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GROWTH OF BURNING TO DETONATION
IN LIQUIDS AND SOLIDS

(Annual Summary November 1968-December 1969)

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ABSTRACT

The initiation and propagation of explosion in liquids and solids has been studied with special reference to the role played by discontinuities in promoting sensitivity and the deflagration detonation transition. The growth of fast reaction in single crystals of lead and silver azide has been investigated using high speed photography. It was found that sufficiently thin crystals of these explosives burn and the dependence of deflagration velocity on crystal dimension was determined. Fracture and break-up of the crystals can occur ahead of the reaction front: in some situations these processes can stop the growth of reaction in lead azide. The effect of collapsing a bubble by a weak shock (~ 1 kbar) in the neighbourhood of the azides has been studied. Adiabatic heating of the gases in the bubble was identified as the major factor in causing initiation. Experiments on lead azide have shown that its explosion temperature depends on crystal size. In separate experiments it has been observed that thermal decomposition occurs when a fracture propagates through a crystal. The amounts and kinetics of the decomposition have been recorded for various crystal types, and temperatures associated with the fracture process evaluated. In liquid explosives the role of cavities on the transition to, and propagation of, a low velocity detonation has been studied for various liquids in both thin film and three-dimensional confinement.

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INTRODUCTION

An investigation is being made of deflagration and growth to detonation in liquids and solids with special reference to the role of small discontinuities in promoting sensitivity and the Deflagration, Detonation Transition.

The research of the last year covered a range of experimental studies and these are discussed under separate sections below. The first describes work on lead and silver azide crystals. Techniques have been developed in the laboratory for growing suitably large single crystals for these studies. Initiation of reaction was by shock and hot wire methods: the growth of reaction was recorded using high speed framing cameras. It was found that sufficiently thin crystals of both lead and silver azide burn and the dependence of deflagration velocity on crystal dimension was determined. High speed micro-photographic studies have shown that fracture and break-up of a crystal can occur ahead of the reaction front. In some situations these processes can stop the growth of reaction in β -lead azide. The study of the initiation of explosion in silver and lead azide by the collapse of cavities has continued. Finally the explosion temperature of lead azide has been found to depend on the size of the crystal and this work is discussed.

The second section describes a study of fracture-induced decomposition in brittle crystalline solids. The work as presented here is the basis of a paper prepared for publication. An experimental study was made of the thermal decomposition produced by the release of elastic strain energy when a fast cleavage crack runs through a brittle crystalline solid. The amounts of decomposition were measured for cleavages in crystals of calcium, magnesium and lead carbonates and sodium and lead azides. By relating these amounts to the fracture velocity and the kinetics of thermal decomposition of each material measured independently, a figure for the crack tip temperature can be deduced in each case. The significance of this temperature and its relevance to the possibility of generating fast self-sustaining reactions in solids is

considered. The relative magnitudes of the crack temperatures can be semi-quantitatively related to the plastic properties of the material as deduced from measurements of their indentation hardness on the cleavage plane. The decomposition of the organic compound pentaerythritol tetranitrate was also investigated.

The third section discusses our work on liquid explosives. Earlier work on thin films of nitroglycerine has shown the importance of cavities, bubbles and solid particles present in the explosive on both the initiation of reaction and also the transition to detonation. Recent work has been concerned with high magnification studies of the region where a flame front interacts with a region of cavitation. An extension was also made to other liquids and to a three-dimensional situation.

An apparatus for firing micro-particles at high velocities (up to about 10 Km/sec) is now in use in the laboratory, and is being used to find the minimum impact energy for initiation.

Background work on strength and fracture propagation in crystalline inert solids is still in progress in the laboratory.

(i) Initiation and Propagation of Fast Decomposition in Single Crystals of Lead and Silver Azide; Explosion Temperature of Lead Azide

The purpose of this work is to understand the mechanism by which fast reaction is initiated in primary explosives and the processes which are responsible for its propagation. The work is important since there is still controversy regarding the nature (i. e., whether thermal or not) of the origin of explosion. The research has mainly been with single crystals since this reduces the number of variables involved compared with agglomerates of crystals. Methods have been developed for growing large and uniform crystals. For lead azides good quality crystals up to about 4 cm. in length and 0.7 mm. diameter have been grown.

The propagation of reaction in these crystals was followed with a sub-microsecond framing camera (Beckman & Whitley, Model 189) using a back-lighting system. Reaction was initiated in various ways including shock and hot wire methods. A typical sequence showing the growth of reaction in a lead azide single crystal is shown in figure 1. The framing interval was 1 microsecond and the dimensions of the crystal were $16.7 \times 0.175 \times 0.022$ mm. The average velocity of propagation in this crystal is about 1050 m/sec. The fact that the products of decomposition have periodic changes in density is caused by vibrations in the glass slide under the crystal. This effect is removed if the crystals are mounted so that the crystal projects outwards from the edge of the slide. Figure 2 shows schematically the two ways in which single crystals of explosive have been mounted for initiation by exploding wires.

Measurements on other crystals in this size range confirm the velocity of burning found in this sequence. In frame 16 there is an indication of mechanical effects such as fracture occurring ahead of the flame front. This process has recently been studied in detail using a high magnification optical arrangement. Several examples of fractures propagating ahead of a flame front have been observed. The sequence shown in figure 1 was not typical as regards the location of initiation which occurs at a point P about 2.2 mm. from the wire. In all other hot wire initiation experiments the explosion started exactly under the wire.

In thin β -lead azide crystals the effect of deformation ahead of the flame front can hinder the growth of reaction, and in very thin crystals the reaction may fail to propagate throughout the whole crystal. It is believed that this failure is due to the formation of discontinuities in the crystal by stress wave effects.

Figure 3 illustrates how mechanical break-up of a crystal can stop the growth of reaction in a thin β -lead azide crystal. This crystal was mounted as in the arrangement 2 in figure 2. The framing interval is again 1 microsecond. Initiation in the crystal (C) was by a hot wire (W). In frame 5 a fracture (F) cuts across the crystal. This fracture acts as a barrier to

further reaction. Mechanical break-up also occurs at the far end of the crystal caused by the reflection of stress waves which cause "scabbing"; that this process occurs well ahead of the burning is confirmation that the stress wave velocity exceeds the burning velocity.

Table I contains the results of two experiments in which fracture stopped fast reaction. The combined length of the collected fragments of the azide forms a considerable proportion of the initial length. Failure to propagate a fast reaction has also been observed in experiments with thin tapered β -lead azide crystals; the reaction failed when the crystal dimensions became very small.

Table I

Original size of crystal mm.	Length of crystal fragments after growth of reaction stopped	Combined length of fragments
10.0 x 0.056 x 0.012	3.4, 1.4, 1.3, 1.2, 0.2, 0.2	7.7
7.1 x 0.062 x 0.012	3.9, 0.5, 0.4	4.8

The effect of stress waves in β -lead azide crystals was further studied in shock initiation experiments using a gap-test type arrangement in which the crystals were mounted on thin phosphor bronze sheets below which was a donor charge. It was found that a shock of intensity of only a few kbars produced initiation of explosion in the crystal at the barrier/crystal interface. For shocks of smaller intensity which failed to produce reaction at the interface the initiation did not occur at all although the crystal frequently fragmented extensively.

In the above experiments it was not possible to observe the initiating shock, and thus the delay between the transition of the shock and the initiation of reaction was not accurately known. In order to detect the presence of the transmitted shock and also be able to measure its pressure a series of experiments were made under water. Shocks of intensity of only a few kbars were readily visible in the water and it was found that only

a very small delay occurred between transmission of the shock into the crystal and the initiation of explosion. Shock pressures were estimated from the measured water shock velocities.

An interesting observation from these experiments was that the sensitivity of the crystals increased for the water confinement. In some cases initiation of reaction also occurred at points away from the interface. The reason for this increased sensitivity is thought to be due to the formation of cavities on the surface of the crystals by precursor shocks in the crystal. These cavities are then collapsed on to the surface of the crystal by the following water shock (its speed is less than the shock waves in the explosive). Initiation of reaction occurs at the points of cavity collapse.

The cavity collapse model has been examined by placing bubbles (in the range 50 μ to 1 mm) on individual single crystals confined by water: these bubbles were then collapsed on to the crystal by sending a small shock (~ 1 kbar) over them. The whole process was filmed at microsecond framing rates using a Beckman & Whitley (Model 189) camera. A typical sequence is shown in figure 4. The bubble reaches minimum volume in frame 10 and growth of explosion in the crystal starts. In experiments in which bubbles were not present explosion was never observed for shocks of this strength.

