

APPROXIMATIVE QUANTITATIVE ASPECTS OF A HOT SPOT, PART II. INITIATION, FACTORS OF SAFE HANDLING, RELIABILITY AND EFFECTS OF HYDROSTATIC PRESSURE ON INITIATION

CARL-OTTO LEIBER

*Bundesinstitut für chemisch-technische Untersuchungen, D-5357 Swisttal-Heimerzheim
(F.R.G.)*

(Received July 24, 1985; accepted in revised form January 13, 1986)

Summary

The order of sensitivity in the falling weight test is calculated as a function of bubble size for a liquid explosive/bubble system. The results compare favorably with experiments, and indicate that sensitivity in such cases is not some unique property of the liquid explosive itself, but rather is a property of the liquid/bubble system. Chemically caused differences of sensitivity may be present, but are not easy to evaluate due to the poor statistical significance of go/no go experiments. Some comments on this problem are given, along with considerations of complicated initiations and the effects of hydrostatic ambient pressure on initiation. The algorithm presented previously is a guide delineating occurrences which are significant in initiation.

Introduction

The idea that initiation and the onset of the chemical reaction in gases is governed by the volume homogeneous (shock-) heating process, fails in the case of condensed explosives at low pressures, as Nernst [1] has already pointed out. Therefore safety is not predictable in terms of thermal explosion or reaction kinetics by itself. Convincing examples are the thermally stable lead azide (stable up to 315°C), which nevertheless is easily initiated by a weak impact, and a low velocity detonation (LVD) of liquid (and solid) explosives initiated by impact pressures of between 1 and 2 kbar. In both cases pressure heating occurs to the extent of a few degrees; it even is practically absent if an explosive increase of pressure of 5–10 bar initiates warm (60°C) nitromethane (NM) [2].

In the following years the idea was born that statistically distributed dissipative centers within the volume may be activated by an external stimulus, finally leading to a quasi-volume homogeneous chemical reaction. Today this concept is known in liquids as hot spot initiation, where the dissipative centers are realized by dynamic activated bubbles or voids. It is noteworthy that the pronounced effect of bubbles on sensitivity has been denied in the

twenties [3], since it was thought, from Le Chatelier's ideas, that overall sensitivity is governed by thermochemistry. Present-day safety considerations are based on more theoretical predictions and it is of importance to have a physical model of initiation for guidance in practical situations which may occur and be potentially dangerous.

The aim of this paper is to apply the previously published paper "Approximative Quantitative Aspects of a Hot Spot" (*J. Hazardous Materials*, 12 (1985) 43-64) to practical problems of safety. In the following the formulas, tables and figures of this paper are identified by a prescript I.

Formulation of the Roth-von Neumann suggestion

Roth [4], in the course of accident investigations, introduced the concept of cavitation in liquids as a causative agent in some cases. From other considerations, von Neumann [5] suggested that the

"detonation wave initiates the detonation in the neighboring layer of the intact explosive by the discontinuity of material velocity which it produces. This acts like a very vehement mechanical blow (~ 1500 m/s), and is probably more effective than high temperature."

It is curious, that this idea, which is in opposition to the thermal- and precursors-initiation view, was largely ignored in the following years, in spite of the fact that Roth [6] had found, in the case of crystalline explosives, that particle velocity is more decisive for initiation than any other parameter.

We will now combine the idea of Roth with that of von Neumann, and assume simply that a cavity or bubble is pushed by a high speed blow. Imparting to the bubble, originally at rest, a particle velocity u_p , we have from eqn. (I-49) together with eqns. (I-2), (I-5) and (I-6) for the dissipative power of the bubble motion:

$$N(t) = -\delta_{\text{tot}} \sqrt{3\gamma' p_0 \rho_\infty} \dot{V}^2 / 4\pi R^2 \quad (1)$$

Using eqn. (I-10) to connect the velocity of the bubble surface, \dot{R} , with the particle velocity, $u_{p\infty}$, of the surrounding medium we get, together with eqn. (I-9), an expression for the loss power in terms of the radius of the bubble, R , the loss of bubble motion, δ_{tot} , the appropriate polytropic index of the bubble content, γ' , the medium density, ρ_∞ , and the surrounding pressure, p_0 ,

$$N(t) = -4\pi R^2 \delta_{\text{tot}} \sqrt{3\gamma' p_0 \rho_\infty} u_{p\infty}^2 \quad (2)$$

