITH STRIPS IN AIR AT LOW PRESSURE AND AT ATMOSPHERIC PRESSURE

mass of striker (g.)	height of fall (cm.)	energy of impact (g.cm.)	efficiency in air	
			at pressure of 10^{-2} cm. Hg	at atmospheric pressure
230	20	4600	12/14 (86 %)	36/40 (90 %)
45	14	630	5/5	3/3

It is clear that the explosion efficiency is still high when the air pressure is lowered to 10^{-2} cm. Hg. At this pressure the amount of air entrapped, and consequently the quantity of heat developed, must be extremely small. Simple calculations show that the mass of gas in each bubble entrapped at 10^{-2} cm. Hg is about 2×10^{-11} g. The calculated temperature rise obtained from adiabatic compression from this initial low pressure is some twenty times greater than that from compression at atmospheric pressure. It seems, therefore, that it is the actual temperature rise rather than the quantity of heat developed (or perhaps a combination of these two factors) which is important in initiating the explosion at the low energy of impact (630 g.cm.). The quantity of heat developed in the bubble may be calculated and is about 10^{-7} cal. The reason for the different behaviour of cavity impacts in this respect is not clear, but may be associated with the smaller amount of air which is entrapped by the cavity.

Droplet experiments in low-pressure atmospheres of oxygen, nitrogen and air

A series of experiments similar to those described in the previous section was carried out with nitroglycerine distributed as droplets in low-pressure atmospheres of oxygen, nitrogen and air. The droplets were spread on the anvil which was previously coated with a very thin film of grease. Such a film does not affect the sensitivity to impact in the case of liquid explosives. It has been shown in a previous paper (Bowden *et al.* 1943*b*) that for the experiments with droplets the explosion efficiency is determined mainly by the velocity of approach of the striker and not primarily by the energy of the blow. It was found that by taking velocity of approach as criterion, the order of explosion efficiency in the different gaseous atmospheres is:

low-pressure oxygen (10 cm. Hg) > air at atmospheric pressure
> low-pressure atmosphere of air (10^{-3} cm. Hg) > nitrogen at atmospheric pressure.

These results support those obtained from the experiments with nitroglycerine distributed as strips, in that they show the presence of an effect due to the chemical nature of the atmosphere; explosions are more readily obtained in air at atmospheric pressure than in nitrogen at the same pressure. Furthermore, the results show that explosions may be obtained when the initial pressure of the gas is as low as 10^{-3} cm. Hg.

THE ACCIDENTAL TRAPPING OF GAS SPACES DURING FLAT IMPACT

Figures for the explosion efficiency of thin continuous films of nitroglycerine to flat-surface impact have already been given in an earlier section. When transparent strikers or anvils were used it became evident that under the normal conditions of flat-impact experiments, air bubbles are readily trapped in the nitroglycerine film during the impact of the surfaces. As pointed out above, the presence of entrapped gas has a profound effect on the sensitivity. The question therefore arises as to how far the impact sensitivity of nitroglycerine reported in the literature and in table 1 is influenced by this factor. It might explain in part the wide discrepancies between the values obtained by different workers. The experiments with glass strikers and anvils showed that even at low velocities of approach of the striker it was almost impossible to exclude air spaces. The results described above suggest that the adiabatic compression of these gas spaces may be responsible for initiation. In order that this might be tested, further experiments were carried out under conditions in which air bubbles were (*a*) intentionally entrapped and (*b*) removed.

In these experiments the striker did not fall directly on the nitroglycerine film. In the (*a*) series, a thin film of nitroglycerine was placed on the anvil and a brass disk allowed to rest on the top of it. The fall hammer then struck the top disk (see figure 1*b*). Parallel experiments with a glass disk showed that almost invariably

some air was entrapped between the disk and the anvil previous to impact. In the (b) experiments a thick lens of nitroglycerine was placed on the carefully cleaned anvil. The clean brass disk was also wetted with a thick film of the explosive and then lowered slowly and obliquely on to the anvil. The excess nitroglycerine was sucked away with a syringe. Again parallel experiments with a glass disk showed that air bubbles were *usually* eliminated by this technique.