In the last annual report (EOOAR-68-0001) photographic sequences were shown of cavities being collapsed by shocks passing over them. Three stages of the collapse process were identified as being of possible importance to explosive initiation. Briefly, these may be listed as (i) rapid collapse of the bubble causing adiabatic heating of the gases inside, (ii) involution of the bubble to form high-speed micro jets (velocity a few 100 m/s), (iii) production of an expansion shock (strength ~ 1 kbar) during the rebound stage.

It is possible to distinguish the relative importance of the above three processes by suitable choice of the geometry of the experimental situation, (for example, by changing the position of the bubble and/or the direction of the shock with respect to the crystal). The results of these

experiments showed that the high temperature produced in the bubble was the major factor causing initiation. By measuring the minimum volume ($\sim \frac{1}{60}$ th of initial value) of the bubble before it initiates the crystal an estimate of the temperature in the bubble can be made. For a bubble containing air a typical estimate is about 1500°K . A paper on the early stages of this work has already been published (Bowden & Chaudhri, 1968).

Figure 5 shows a recent sequence in which bubbles of different sizes were attached to a silver azide crystal. The diameter of the biggest bubble is 1.75 mm, while that of b_1 , b_2 , b_3 and b_4 are $50\ \mu$, $80\ \mu$, $80\ \mu$ and $250\ \mu$ respectively (measurements taken directly, not from the photographs of figure 5). It can be seen in frame 3 that the smallest bubble caused initiation first, whereas at this stage there is very little change of volume of the biggest bubble. Later in frame 4 initiation takes place where the other small bubbles were sitting; the biggest bubble has still not reached minimum volume.

Air bubbles down to $50\ \mu$ caused initiation of silver azide if they collapsed in contact with the crystal surface. Experiments with butane (a lower value for γ the ratio of the specific heats) in the bubbles gave initiation for millimetre sized bubbles but not for small ones in the range 50 to $220\ \mu$. This result supports the suggestion that adiabatic heating during the collapse process is a major effect.

The minimum thermal energy input to initiate silver azide has been estimated from experiments of the type discussed above. The conclusion is that if approximately 2×10^{-11} calories of thermal energy are applied to an area $1\ \mu^2$ within a sufficiently short time then initiation of reaction can result.

The velocity of deflagration was measured in all the various types of experiments discussed above. The main factor controlling the burning velocity appears to be the thickness of the crystal. Measurements on β -lead azide show an increase in velocity from 1000 to 1600 m/sec as the thickness increases from 20 to 60 microns. For crystal thicknesses

in excess of 60 microns the results are mainly for the α -form of lead azide. This crystal shows a similar trend of increasing velocity with thickness. However, above 215 microns and up to the largest size so far studied (670 microns) the propagation velocity remains approximately constant at about 2900 m/sec.

The suggested explanation for the propagation of reaction up to 2,900 m/sec in lead azide single crystals is that energy from the decomposing layers is transmitted to neighbouring undecomposed layers by conduction of heat. In a thin crystal (in which the reaction speed is less than about 2,000 m/s), the heat losses are considerable and the temperature of the reacting crystals (at the products/undecomposed crystal interface) controls the rate of propagation. As the thickness of the crystal is increased the temperature of the crystal increases, which results in a higher propagation rate. However the propagation velocity will not continue to increase after the velocity has become equal to the maximum velocity with which heat can be conducted from one monolayer to the next even though the temperature of the crystal may continue to rise with the thickness. This means that the upper limit of the propagation velocity should be equal to the velocity of sound in the crystal. It should be pointed out that this upper limit is only for the crystals in which the shocks produced due to fast decomposition are not strong enough to cause significant shock heating effects. Our experimental results support this model.

Explosion temperature of lead azide

A thermal enclosure has been constructed which allows microscopic examination of an explosive crystal while it is heated and its explosion temperature and time to explosion measured. Single crystals of α -lead azide were used in this study. The crystals were inserted when the furnace was already at a chosen temperature. A dependence of explosion temperature

on crystal dimension was found. Below 3 μ thickness the crystals did not explode, even for temperatures as high as 570°C. 4 μ crystals exploded at 420°C. This temperature gradually decreased with increasing crystal thickness (approximately exponentially) reaching a value of 390°C for 34 μ thick crystals. Since the decomposition, even at high temperatures, for lead azide is surface controlled (this would indicate that there should be no dependence of explosion temperature on size) the observed size dependence is thought to be related to defects. The microscopic evidence supports this.

(11) Fracture-Induced Thermal Decomposition in Brittle Crystalline Solids

The continuing importance of the Griffith criterion in the theory of fracture stems from the fact that, because it is simply a statement of the principle of conservation of energy, it is capable of progressive enlargement as more and more terms are found to be important in particular fracture situations. Thus the original theory was applied to the case of a perfectly brittle solid in which the elastic strain energy at the point of rupture is converted into the excess energy of the two new surfaces formed. This simple energy balance was subsequently modified by Mott (1948) to include an additional term for the kinetic energy of the fragments produced in the fracture process and this treatment demonstrated how the fracture velocity is limited by the elastic properties of the material to some fraction of the velocity of sound in that material. This was later shown to be equal to the velocity of surface waves (Rayleigh waves) on the new surfaces formed (Broberg, 1964).

Further progress came with the recognition that most materials are far from ideally brittle and that some of the elastic strain energy can be dissipated during fracture, by plastic flow which, in the case of crystalline materials, takes place by the generation and movement of dislocations and in amorphous materials by viscous flow. This term in the energy balance is normally large in comparison with the surface energy term, as first pointed out by Orowan (1949) and subsequently developed by Orowan (1952) and Irwin (1958).

The method of balancing energy released with energy consumed is capable of unlimited application. Moreover, the amount of elastic energy available is fixed by the elastic properties of the material and the relative contributions to the various dissipative processes may be dependent upon the temperature. This problem has recently been studied for the case of viscoelastic materials (Williams, 1966).

In the study described here we considered the possibility that, in a fracture process, some of the energy released may be used in promoting chemical reactions in thermally unstable materials. We have also attempted to assess the role of fracture in very fast reactions in solids.

Two groups of compounds have been studied; in one the materials decompose with an absorption of heat (endothermic) and in the other with an evolution of heat (exothermic). The first group comprises calcium, magnesium and lead carbonates and the second sodium and lead azides. The materials in both groups decompose on heating to produce a single gaseous species and a solid residue and in this respect the reactions are chemically 'simple'.

We may write the condition for crack growth in terms of a Griffith type energy balance in the following way,

$$\frac{d}{dc} \left\{ E_{el} - [E_s + E_{ke} + (E_{pl} + E_{chem})] \right\} \gg 0$$

where c is the length of the crack and the subscripts for the energy terms represent the contributions of elastic, surface, kinetic, plastic and chemical energies respectively. By bracketing the plastic and chemical energy terms together we imply that the elastic energy which is not consumed in the surface and kinetic energy terms will be divided between the plastic and chemical terms in a way which depends upon the ductility of the material at the temperature of the experiment.

Here we describe experiments to measure the amount of thermal decomposition produced by fracture and discuss the results in terms of the relative plastic properties of the materials studied and the energetics of the decomposition process.

To reduce the uncertain effects of crack velocity on the mobility of dislocations in these materials, we have used an energetic fracturing technique in an attempt to drive the crack at maximum speed through the crystal, in this way minimising the dissipation of energy in plastic flow with the hope that more will be made available for thermal decomposition.

Experimental

Apparatus. The amount of decomposition produced by fracture is small necessitating rather sensitive experimental techniques for detection. This was achieved with the apparatus shown schematically in figure 6. It consists of a high vacuum system in which background pressures of less than 1 pbar are normally attained. This provides sufficient sensitivity for the detection of an amount of decomposition corresponding to considerably less than one mon. molecular layer of new fracture surface. Decomposition products were detected and measured with a fast scanning mass analyser of the quadrupole mass filter type and since no synchronisation between the fracture event and mass scan was available, the mass spectrum was scanned continuously and repeatedly (scan rate, 1 msec/a.m.u.) while the fracture was made, and recorded photographically.

The crystal was mounted on an anvil with one of its cleavage planes vertical and fractures were made with a blunt chisel located in a V-notch cut in the top edge as shown in the inset (a) to figure 6. In most cases the chisel was struck energetically with a hammer blow but in a few experiments a more precisely shaped energy pulse was used. This was obtained by using a small explosive charge loaded into a hollow chisel and as close to the point as possible to reduce attenuation in the shank, inset 6 (b). We believe that by using such an energetic method of fracture the cracks produced reach maximum velocity and this seems to be confirmed from an examination of the features on the new surfaces formed. The effect of crack velocity was studied qualitatively by replacing the loading arrangement with one in which the chisel could be lowered more slowly into the V-notch producing a less energetic fracture.