In the generalized case, eqn. (I-50), the dissipative power is proportional to $\delta V'^2$. Relating this dissipative power to the instantaneous volume of the bubble, V , one gets

$$N/V \propto \delta |V'^2/V| \quad (3)$$

$|V'^2/V|$ is plotted in Fig. 1 as a function of the generalized time, τ , and various losses, δ . Figure 1 shows the idea of hot spots as poles of power

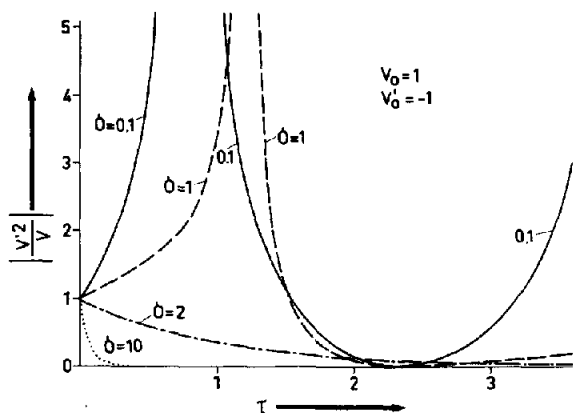


Fig. 1. The demonstration of the Roth—von Neumann suggestion. A generalized unit bubble of initial volume $V_0 = 1$ and loss δ is pushed by a velocity blow corresponding to $V'_0 = -1$. As can be seen, for low losses poles of loss power exist per the instantaneous volume V , which disappear for larger losses. As shown later, this is not a key for determining safety, since these poles depend on the stimulation V'_0 , and not on the loss δ alone.

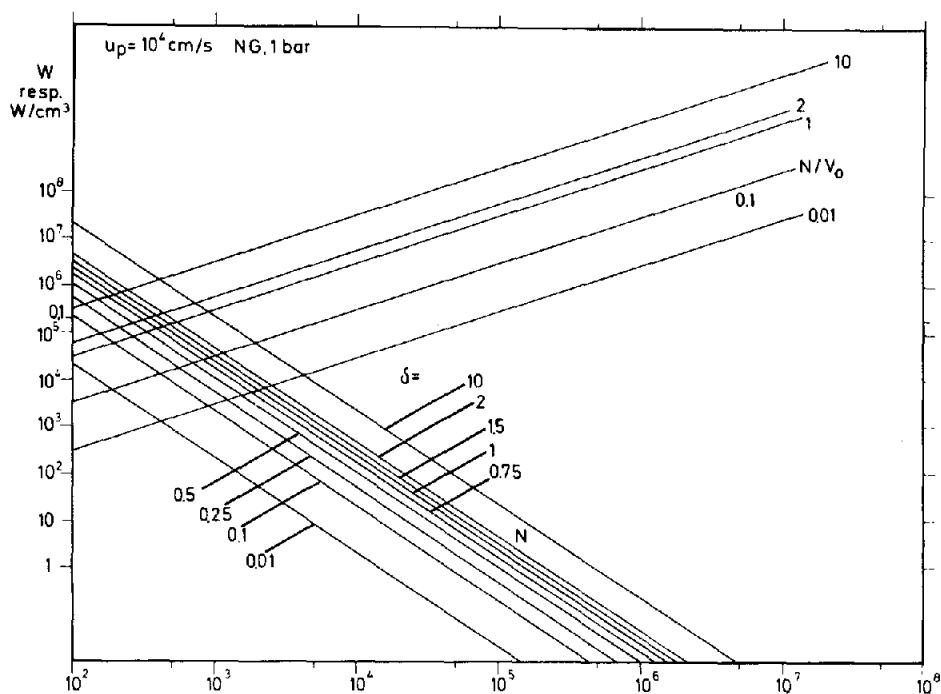


Fig. 2. Loss power, N , and volume-specific loss power, N/V_0 , where the initial volume, V_0 , has been used, for resonant bubbles of various losses in NG. These bubbles, originally at rest, have been pushed by a discontinuous particle velocity blow of $u_p = 100$ m/s.

loss in locus and time as the void collapses. Larger losses prevent collapse under given conditions.

As an example, the order of magnitude of the dissipated power is shown in Fig. 2 for a bubble of resonance frequency f in nitroglycerine (NG) pushed by a particle velocity $u_p = 100$ m/s as a function of the loss. The dissipated power decreases as the size of the bubble decreases, whereas the power loss per initial volume of the bubble increases as bubble size decreases. It seems quite likely that power losses of MW/cm³ force the onset of chemical reaction if it is at all possible. The radiation loss is phase locked to the dissipative power loss; this is the physical reason why pressure and reaction waves are usually coupled. If reaction is marginal, a decoupling of pressure and reaction wave may occur, which is not foreseen in the classical approach to detonation. In classical detonics, see Becker [7], the existence of coupling between pressure and reaction was considered to be the key problem of detonation, but no explanation has ever been given.