With a fall hammer of 1 kg. falling some 60 cm. (energy of impact 60,000 g.cm.) the results for the explosion efficiencies were as follows:

(a) gas spaces intentionally entrapped 10/10 (100 %),

(b) gas spaces probably absent 2/35 (6 %).

This figure of 60,000 g.cm. may be taken as an upper limit only, since it was found that with this particular hammer a considerable amount of the energy was absorbed in plastic deformation of the rear end of the brass striker.

The results show that the presence of a gas space greatly increases the probability of explosion.

There is evidence that if the impact energy is very great the nitroglycerine may be detonated by impact in the absence of gas spaces. A layer of nitroglycerine was enclosed between a brass disk and a glass slide (arrangement similar to figure 1*b*) and the film closely scrutinized to ensure that no bubble was entrapped. The glass slide was 'stuck' to a brass anvil with a thin layer of nujol and the disk subjected to the impact of 5 kg. falling 120 cm.—energy of impact about 10^6 g.cm. Regular explosions were obtained. In this case, initiation may be due to shock or to a temperature rise within the rapidly flowing liquid.

Recently, Cherry (1945) has made a mathematical analysis of the liquid flow between two approaching surfaces. He has shown that, if allowances are made for the elastic deformation of the approaching surfaces, the temperature rise in the liquid film under moderate conditions of impact is only a few degrees Centigrade. Eirich & Tabor (1945) arrive at the same conclusion. According to Cherry's calculations there is very little actual 'shock' on impact, since before contact the surfaces suffer considerable elastic deformation. This deformation absorbs the major part of the energy of impact so that only a small proportion is actually absorbed by the explosive liquid; consequently the rise in temperature within the film at the lower energies of impact (up to 10^4 g.cm.) is in most cases no more than 50° C. It is only at very high energies of impact (about 10^6 g.cm.) that the theoretical temperature obtained during the shearing of the liquid as it escapes between the surfaces reaches several hundred degrees, near the periphery of the striker. It is therefore improbable at low or moderate energies of impact that the initiation is due to a viscous heating of the rapidly flowing liquid. This can only be true at very high energies of impact, e.g. 10^5 – 10^6 g.cm.

In view of the effect of air bubbles entrapped in thin films, it is interesting to note that in previous impact experiments (Bowden *et al.* 1943*a*), where the striker fell upon an open film of nitroglycerine, it was found that strikers of large area

are more efficient than small ones. With brass strikers 0.6 cm. in diameter it is very difficult to initiate the explosion at all, even with very high energies of impact. If the diameter is increased to 2.5 cm., both the sensitivity and the probability of explosion are very greatly increased. With the striker of greater diameter, the probability of entrapping air is obviously greater.

Also it is found that very thick films of the liquid are less sensitive than thin ones. In thick films the bubbles would be more mobile and could more readily escape before the pressure rose to a high value. If the film on the anvil is too thin, the sealing and compression are inefficient and again the probability of detonation is lower.

THE DETONATION OF LIQUID EXPLOSIVE OTHER THAN NITROGLYCERINE

Previous work (Bowden *et al.* 1943*b*) has shown that provided an explosive is in the liquid state, either molten or dissolved in solvents, its behaviour is similar to nitroglycerine, both as regards its high sensitivity to cavity impacts and its propagation mechanism.