These methods were used for all materials except lead azide which was available only in needle shaped crystals of up to 1 cm length. These were fractured by a three point bending technique in which the crystal was laid across two supports at its ends and the fracture made by driving a wedge through the crystal at its mid point.

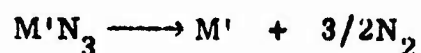
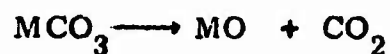
Materials. All of the carbonate crystals used were of natural origin. The calcium carbonate was calcite of optical quality. Magnesium carbonate was magnesite available from two sources, Vikersund (Norway) and Oberdorf (Austria). Those from the latter source contained less occluded impurities, water and nitrogen being the main impurities in the Norwegian crystals. Crystals of lead carbonate were obtained as the mineral cerussite from Tsameb (S.W. Africa). The carbonates were all prepared in a form suitable for the experiments by cleavage.

Sodium and β -lead azide crystals were grown from aqueous solution in a form suitable for fracture. The sodium azide specimens were prepared by cleaving to the correct size as for the carbonates. The lead azide was used as grown.

Decomposition kinetics. The parameters in the rate equations for the thermal decomposition of all the materials were determined in an independent set of experiments in which the rates of decomposition (evolution of gas) were measured as a function of temperature. The apparatus was essentially similar to that already described in figure 6, except that the arrangement for fracturing the crystals was replaced by a small heater maintained at a known temperature into which the crystal could be inserted. The sensitivity of the method is again such that fractions of a monolayer decomposition per cm^2 can be measured.

Results

The decomposition which occurs during high speed fracture may be represented by the following chemical reactions:



where $M = \text{Ca, Mg and Pb}$ and $M' = \text{Na and Pb}$. The results are summarised in the left hand portion of Table II: the number of molecules of gas resulting from decomposition has been calculated from the pressure rise on fracture, the volume of the system and the sensitivity of the mass spectrometer. The average number of molecular layers decomposed is deduced from the molecular density on the cleavage plane. The values given are average since the increase in area due to such cleavage features as step formation and river patterns has not been taken into account.

The possibility that at least some of the gas evolved was occluded or dissolved in the crystal was investigated by fracturing crystals at different speeds. These experiments showed that the amount of gas evolved varied by a factor of about 100 up to a constant maximum value per unit area for the most energetic fractures and it is these values which are shown in the table. A series of experiments on magnesium oxide single crystals showed that while no decomposition products could be detected, which was expected because of the high thermal stability of MgO , in some cases occluded gas characteristic of the atmosphere in which the crystals were grown was observed. This could be associated with the occurrence of hexagonal holes in the fracture surface which were presumably filled with the gas before fracture.

The thermal decomposition of the crystals used in the present investigation produces the same reaction products as those observed during fracture. The decomposition rate may be expressed by an Arrhenius relation of the form:

$$\text{Rate} = A \exp \left[\frac{-Q}{RT} \right]$$

where A is the pre-exponential (frequency) factor, R the gas constant and T the absolute temperature. The experimental data is plotted as a series of Arrhenius plots in figure 7 and the values for the parameters A and Q are shown in the right hand half of Table II. In the discussion we shall assume that the kinetic parameters obtained from such data are material constants of the crystals; that they are unchanged by the conditions of the experiment and even apply to the extremely rapid decomposition occurring during fracture.

Table II

Fracture Data			Thermal Decomposition Data	
Material	Amount decomp. molecules m ⁻²	Av. no. of molecular layers decomposed	Pre-exponential factor A. m ⁻² sec ⁻¹	Activation Energy for decomposition 10 ² kJ mole ⁻¹
Calcium carbonate (calcite)	2 x 10 ¹⁷	0.09	1.2 x 10 ⁴⁶	3.82 ± 0.25
Magnesium carbonate (magnesite)	1 x 10 ¹⁸	0.37	2.3 x 10 ³¹	1.76 ± 0.03
Lead carbonate (cerussite)	7 x 10 ¹⁸	ca. 2	4.8 x 10 ⁴⁶	2.39 ± 0.12
Sodium azide	1 x 10 ¹⁷	0.02	3.0 x 10 ³⁸	1.93 ± 0.26
α-lead azide	3 x 10 ¹⁹	ca. 10	7.4 x 10 ³⁰	1.25 ± 0.12

This is not necessarily the case. For instance we have shown recently that the activation energy for decomposition of calcite is very sensitive to the defect structure of the material (Fox & Soria-Ruiz, 1969). In the table the values of A and Q are for freshly cleaved unannealed crystals. With magnesite crystals the decomposition did not seem to depend upon such factors so that the values of A and Q are independent of the state of the crystal. On the other hand the decomposition kinetics of lead carbonate are complicated by a series of intermediate decomposition products involving lead carbonate and lead monoxide, the composition of which depends upon the temperature of decomposition (see for example Young, 1966). This material is therefore unsuitable for this type of study in which we have tried to choose reactions which take place in a single step. However, the results are included because they illustrate the general features of fracture-induced decomposition.

The complexity of the decomposition reactions in the carbonates is to a large extent mirrored in their decomposition behaviour on fracture. For instance the evolution of CO_2 is so fast in calcite and magnesite fractures that the rate of rise cannot be followed with the present recording technique which has a time resolution of rather better than 0.1 seconds. However for cerussite fractures CO_2 is evolved over a period of several seconds. Furthermore after fracture of magnesite the pressure of gas was constant but decreased in the presence of calcite probably due to recombination of the CO_2 with the fracture surface. This recombination behaviour has been observed previously in the decomposition of calcium carbonate (Hyatt et al., 1958). The general behaviour of the three carbonates is shown schematically in figure 8. No such complications are observed in fracture experiments with the azides.

Discussion

The results described in this work show that fast fractures in brittle crystalline solids may be accompanied by chemical decomposition if the material is thermally unstable. If we assume that this decomposition takes place by the same mechanism as that which occurs during simple

thermal decomposition, we may calculate directly the effective temperature at the crack tip. This may be done by using the thermal decomposition rate equation, a knowledge of the amount of decomposition and the time taken for the crack to traverse the specimen. This latter was not measured directly in the present series of experiments but was calculated from the fracture velocities of the materials. For some of these the fracture velocities are given in the literature; for others the velocities were assumed to be one half of the longitudinal stress wave velocity calculated from the expression $v_1 = (E/\rho)^{1/2}$ where E is Young's modulus and ρ the density of the material. Measurements of E for the azides have been described recently (Fox 1969). Examination of the fracture surface markings suggest that in the present experiments the cracks travelled at near maximum velocities; moreover no appreciable difference in amount of decomposition was observed in calcite for crystals fractures by impact and by the detonator methods.

In addition, some estimate of the width of the zone around the crack tip is required before the calculation can be carried out, since it is this region only which decomposes as the crack passes through the specimen. This quantity is unknown but in the present calculations, we assume it to be of the order of molecular dimensions and in fact equal to one unit cell dimension on the fracture plane. This choice is arbitrary and will, together with some uncertainty in the actual fracture velocity, affect the values obtained for the crack tip temperature.

From the amount decomposed per unit area and the time taken for the crack to traverse a unit cell dimension, the rate of decomposition is then obtained. A typical calculation, in this case for calcite, is as follows:

$$\begin{aligned} \text{Rate of decomposition} &= \frac{\text{number of molecules decomposed/unit area}}{\text{time for crack to traverse one unit cell}} \\ &= \frac{2 \times 10^{17}}{1.8 \times 10^{-13}} \\ &= 1.1 \times 10^{30} \text{ molecules m}^{-2} \text{ s}^{-1}. \end{aligned}$$

Putting this value into the rate equation and using the values of A and Q from Table II, we obtain:

$$1.1 \times 10^{30} = 1.2 \times 10^{46} \exp \left[\frac{-3.82 \times 10^5}{R.T.} \right]$$

$$\text{whence } T = 1250 \text{ K}$$

The results are shown in Table III in which the materials are divided into two categories, those which decompose endothermically and those in which heat is evolved on decomposition. For the latter group, the possibility exists of the reaction becoming partially self sustaining and this we believe is the case for lead azide in which an apparently large amount of decomposition per unit area gives rise to an unrealistically high temperature which in this case does not represent the true crack tip temperature. We may expect the values for the temperature calculated for the first group of materials to be, within the limits of the assumptions made, more realistic. (The seemingly unrealistic temperature for magnesite may be due to the uncertainties in the width of the reaction zone and the crack velocity. The calculation of T for magnesite is particularly sensitive to these quantities because of the low value of the pre-exponential factor A for magnesite decomposition. For instance errors of a factor of two in the reaction zone width and the fracture velocity decrease the crack tip temperature to 7580 K).