Comparison with experiments

According to the foregoing, sensitivity does not seem to be a unique function of the chemical properties of the liquid explosive; Figure (I-7) suggests that sensitivity should be governed by bubble size.

Roth [8] carried out experiments using the falling weight test to investigate the effect of the size of an air bubble on sensitivity. He sealed an air bubble in a bag containing nitroglycerine (NG), and this assembly was

TABLE 1

Comparison of the experimental and theoretical sensitivity hierarchy of a liquid explosive/bubble system for NG and GDN [8]

Radius, R , of air bubble (cm)	Experimental energy of fall, E^a (mkp/cm ²)	Experimental	Calculated
<i>NG</i>			
—	>26.5	$E_{0.05}/E$	$(N/N_{0.05})$
0.05	1.86	1	1
0.1	0.8	2.33	2.71
0.2—0.25	0.3	6.2	
0.25			10.25
0.25—0.5	0.25	7.44	
0.5			28.7
>0.5	< 0.06	>37.2	
<i>GDN</i>			
0.15	>1.86	$E_{0.15}/E$	$(N/N_{0.15})$
0.25	1.1	~1	1
>0.5	0.2	>1.7	2.2
		~9.3	8.2

^aFor 1 explosion in 6 trials (1 mkp \approx 9.81 J).

TABLE 2

Experimental order of sensitivity of a liquid explosive with one 1 cm diameter air bubble: Calculations to determine possible chemically caused differences of sensitivity

	Energy of fall E^a (mkp/cm ²)	Loss power $\bar{N} \propto R^2 \delta_{\text{diss}} \sqrt{\rho_{\infty}} E$ (10 ⁻⁶)	$\bar{N}/\bar{N}_{\text{NG}}$
NG	0.06	265	1
DEGN	0.14	522	2
GDN	0.2	781	3
NM	>1.86	>5882	>22

^aRoth [8].

completely immersed in another liquid. In these circumstances we may apply our algorithm to this type of experiment. As a measure of sensitivity Roth used one explosion in six trials. For this limit he has given a specific energy of impact (mkp/cm²). Since he performed these experiments with a constant drop weight, the corresponding $u_{p_{\infty}}^2$ in the liquid is proportional to the specific energy of impact. He determined the specific energy of impact as a function of bubble size for NG and glycoldinitrate (GDN), as shown in Table 1. Furthermore he determined the sensitivity of different liquid explosives containing an air bubble of about 1 cm diameter, as shown in Table 2.

If we assume that the same power loss in the same liquid produces the same chemical effects, then the order of sensitivity should be governed by eqn. (2); the order is given from the experiments in terms of E_{ext}/E and this ratio should correspond to the ratio $(\delta_{\text{diss}} R^2)/(\delta_{\text{diss}} R^2)_{\text{ref}}$. These values are compared in Table 1, where the dissipative losses have been calculated according to the Nishi algorithm by using the values given in Tables I-1 and I-2. Within the expected accuracy, the appropriate order of sensitivity has been calculated for NG and GDN.

Chemically caused differences of sensitivity

Chemically caused differences in sensitivity can be found by comparing the power losses for a constant size air bubble in different liquid explosives. Using eqn. (2) we consider the expression $\delta_{\text{diss}} R^2 \sqrt{\rho_{\infty}} E_{\text{exp}}$. Table 2 indicates that the dissipative loss power in DEGN is approximately twice that in NG. Therefore an order of chemical sensitivity NG/DEGN/GDN/NM $\approx 1/2/3/>22$ is most likely. At first glance this result is not completely consistent with the findings of Bowden and Yoffe [9]. These authors report that the sensitivity of various substances in the liquid or plastic state are roughly the same if tested by a cavity striker falling 10 cm, where the radius of the cavity is $R = 5 \times 10^{-3}$ cm. In this assembly the first explosion of NG was observed at a height of fall of 0.5 cm, and 100% efficiency was obtained for 10 cm.

Calculating for $R = 5 \times 10^{-3}$ cm the values of $\delta_{\text{diss}} \sqrt{\rho_{\infty}}$, these values indeed do not differ widely. At the upper extreme we calculate 0.256 for NG, 0.152 for liquid TNT, ranging down to 0.095 for NM; a factor of 3.