Nitroglycol, as might be expected, is extremely sensitive to the impact of a cavity striker, an explosion efficiency of 100 % being obtained at an energy of impact of 300 g.cm., i.e. 30 g. falling 10 cm. Gas-space experiments with nitroglycol (bubbles, strips and droplets), show that, in these circumstances, its behaviour is hardly distinguishable from that of nitroglycerine. Similarly, T.N.T., picric acid, trinitroanisole, tetryl, P.E.T.N. and R.D.X., at temperatures just above the melting-point, are sensitive to cavity impacts of an energy of about 300 g.cm.—30 g. falling 10 cm. At these low energies, however, the propagation of the explosion is very limited. T.N.T. may also be decomposed by cavity impact when it is dissolved in various solvents. For example, using nitrobenzene as a solvent at 50° C, a 45M % T.N.T. solution may be obtained, and decomposition occurs with an impact energy of 1000 g.cm. Using a 35M % T.N.T.-dioxan solution at room temperature, decomposition was obtained at an impact energy of about 5000 g.cm. The effect of solvents such as toluene, benzene, ethyl alcohol and nitrobenzene on the sensitivity of nitroglycerine to cavity impact was also studied, and it was shown that the explosion efficiency was still 100 % with a 62M % nitroglycerine-toluene mixture at an energy of impact of 500 g.cm. Blasting gelatine (9 % nitrocellulose), when spread as thin films on a metal anvil and subjected to a cavity impact, gave an explosion efficiency of 90 % with a 40 g. striker falling 15 cm. (energy 600 g.cm.), and explosions were obtained with impact energies as low as 70 g.cm. A similar result was also obtained with dynamite. Further work has been done with five other liquid explosives—methyl nitrate, ethyl nitrate, tetranitromethane, nitromethane and diglycol dinitrate.

Methyl nitrate and ethyl nitrate. The sensitivity of methyl nitrate to impact in the presence of gas spaces is of the same order as that observed for nitroglycerine. Using a 40 g. cavity striker, explosions could be obtained from a height of fall of

1 cm. (energy 40 g.cm.). When flat surfaces were used and a small air bubble introduced into a thin film of the explosive, it was possible to obtain explosions with a 60 g. striker falling 5 cm. (energy 300 g.cm.). Most of the explosive confined between the impacting surfaces was consumed. This high sensitivity may be contrasted with the behaviour of methyl nitrate when spread as a thin film and subjected to impact between flat steel surfaces when no gas spaces are present. Under these conditions no explosions were obtained with 1.8 kg. falling 100 cm. (energy 1.8×10^5 g.cm.).

Ethyl nitrate, on the other hand, was found to be much less sensitive to impact when cavity strikers were used. The lower limit for the sensitivity appears to be about 800 g.cm. Even at high energies of impact the explosion did not propagate and the reaction was confined to the cavity.

Tetranitromethane was interesting for, although it behaved in a fashion fundamentally similar to that of nitroglycerine, there were marked differences. It was found that pure tetranitromethane was remarkably insensitive to flat-surface impact, cavity impact or spark. It is well known that mixtures of this substance with hydrocarbons are explosive, and on mixing it with a small quantity of toluene it was in fact readily initiated by a spark and gave a loud and powerful explosion (cf. Sidgwick 1937). Furthermore, the mixture was found to be sensitive to cavity impacts of the order of 900 g.cm. This reactivity is presumably due to the combustion of the toluene, the tetranitromethane acting as an oxidizing agent. If the volume composition of the mixture is less than about 12 % toluene, no propagation of explosion initiated by sparking is observed. Above 12 %, explosions are observed which are remarkable for their brisance, and which appear to develop, at least at low toluene percentages, in a manner similar to that of nitroglycerine. When the concentration of toluene is greater than 60 %, the passage of a spark no longer produces an explosion. Explosion by impact in the absence of gas bubbles is difficult to obtain (cf., however, the work of Stettbacher (1930), who reports an extremely high sensitivity to flat impact). Flat-surface impacts on thin films of mixture failed to produce an explosion, even at energies of the order of 10^4 g.cm. As mentioned before, however, when the striker contained a cavity as in figure 3, explosion occurred at impact energies of 900 g.cm., but the efficiency was low.

Nitromethane. It was possible to obtain explosions with a 40 g. cavity striker falling 10 cm. (energy 400 g.cm.). When small air bubbles were introduced into a thin film of nitromethane, and the explosive then subjected to flat impact, explosions were observed with a 60 g. striker falling 20 cm. (energy 1200 g.cm.). The explosions obtained were weak and did not propagate to any considerable extent.

Diglycol dinitrate. Using cavity strikers, an explosion efficiency of 10 % was observed with a 40 g. striker falling 10 cm. (energy 400 g.cm.). When small air bubbles were introduced into thin films of the explosive and subjected to flat impact, explosion occurred with a 50 g. striker falling 12 cm. (energy 600 g.cm.).