The physical significance of the crack tip temperature is not clear, especially for those materials in which only a fraction of a monolayer is decomposed. Thus for maximum velocity cracks, chemical bonds are traversed by the crack in a time comparable to that required for one vibration of the bond. For this reason there is no possibility of thermal equilibrium being attained. Consequently 'temperature' can only be defined in terms of the average energy required to break the bonds of the molecules decomposed. We call this the equivalent temperature.

The relative crack tip temperatures. Calcium carbonate is more stable on heating than magnesium carbonate, i.e., the temperature required to produce a given rate of decomposition is higher for calcite than for magnesite. This is reflected in Table II which shows a five-fold difference in the amount of decomposition in the two materials. However the calculated crack tip temperature in magnesite seems disproportionately high compared with that for calcite. Furthermore, lead azide is more stable than sodium azide if judged by the slow thermal decomposition behaviour of the two materials (Fox, 1969) although the crack tip temperature in the latter is now

Table III

Material	Equivalent crack tip temperature K	Energy release on decomposition Jm^{-2}	Hardness V. H. N. kg. mm ⁻²	Fracture velocity km s^{-1}	Time taken to traverse one unit cell. 10^{13} s.
<u>I Endothermic</u>					
Calcium carbonate calcite	1250		160	3.60*	1.8
Magnesium carbonate magnesite	1.5×10^4		460	3.45*	1.8
Lead carbonate cerussite					
Magnesium oxide	$< 1900^{++}$		845	$5.10^{\dagger}$	0.8
<u>II Exothermic</u>					
Sodium azide	507	3.5×10^{-3}	10	$0.48^{\dagger}$	31.7
α -lead azide	very large	24	130	$0.97^{\dagger}$	6.4

* Calculated from measurements of the longitudinal stress wave velocity
(Peselnich and Robie, 1963; Simmons, 1964)

+ Calculated from measurements of Young's modulus (Fox, 1969)

$\dagger$ From the measurements of Field (1965)

$^{++}$ Calculated from the limits of detection of the apparatus (10^{16} molecules m^{-2})

much lower than in the former. From this there would seem to be no consistent relationship between chemical stability and crack tip temperature. This can be rationalised by a consideration of the relative plasticities of each material.

In the introduction we have implied that the available elastic strain energy which is not used in surface and kinetic energy will be divided between plastic and chemical dissipation terms in a way which depends upon the plasticity of the material. For example, if less energy is used in plastic deformation more will be available for thermal decomposition. By propagating cracks at their maximum velocity we have attempted to eliminate the uncertain effects of strain rate dependence of dislocation velocity in order to compare the plastic properties of each material under conditions in which velocity effects are strictly comparable from one material to the other (Tetelman, 1963).

Tetelman has shown theoretically that the most effective method of dissipating energy plastically during crack propagation is by multiple cross glide on to planes adjacent to the fracture plane. He has also shown how the amount of energy dissipated by this method varies with crack speed. Experiments on sodium chloride (Schmidt, 1966) have shown that for maximum velocity cracks, the range of dislocations is limited to about 1 μm on either side of the cleavage plane. In this work we have obtained a semi-quantitative comparison between the plastic behaviour of each material by making indentation hardness measurements on the fracture faces of the crystals. These were made using a Leitz Durimet hardness machine at a load of 10 gms (loading time 90 secs) and the results are given in Table III.

The hardness of a material is a measure of its resistance to plastic deformation and it can be seen from the table that the harder the material the higher is the temperature generated at the crack tip. This implies that the smaller the amount of energy which can be dissipated in plastic flow in the crystal the more there is available for thermal decomposition. The correlation is at best rather qualitative since there is a vast difference in the rate of deformation during fracture compared with the hardness test.

Furthermore the hardness of the material will, in general, bear a complex relationship to its plastic properties depending on the symmetry of the crystal and the slip systems which can be operated by the mechanical deformation.

Calcium and magnesium carbonates and sodium azide are all rhombohedral (hexagonal); the hardness for all these materials has been determined on the (100) $\{10\bar{1}1\}$ cleavage face. One might then ask why they differ so markedly in their hardness values. The etching of dislocations around hardness indentations in the two carbonates shows that the major difference in deformation behaviour lies in the fact that while calcite readily twins on $\{110\}$ planes, this is not the case for magnesite. The very low hardness value for sodium azide is not yet explained.

The temperature rise due to plastic flow. Since the early work of Taylor and Quinney (1934) which demonstrated that almost all the energy of dislocation movement was dissipated as heat, several attempts have been made to measure the temperature rise produced by this mechanism when plastic materials are fractured. For instance, a recent detailed study of fractures in polymethylmethacrylate by Doll (1967) has shown that the temperature rise in the plastic zone is only about 20°C . This low value is characteristic of the dissipation of energy by plastic flow which is dissipated over a relatively large volume of material depending upon the crack velocity. It is not to be compared with the temperature referred to here as the effective crack tip temperature.

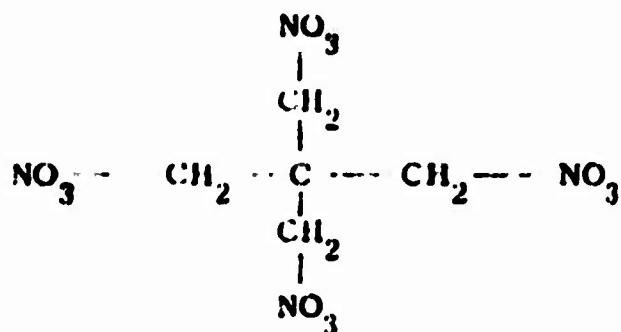
Fast reactions in solids

Because decomposition accompanies fractures in some solids, it is interesting to consider the possibility of inducing self propagating reactions by this method. For explosive reactions, the mechanism has the advantages of predicting the correct reaction speeds, i.e., of the order of kilometres per second and furthermore involves surface decomposition which is known to be rate controlling for many types of solid state reaction (Montagu-Pollock, 1962; Walker et al., 1966).

The carbonates decompose endothermically which precludes the possibility of these reactions becoming self sustaining. On the other hand the azides are exothermic materials and it can be seen from Table III that considerably more energy is liberated by lead azide than by sodium azide. Lead azide is, indeed, very prone to react with explosive violence under the stimulus of the low stress levels required to produce fracture in these crystals. On the other hand, sodium azide which is much less exothermic, liberates much less heat on fracture (Table III) and is not explosively reactive under these conditions.

The problem of explosive reactions induced by fracture in solids has been treated in greater detail elsewhere (Fox, 1969).

The behaviour of more complex molecules. Finally we consider the behaviour of a much more complex molecule during the fracture of its crystals. Pentaerythritol tetrannitrate is a symmetrical molecule of the structure shown. It crystallises with tetragonal symmetry to produce crystals of simple morphology.



However, it is clearly capable of much more complex modes of thermal decomposition. On fracturing the crystal, the molecule cleaves at the four central C-C bonds producing fragments of the type $-\text{CH}_2 - \text{NO}_3$ and also small amounts of the fragments $\text{NO}_3 - \text{CH}_2 - \text{C} - \text{CH}_2 - \text{NO}_3$. These fragments rapidly degrade to CO and NO via intermediate amounts of other fragments of low molecular weight. Since the decomposition kinetics are so complex it is not possible to deduce an equivalent crack-tip temperature. However the experiments show that, as with the simpler compounds studied, crack propagation is accompanied by marked molecular decomposition.

(iii) The Initiation and Growth of Explosion in Liquids

In earlier papers from this laboratory (Bowden & McOnie, 1965, 1967; McOnie, 1965) we discussed initiation and growth of explosion in thin liquid films of nitroglycerine. Initiation of deflagration was by rapid condenser discharge across a spark gap. This work stressed the importance of cavities on both the initiation and transition to detonation in liquid explosives. These cavities were sometimes present originally in the film but were also formed ahead of the reaction front as the burning developed. Bowden and McOnie used an A.W.R.E. C_4 continuous access high speed framing camera capable of a minimum interframe time of 5 microseconds. Recent studies have extended this work using rotating mirror cameras capable of sub-microsecond framing intervals (Beckman & Whitley 1989, A.W.R.E. C_5) as well as with the previous C_4 camera.