It therefore depends on experimental conditions whether chemically caused differences are evident or not. The physical reason for this is that the power loss per unit volume is increased.

Statistical significance of go/no go-tests

In a falling weight test an explosion (go) occurs, or does not occur (no go), and the reliability of such a procedure is not at all comparable with the required reliability.

Suppose that the probability of an explosion in a single experiment amounts to p , then the probability of failure is $q = 1 - p$. The probability, P_c , of exactly c explosions occurring in N trials is given by,

$$P_c = \frac{N!}{c!(N-c)!} p^c (1-p)^{(N-c)} \quad (4)$$

where $0!$ is defined to be 1.

Several measures of sensitivity are possible, depending on sensitivity requirements:

(a) One may take as an indication of "safety" 0 explosions in N trials, so one gets with a single-event probability p

$$P_0 = (1-p)^N \quad (5)$$

(b) Another possibility is, as Roth did, to take 1 explosion in N trials as a measure

$$P_1 = Np(1-p)^{(N-1)} \quad (6)$$

(c) Or, one asks for a 50% value, so that exactly $c = N/2$ explosions in N trials are obtained

$$P_{N/2} = \binom{N}{N/2} p^{N/2} (1-p)^{N/2} \quad (7)$$

(d) Also one may say, that in N trials *at least* $c = 1$ or *more* explosions occur, and the probability to get this amounts to

$$P_{\geq 1} = \sum_{c=1}^N P_c = 1 - P_0 = 1 - (1-p)^N \quad (8)$$

(e) An explosives manufacturer requires N explosions in N trials, and this probability is:

$$P_N = p^N \quad (9)$$

In Fig. 3 the probabilities of getting these desired events are plotted for the single-event probability, p , for the case of $N = 6$ trials. By comparing these cases it is seen that Roth's indications, one explosion in 6 trials, are more decisive for the single-event probability.

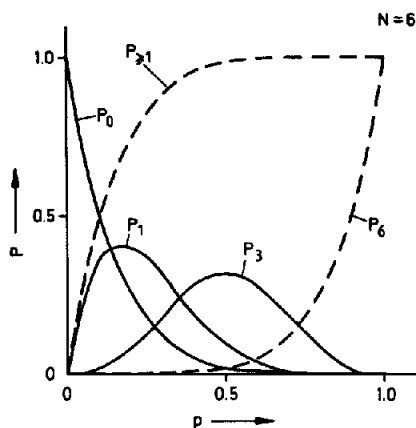


Fig. 3. If the single-event probability is p , then P_0 gives the probability of getting exactly $c = 0$ events in $N = 6$ trials ($0/6$), P_1 exactly $1/6$, P_3 exactly $3/6$, P_6 exactly $6/6$, and $P_{>1}$ at least 1 or more events in 6 trials. In go/no go-tests the single-event probability p can only be evaluated by sets of experiments.

The single-event probability, p , can be evaluated only by a number, N , of experiments. One may be interested in the maximum value, p_{\max} , for a given confidence $P_v = 1 - \alpha$ in the case $c = 0$. According to eqn. (5) for $0 \leq p \leq p_{\max}$, $(1 - p_{\max})^N = \alpha$ holds. This means that with a confidence of $P_v = 0.95$ in $N = 50$ no go tests throughout ($c = 0$), $p_{\max} = 1 - \exp(\ln 0.05/50) = 0.058$, and for $P_v = 99\%$, $p_{\max} = 0.088$ is even obtained.

To insure with a probability P_0 that the single event probability is below a maximum value p_{\max} ,

$$N = \text{Int.} \frac{\log P_0}{\log(1 - p_{\max})} + 1 \quad (10)$$

no go tests throughout are necessary. To settle $p_{\max} = 10^{-7}$ with a confidence of $1 - P_0 = 0.95$, $N = 3 \times 10^7$ of the said tests are necessary. Evidently it is impossible to settle safety limits by go/no go tests in practical situations.

One may ask further how many experiments must be performed to obtain at least one event or more, if the single-event probability amounts to p . According to eqn. (8) we may undertake

$$N = \text{Int.} \frac{\log(1 - P)}{\log(1 - p)} + 1 \quad (11)$$

experiments, for getting at least one go with a probability P . It is therefore

possible to perform many trials, in spite of a relatively poor safety, until the first event, i.e. an accident occurs. It is even possible to have a fabrication process with an inherently unsafe system (lets say explosion probability $p = 10^{-3}$), with only after some thousands of operations the real character of the system coming out (in this example $N = 2995$ operations are necessary to get at least one or more events with the probability of $P = 0.95$).