It is apparent that all the liquid explosives which have so far been investigated are very sensitive to impact when small gas spaces are present in the explosive.

It is possible that the high sensitivity of methyl nitrate when compared with ethyl nitrate is due to its high vapour pressure, and this suggests that the initiation of the explosion may occur in the vapour phase.

These particular experiments have been confined to liquid and plastic explosives, but it is possible that the inclusion and adiabatic compression of small gas spaces may play a larger part in the initiation of solid explosives than is generally recognized.

DISCUSSION

The experiments show that impact sensitivity of nitroglycerine (and other explosives in the liquid state) is increased enormously if tiny gas spaces are present in the liquid or are trapped in it during the impact. This effect is illustrated diagrammatically in figure 5, where the energy required to initiate the explosion is plotted against the explosion efficiency. The amount of air which is capable of bringing about the increase in sensitivity is minute. In the experiments where the explosive is distributed as strips, the entrapped air spaces may have a volume of about

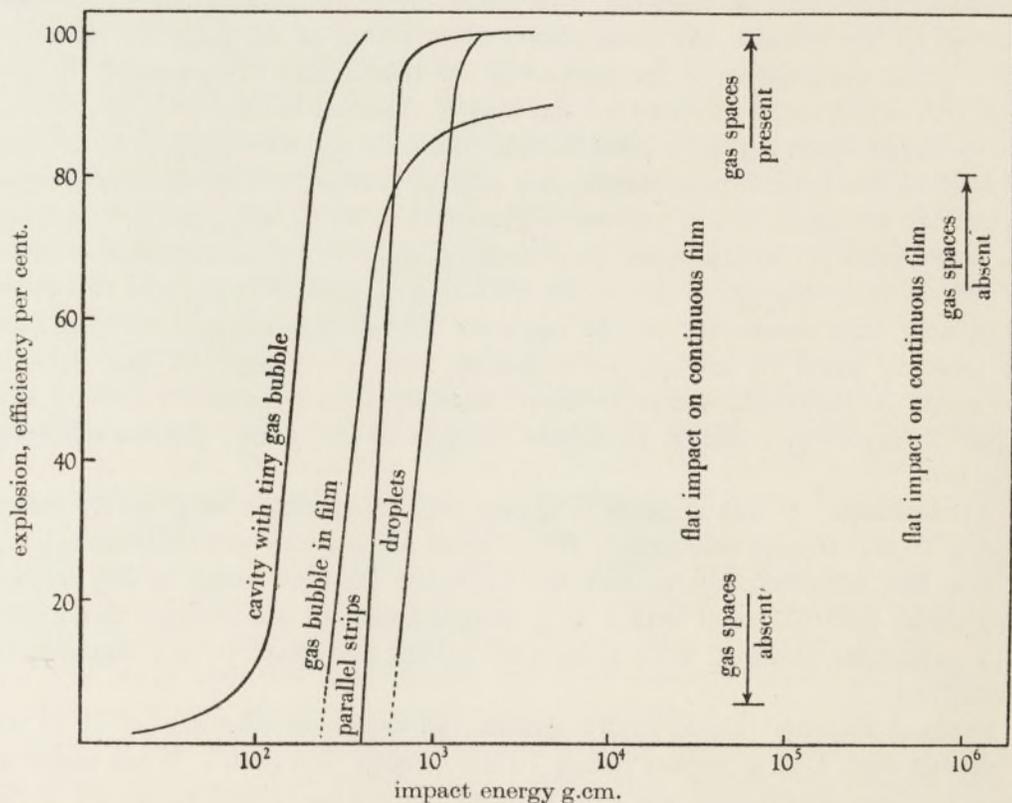


FIGURE 5

10^{-4} c.c. (mass 10^{-7} g.) before compression, and these will cause explosion with a low impact energy (250 g.cm.). The undiminished sensitivity of the strips when struck in a low-pressure atmosphere shows that the mass of air required to sensitize the explosive may be as little as 10^{-10} g. and the volume when compressed about 10^{-11} c.c.