At the time of the earlier papers the cavitation fields set up in the thin film situation were not fully understood. High speed camera studies with inert liquids such as water have now shown the way precursor waves in the confining solids create the cavitation in the liquid. The evidence at present is consistent with the view that of the stress waves generated during the spark discharge (and the burning in the explosive situation) it is the Rayleigh surface wave which is responsible for the cavitation. The use of higher framing rates combined with higher magnification has also allowed the interaction between the flame front and the cavities to be studied in detail. Since the burning progresses at velocities of only a few hundred metres/sec, the precursor waves in the confining plates travel well ahead of the burning and cavitation in the liquid results. However, the burning sends compression shocks into the liquid and these have the effect of removing cavities ahead of the flame front. With nitroglycerine the burning accelerates and eventually reaches the region of cavitated liquid. At this stage transfer to a low velocity detonation occurs. In the earlier work transition to detonation occurred between two successive frames and it was not possible to distinguish the precise sequence of events. Latest photographic evidence shows that the transfer occurs just before the flame front enters the

cavitated region at points in the zone where cavities have recently been very rapidly collapsed. This gives strong evidence for a mechanism involving heating of the liquid by the adiabatic collapse of cavities.

The low velocity detonation travels at a velocity of about 1100 m/sec with perspex confining plates. With glass confining plates this velocity is higher at a value of about 1600 m/sec. There is some evidence that the increased surface area provided by the cavities and the relative ease with which products can traverse them, aids the propagation of explosion at this stage. The records also show that a burning front passes back towards the centre of the liquid film at a velocity of about 300 m/sec: this indicates that only partial burning occurred in the initial stages of deflagration.

Various other liquid explosives have been examined in this thin film confinement. In many cases (for example, nitromethane/nitric acid mixtures, hydrogen peroxide/ethanol mixtures, D. E. G. D. N.) the burning accelerates to a velocity of about 270 m/sec but does not exceed this value. This proves to be too low for the flame front to reach the rear of the cavitated region and transition to detonation does not occur. It appears that the sealing of cavities by the compression shocks is an important process since this clears the liquid ahead of the burning front.

Nitroglycerine has been examined in a 3-dimensional situation in which the effect of confining solids and reflected waves was minimised. This system also shows the importance of cavities, bubbles and occluded particles on the transition process. When the liquid is homogeneous and remains so ahead of the flame the reaction progresses throughout as a deflagration.

(iv) Micro-particle Impact of Explosive Materials

A micro-particle accelerator (130 KV) has been constructed in the laboratory capable of firing micron sized particles at velocities of up to about 10 Km/s. Since the particle size and velocity can both be measured to a few percent, the kinetic energy carried by the particle and the pressures

generated during impact can be estimated reasonably accurately. The apparatus should prove useful in finding the minimum energy input parameters required to initiate reaction.

(v) Fracture of Solids: Explosive and Inert

A programme of work is in progress in the laboratory for studying fracture growth in solids. Many of the results provide useful information for certain aspects of the explosives work. The results of this study can be briefly summarised as follows:

(1) In brittle solids cracks can quickly accelerate to high speeds. Velocities of the order of 1000 m/s can be reached in times of the order of a microsecond.

(2) For many brittle solids a maximum velocity of crack propagation exists. This velocity can be very high (1500 m/s in soda glass, in excess of 5000 m/s for magnesium oxide).

(3) The maximum speed in isotropic solids is about 0.3 of the dilatational wave velocity, at that velocity crack forking can occur. In crystalline solids with well-defined cleavage planes values of about 0.5 have been recorded (see Field & Heyes 1965; Bowden & Field, 1967).

(4) Crack motion can be strongly affected by stress waves. The interaction may even cause crack forking.

(5) Very intense stress waves can cause initiation of many individual cracks along their path. In these circumstances a fracture front can travel at the stress wave speed even though the individual cracks travel somewhat slower.

For studies of crack motion high resolution techniques are required. In our work we have used various experimental approaches including high-speed photography, an ultrasonic technique in which high frequency waves (typically 5×10^6 c.p.s.) modulate the growing fracture effectively leaving "time-markings" on the fracture surface, and electrical methods. Recently a study has started of crack motion in explosive single

crystals using high-speed photography and the ultrasonic method. The highest crack velocities so far recorded in both P. E. T. N. and lead azide are about 700 m/s. The maximum velocity observed in silver azide appears to be somewhat lower at about 200 m/s.

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CAPTIONS TO FIGURES

Figure 1 A sequence showing the propagation of fast reaction in a thin α -lead azide crystal in air. The whole of the crystal is lying on a microscope slide. Framing interval 1.0μ sec.

Figure 2. Schematic representation of the two ways in which single crystals of explosive have been mounted for the high speed photographic studies of growth of reaction for initiation by hot wire.

Figure 3. This sequence shows that in a thin α -lead azide crystal the reaction stops at a crack formed ahead of the flame. Framing interval 1.0μ sec.

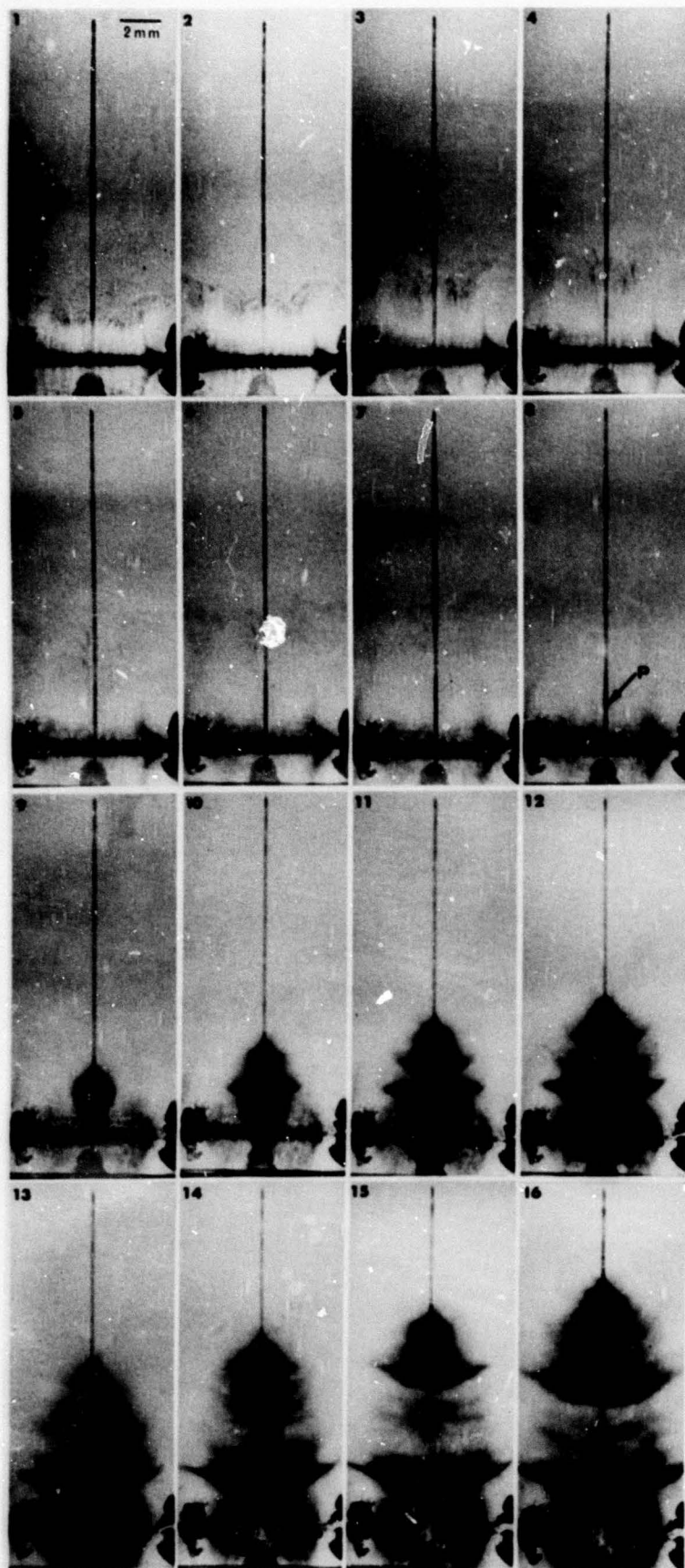
Figure 4. Initiation of explosion in a single crystal of AgN_3 by a bubble collapsing on to the surface. Initiation takes place at the point of contact and when the bubble is near its minimum volume (frame 10). The time interval between frames is 1μ sec. Length of the crystal is 7.3 mm and its diameter 123μ .

Figure 5. This sequence shows that a small air bubble, b_1 , of diameter $50\ \mu$ can lead to initiation when it is collapsed, also that it causes initiation in a much shorter time than for the large air bubble B. Framing interval $1.0\ \mu$ sec. Magnification 3.7X.

Figure 6. Apparatus for measuring the amount of chemical decomposition produced by fracture. BA is a metal bellows assembly which holds the chisel and can be adjusted for correct positioning of the chisel in a V-notch cut into the crystal. W is a window. Inset (a) shows the arrangement for making fractures by a sharp blow applied to the top of the bellows assembly. (b) shows the alternative arrangement in which the fracture energy is supplied by a small electrically operated detonator D positioned as close as possible to the sharp end of a hardened steel chisel C.