For the assessment of safety, further information is helpful, such as empirical knowledge, feeling, practice, or at best a real theoretical insight. Such an insight is the most powerful tool, since the former items of information are lacking in the case of new ventures.

There are two limiting cases of possible strategies for assessment of safety:

- Experience without any theory, only possible for old-fashioned systems to settle a statistical *a posteriori* safety.
- Relevant physical modeling, and discovery of an applicable "true" theory.

This is the only option to settle a predictive *a priori* safety for new systems.

In practical situations, of course, these cases are mixed. The theoretical basis for linking *a priori* events and probabilities (from experience of the past, or from theory) with an actual test result is Bayes' theorem. It is crucial that in the case of explosives numerical *a priori* probabilities are not available. The monograph [11] nevertheless gives an approximate way for incorporating Bayes' theorem. In an actual test we get c events in N trials, so the event probability orders to

$$p \approx c/N \quad (12)$$

Now we perform N' additional, related experiments (not necessarily the same ones) until we get exactly the next event. The safety characterizing probability amounts to

$$p' \approx \frac{c + 1}{N + N'} \quad (13)$$

and as N' increases, p' decreases. This additional experiment may be a real experiment, knowledge, theory, or even feeling. In the latter case a good knowledge, or an assumed good knowledge, is characterized by the size of N' .

Factors of safe handling

As demonstrated, \dot{V}^2 and V'^2 , or better $|\dot{V}^2/V|$ and $|V'^2/V|$, are the decisive terms for safe handling or initiation, respectively. The absolute value indicates that a bubble expands following its collapse. From Fig. 1 one may speculate that there exists an optimum loss for preventing bubble collapse. This, however, is not the case, since in addition the external stimulation is a decisive term. This will be shown here for the case that a pressure step starting at $\tau = 0$ with infinite duration stimulates the bubble system.

If a unit pressure step, p , corresponding to $V_\infty = -1$, see eqns. (I-42) to (I-46), activates a bubble system of different losses, δ , the situation depicted at the top of Fig. 4 results. In this case bubble collapse is prevented for the system of loss $\delta = 20$. As a 10-fold unit pressure step is applied ($V_\infty = -10$), this effect disappears as shown at the bottom of Fig. 4. Apparently conditions of safe handling always depend both on stimulation and loss, and there exists no general rule to establish safety under each circumstance.

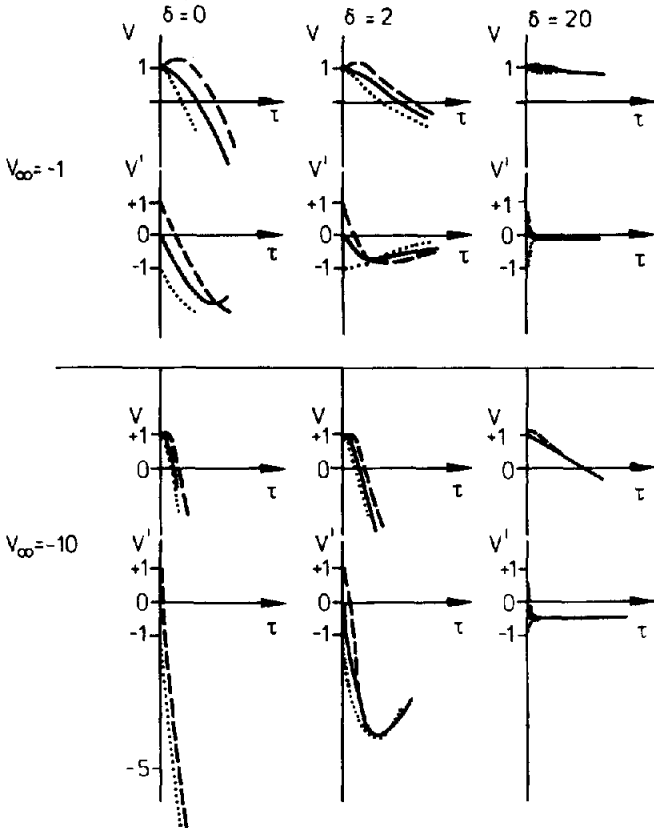


Fig. 4. Stimulation of a bubble system of different losses by an external unit pressure step corresponding to $V_\infty = -1$, and the 10-fold unit pressure step $V_\infty = -10$ of infinite duration. If the initiation is powerful, systems of high loss also collapse, and the influences of the initial conditions progressively vanish.