The size of the bubbles at the first instant of their formation is roughly determined by the geometry of the arrangement of the strips, and may be assumed to be independent of the initial pressure of the air.

There is little doubt that the sensitivity is associated with the adiabatic compression and heating of the air bubble under the impact. However, the high sensitivity at low pressure of air indicates that the quantity of heat developed in the air bubble is a relatively unimportant factor compared with the actual temperature rise in the range investigated. For example, the ratio of the quantities of heat generated by equal compression of similar bubbles from atmospheric pressure and from 10^{-2} cm. Hg may be crudely calculated by multiplying the estimated rises in temperature by the mass of air in each case. Reduction of the pressure to 10^{-2} cm. causes a reduction in mass of the bubble by 1/7500 and results in an increase of the temperature rise by 20. The quantity of heat generated under the low-pressure condition is therefore only about 1/370 of that obtained by equal compression of a bubble from atmospheric pressure. It is possible, of course, that the quantity of heat generated under the low-pressure conditions, though much less than that obtained at atmospheric pressure, is still above the threshold quantity necessary for initiation under these conditions. The fact that in the cavity experiments a decline in explosion efficiency with diminishing pressure was observed is evidence of this. The lower sensitivity in the ether atmosphere than that in nitrogen at the same initial pressure (ratio of temperature rises 1:20), for both strip and cavity experiments, indicates strongly that a fairly high temperature must be reached in the bubble for initiation to be effected.

Again, though it is clear that it is the high temperature reached during the compression of the included air spaces which brings about initiation, it is also evident that the high increase in sensitivity is also due in part to the chemical nature of the gas, viz. to the presence of oxygen. This result emerges from the fact that, if included spaces of nitrogen are substituted for air spaces in the liquid, the explosion efficiency falls off (although the sensitivity is still enormously greater than that obtained in the absence of gas spaces). The importance of the chemical (oxidizing) nature of the included gas has been shown by the results of experiments previously reported (Bowden *et al.* 1943*b*). It was found that the introduction of gas bubbles into the liquid previous to impact greatly increases the sensitivity, but that the explosion efficiencies obtained when nitrogen or carbon dioxide is used are considerably less than when air, oxygen or nitrous oxide is introduced under the same conditions of impact. Further evidence that quite high temperatures are reached inside the bubble during compression is obtained from the electrical and photographic study of the initiation and propagation of the explosion

which will be described in the next paper. It will be shown that initiation of the explosion, whether due to compression of a bubble within a cavity or within a thin film of the liquid, takes place within 50×10^{-6} sec. from the beginning of the exertion of the pressure. This very short time-lag is an indication that high-temperature flashes are reached inside the bubble. A similar conclusion has been arrived at from the theoretical calculations of the pressure produced in the liquid during impact. It is possible that initiation of the explosion occurs in the vapour phase inside the bubble.

It would, of course, be interesting to calculate the time lag between the application of the high-temperature flash to the onset of decomposition. Unfortunately, no figures are available in the literature for temperatures of 400°C and greater. Roginsky (1932) did show that the time lag below 200°C could be expressed by $\tau = 1.5 \times 10^{-10} e^{(25,700/RT)}$. This relation has not been tested above 200°C . At a temperature of 900°C , which corresponds approximately to the calculated temperature rise of the air bubble in the cavity experiments, τ , according to the above equation, would be 10^{-5} sec. Our photographic and electrical study indicates a time lag from 0 to 50×10^{-6} sec.

The readiness with which small air spaces are entrapped in a continuous film of nitroglycerine under ordinary conditions of impact, and the large decrease in sensitivity observed when special precautions are taken to reduce this possibility indicate that the high sensitivity (a few thousand g.cm.) recorded for nitroglycerine in the literature may, in fact, be due to this cause. Furthermore, it appears from the few experiments in which the possibility of the trapping of air spaces during impact has been avoided, that it is difficult to obtain explosions with an impact energy of about 6×10^4 g.cm. At these large energies of impact, Cherry (1945) has shown that the temperature rise due to the viscous flow of nitroglycerine may amount to several hundred degrees, and it is possible that initiation of the explosion at these high energies is due to this effect. It would seem, therefore, that if the inclusion of these gas spaces is avoided, nitroglycerine is an explosive which is comparatively insensitive to detonation by impact.