Figure 7. Arrhenius plots for the thermal decomposition of each material studied. The data for sodium azide is derived from Walker (1965).

Figure 8. Schematic comparison of the evolution of CO_2 from fractures in the three carbonates studied. The maximum values are recorded 'instantaneously' for calcite and magnesite whereas CO_2 is evolved for several seconds after the fracture of cerussite.



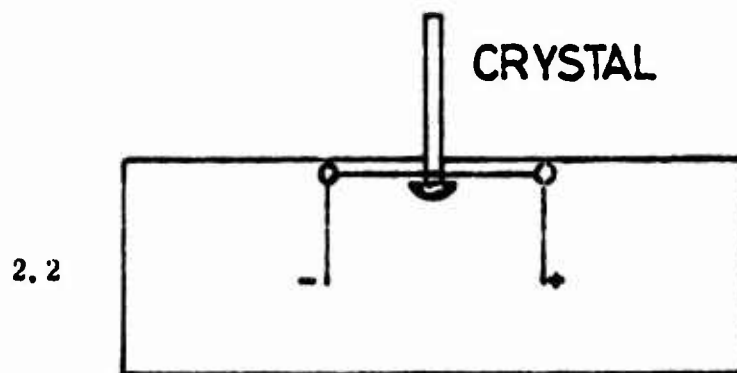
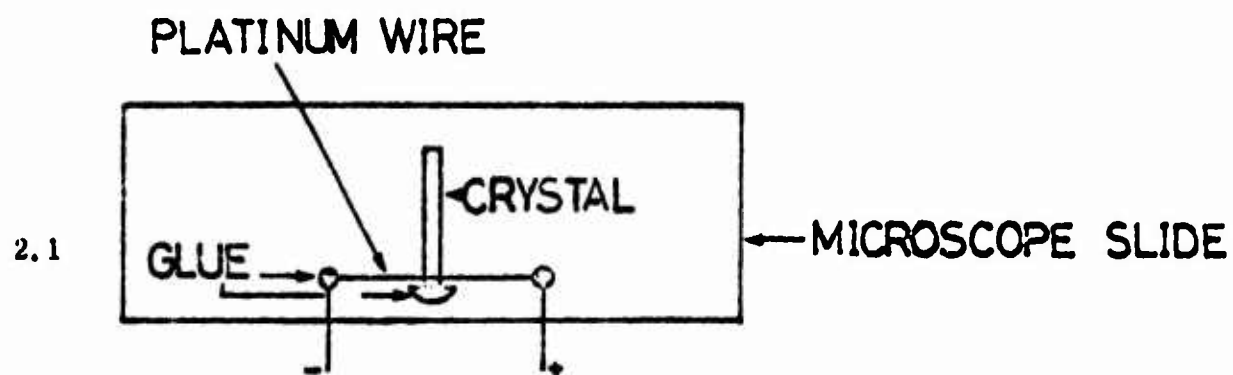
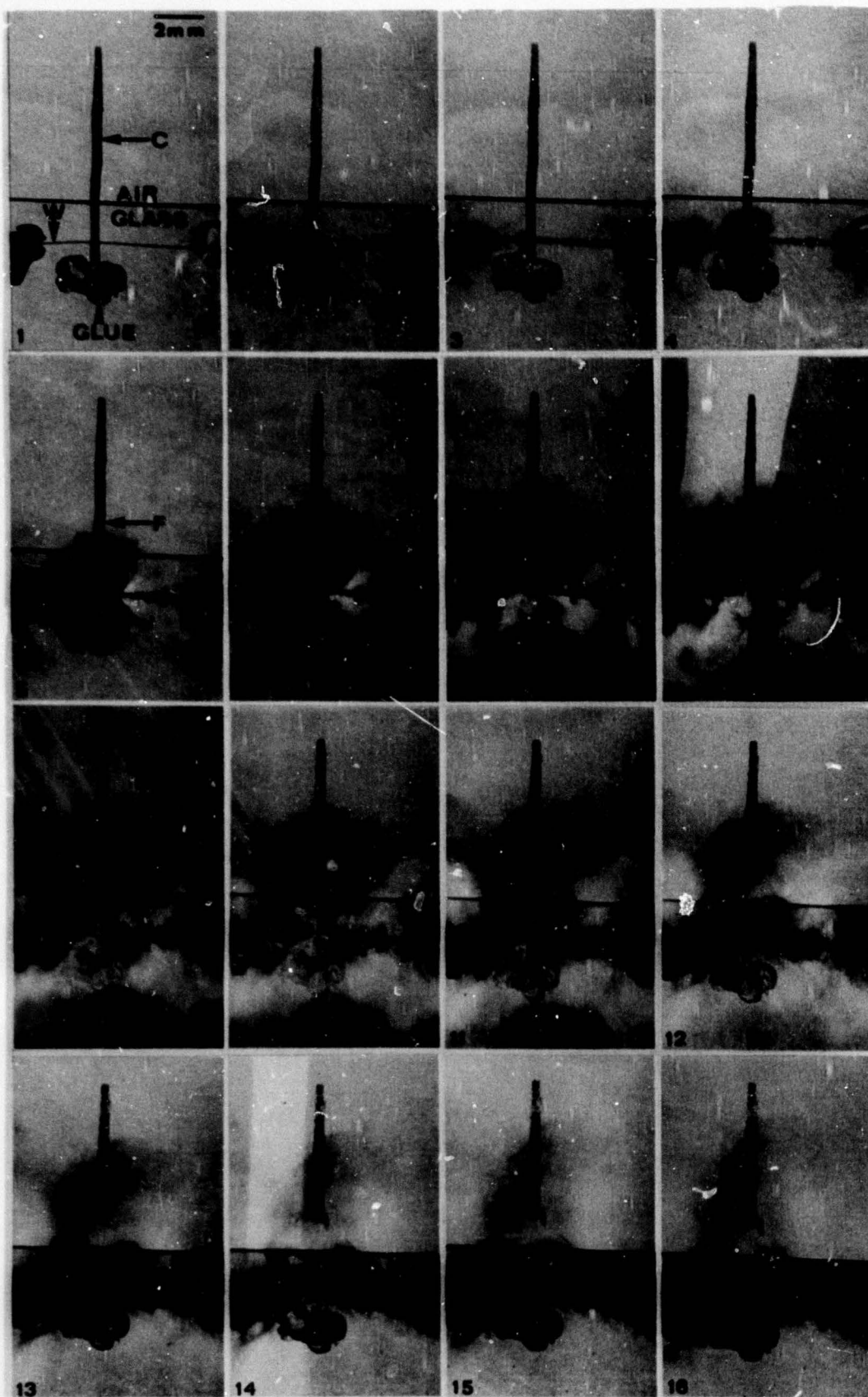
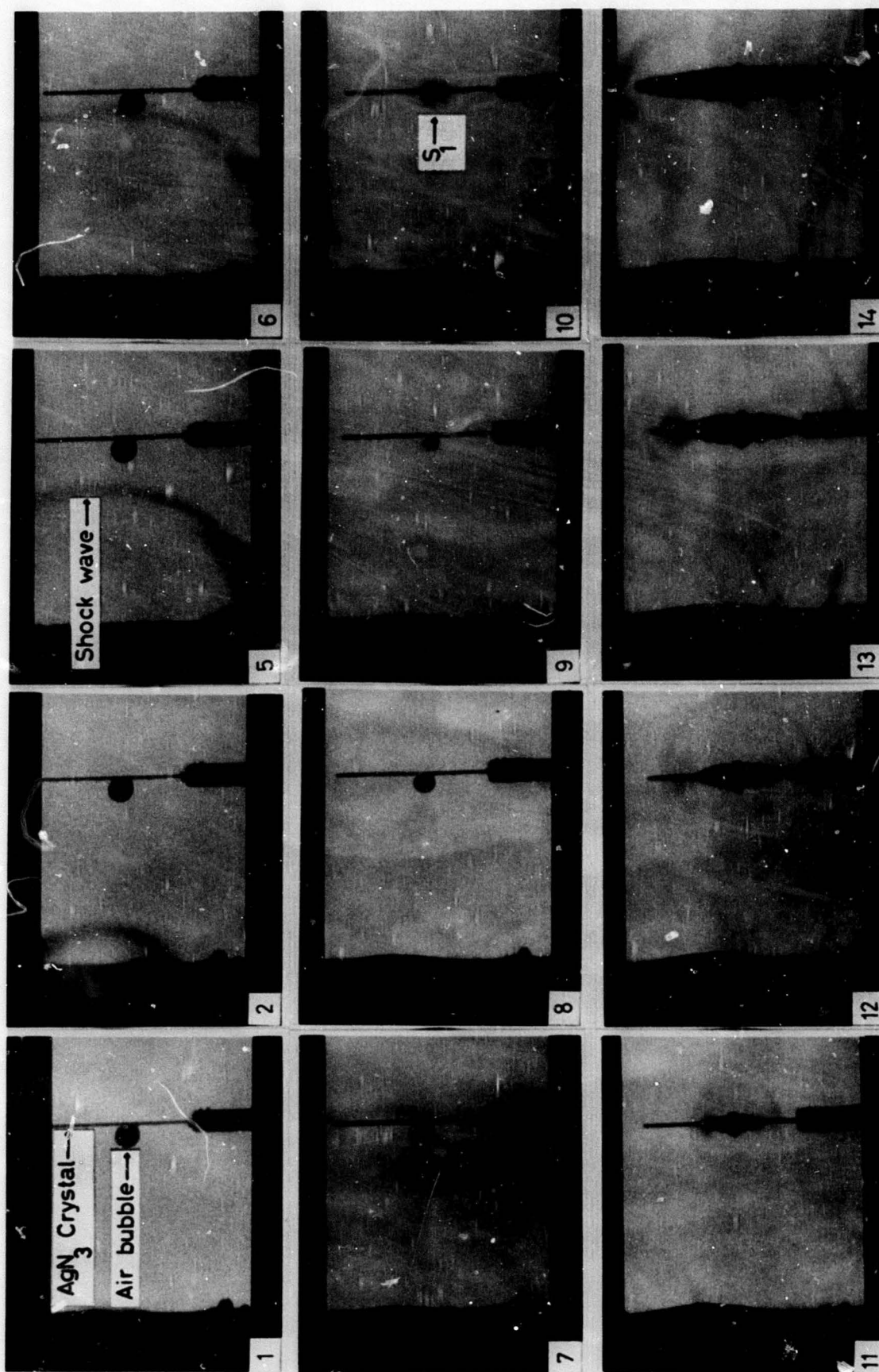
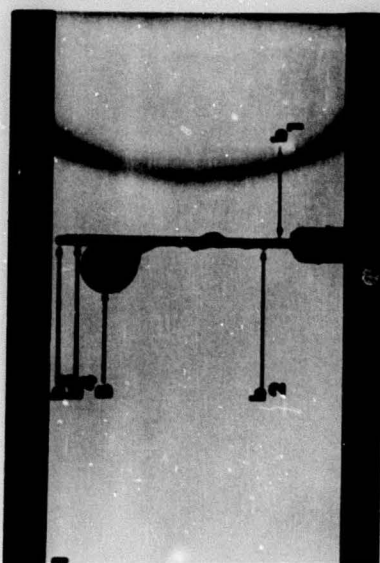
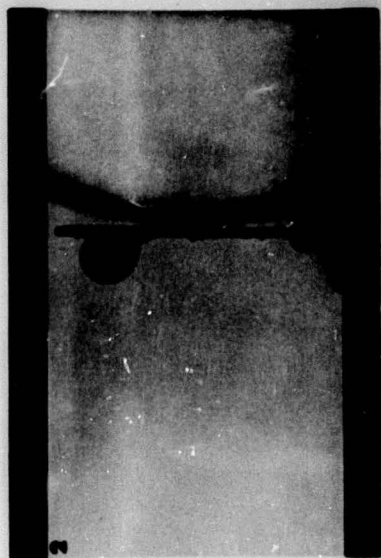
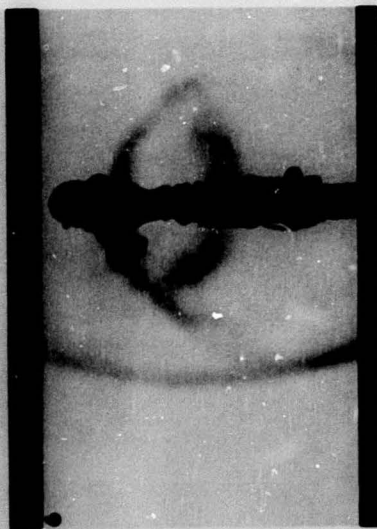
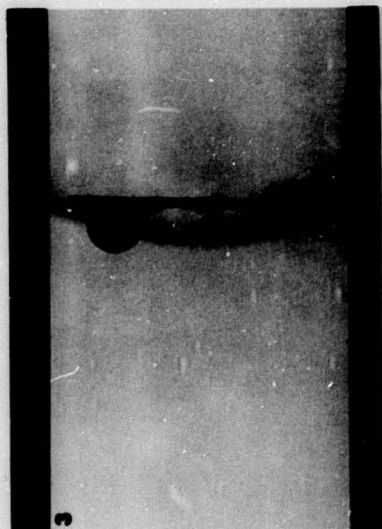


Figure 2







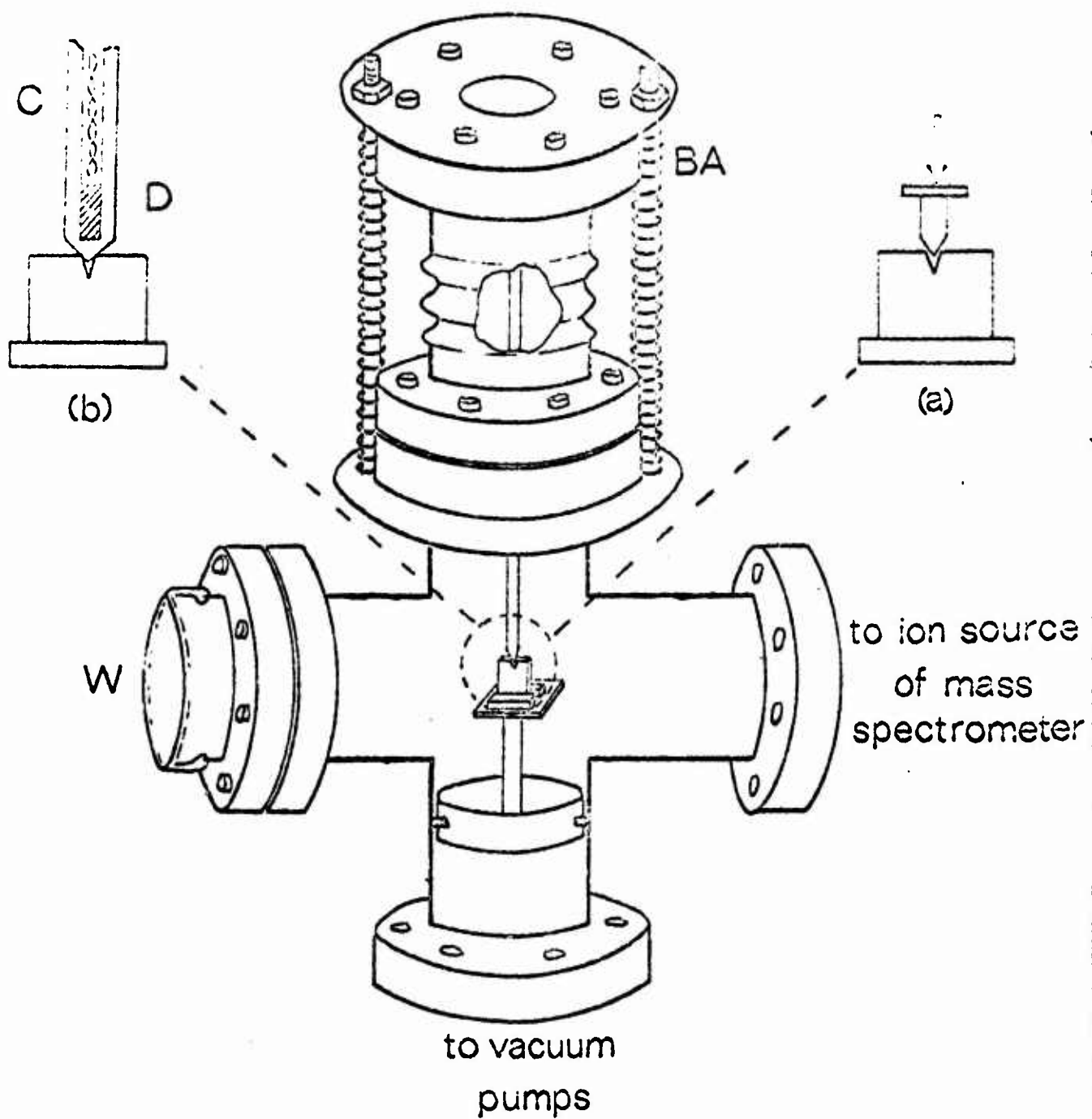


Figure 6

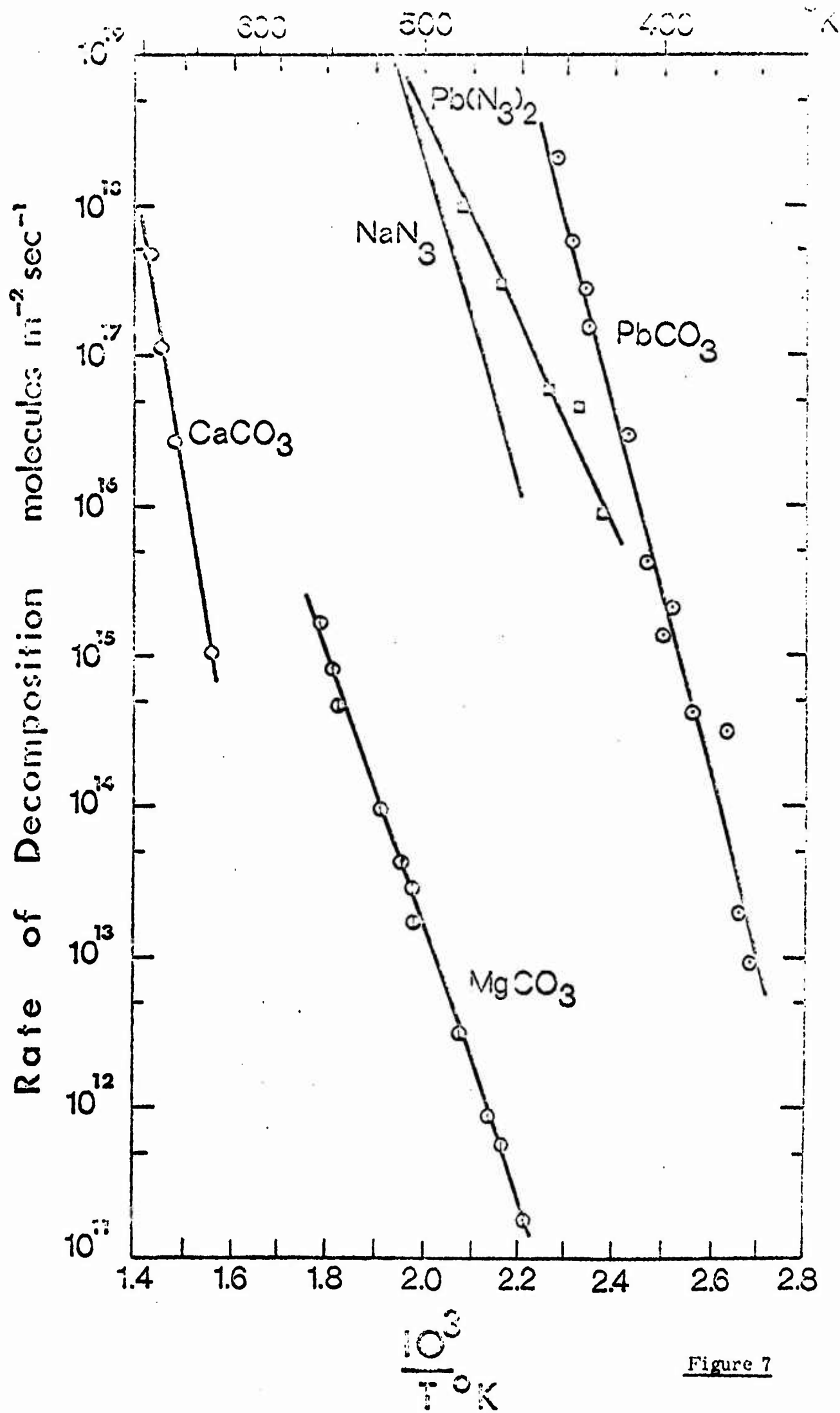


Figure 7

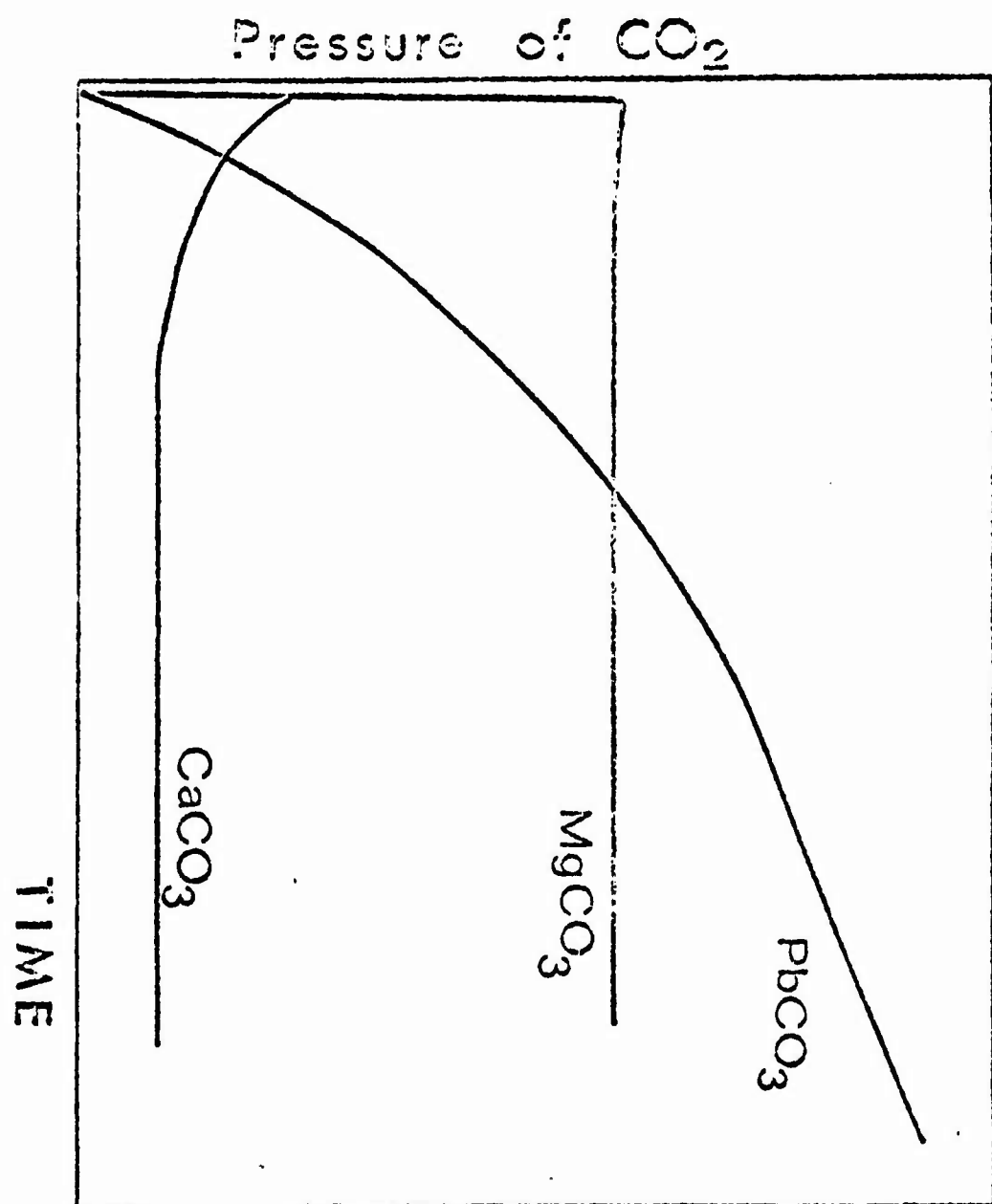


Figure 8

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13. ABSTRACT The initiation and propagation of explosion in liquids and solids has been studied with special reference to the role played by discontinuities in promoting sensitivity and the deflagration detonation transition. The growth of fast reaction in single crystals of lead and silver azide has been investigated using high speed photography. It was found that sufficiently thin crystals of these explosives burn and the dependence of deflagration velocity on crystal dimension was determined. Fracture and break-up of the crystals can occur ahead of the reaction front; in some situations these processes can stop the growth of reaction in lead azide. The effect of collapsing a bubble by a weak shock (~ 1 kbar) in the neighbourhood of the azides has been studied. Adiabatic heating of the gases in the bubble was identified as the major factor in causing initiation. Experiments on lead azide have shown that its explosion temperature depends on crystal size. In separate experiments it has been observed that thermal decomposition occurs when a fracture propagates through a crystal. The amounts and kinetics of the decomposition have been recorded for various crystal types, and temperatures associated with the fracture process evaluated. In liquid explosives the role of cavities on the transition to, and propagation of, a low velocity detonation has been studied for various liquids in both thin film and three-dimensional confinement.			

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