The fact that a wide range of explosive substances is rendered sensitive to gentle impact if small bubbles are present is of some practical interest. Since the bubbles can be so small that they are difficult to see even with a microscope they readily escape detection, and, under suitable conditions, they may constitute a serious hazard.

We wish to express our thanks to Sir David Rivett, F.R.S., and to the Executive of the Council for Scientific and Industrial Research for their stimulating interest and encouragement in the work described in these papers, to the University of Melbourne and to Professor E. J. Hartung for providing facilities and accommodation, and to Imperial Chemical Industries of Australia and New Zealand Ltd and the Munitions Supply Laboratories for providing explosives. We are greatly indebted to Mr A. E. Ferguson, B.E.E., for the design of much of the electrical apparatus, and

to Mr J. S. Courtney-Pratt, B.E., and Mr T. V. Krok, B.E., for assistance with the design of the fall hammers and camera. Our thanks are also due to Mr J. R. Richards, M.Sc. and Mr N. N. Greenwood, B.Sc. for assistance with some of the experimental work.

REFERENCES

- Berthmann, A. 1941 *Chem. Abstr.* **35**, 625.
Bowden, F. P., Eirich, F., Ferguson, A. E. & Yoffe, A. 1943a *Bull. Coun. Sci. Industr. Res., Aust.*, no. 167.
Bowden, F. P., Eirich, F., Mulcahy, M. F. R., Vines, R. G. & Yoffe, A. 1943b *Bull. Coun. Sci. Industr. Res., Aust.*, no. 173.
Cherry, T. 1945 *Rep. Coun. Sci. Industr. Res., Aust.*, A, **116**, no. 8.
Eirich, F. & Tabor, D. 1945 *Rep. Coun. Sci. Industr. Res., Aust.*, A, **121**, no. 9.
Roginsky, S. Z. 1932 *Phys. Z. Sowjet.* **1**, 640.
Sidgwick, N. V. 1937 *The organic chemistry of nitrogen*. Oxford University Press.
Stettbacher, A. 1930 *Z. ges. Schiess- u. Sprengstoffw.* **25**, 439.
Will, W. 1906 *Z. ges. Schiess- u. Sprengstoffw.* **1**, 209.

The period of impact, the time of initiation and the rate of growth of the explosion of nitroglycerine

BY F. P. BOWDEN, M. F. R. MULCAHY, R. G. VINES AND A. YOFFE, *Tribophysics Section, Council for Scientific and Industrial Research, University of Melbourne*

(Communicated by Sir David Rivett, F.R.S. and Sir Robert Robertson, F.R.S.—
Received 12 January 1946—Read 9 May 1946)

[Plates 5–9]

Electrical and photographic methods have been used to measure the period of impact between colliding solids and to study the time of initiation and the rate of growth of an explosion produced by the impact. The measurements were made with liquid explosives, where, as the last paper has shown, the initiation is due to the entrapping of small gas bubbles. Under the conditions of these experiments, the period of impact—that is the time from the first moment of contact of the solid surfaces until they separate or the rebound—is about 200 μ sec.

If one of the surfaces contains a cavity, initiation with nitroglycerine is first apparent as a tiny spot of light inside the cavity. This occurs at the first moment of contact or a few microseconds after. This small flame spreads slowly through the cavity with a velocity of about 20 m./sec., and after a short interval of time (about 50 μ sec.) bursts through the cavity wall and explodes the main film. The explosion is propagated through the film with a velocity > 1000 m./sec., and the residual burning inside the cavity is finally extinguished when the surfaces separate.

When the initiation is due to a bubble entrapped in the coalescing liquid, the measurements show that initiation again begins as a small flame which becomes visible at the moment of coalescence or a few microseconds afterwards. Both the coalescence and the initiation can