For a given stimulation, however, safety is increased by increased loss δ . According to {I} loss is favorably increased by the viscosity of the matrix, η_∞ . This indication is also realized by the historical steps undertaken to increase the safe handling of NG. The more viscous explosive, like blasting gelatine, is less sensitive and horny ballistite as a NG-propellant may be used

for stable burning in ammunition systems, whereas nevertheless it is exploded by suitable impact.

Pressure effects on safe handling

Let a stimulating pressure step, p ,

$$t < 0 \quad - p(t) = 0$$

$$t > 0 \quad - p(t) = -p$$

corresponding to

$$V_{\infty} = \begin{cases} 0 & \text{for } \tau < 0 \\ -\frac{p}{K} = -\frac{V_0}{\gamma'} \frac{p}{p_0} & \text{for } \tau > 0 \end{cases} \quad (14)$$

act on the vibratory bubble system, see eqns. (I-42) to (I-46). p_0 is the initial ambient pressure of the system. If this ambient pressure, p_0 , is increased, say by a factor of 10, then the stimulation caused by the dynamic pressure, p , accordingly decreases by this factor of 10. This case is also illustrated in Fig. 4, where in this example $V_{\infty} = -10$ corresponds to the initial case, and that of $V_{\infty} = -1$ to the case of the 10-fold increase in ambient pressure. Very approximately the V' -spectrum decreases by this factor, depending on the loss.

The pressure dependence of sensitivity, and the limits of safe handling as a function of stimulation and external pressure arises because the transition functions V/V_{∞} and V'/V_{∞} both depend on V_{∞} , see eqns. (I-42) to (I-46). Pressurized systems are therefore less sensitive to the onset of chemical reaction, but more sensitive to pressure build-up due to increased radiation loss. Depressurization should increase the sensitivity to explosion.

Pressure effects on open- and closed-pore systems

Considering in the vibratory system the quantities of mass m (eqn. I-2), and stiffness K (eqn. I-4), significant differences of pressure effects in open- and closed-pore systems are to be expected: In the case of a closed-pore system the initial volume V_0 of the bubble at pressure p_0 will be compressed to the volume V_1 by the ambient static pressure p_1 , whereas in the open-pore system this latter pressure p_1 pressurizes the original volume V_0 .

In the open-pore system, only values of K , b , and δ depend on the pressure

$$K_1 = \frac{\gamma' p_1}{V_0} \text{ versus } K = \frac{\gamma' p_0}{V_0} \quad (15)$$

The resonance frequency, which is connected with the time of bubble collapse, changes according to \sqrt{p} if isothermal compression occurs. Further values of b and δ vary according to the conditions.

In closed-pore systems all coefficients are affected by pressure. Again assuming isothermal compression with $p_0 = 1$ one obtains:

$$m_1 = \rho_\infty \sqrt[3]{p_1/4\pi R_0} \quad (16)$$

$$K_1 = \gamma' p_1^2 / V_0 \quad (17)$$

$$\omega_1 = \frac{1}{R_0} \sqrt{\frac{3\gamma'}{\rho_\infty}} p_1^{5/6} \quad (18)$$

Therefore resonance conditions vary as $(p_1/p_0)^{1/2}$ in the case of open-pore, and as $(p_1/p_0)^{5/6}$ in the case of closed-pore systems. Accordingly the loss, δ , is affected in different ways, see {I}.

The role of the pressurizing gas

It has long been puzzling why a difference is sometimes observed between air and nitrogen pressurization; a difference which cannot be explained in terms of the pressure dependence of the polytropic index, γ' . Actually, the pressure dependence of this polytropic index is a difficult problem to deal with [12], see Appendix.

However, there are some recent results on the role of a gas dissolved in a liquid. Usually the viscosity of any liquid, with the exception of water below 30°C, increases with pressure. This increase of viscosity with pressure depends on the molecular structure of the liquid, and varies between moderate and large. Kuss [13] has shown that there are some gases, if dissolved in the liquid, that do not markedly affect the pressure dependence of viscosity. There are also cases where dissolved gases in a liquid reduce its viscosity by several orders of magnitude. It has also been found that viscosity reduces to a minimum value and then increases again as pressure increases. Gases of a more complex molecular structure are more effective than simple gases.

Dissolved gases also change the density and compressibility of liquids. This is why it is difficult to predict the effects that a particular type of pressurizing gas will have.

Experimental facts on the pressure dependence of initiation

In spite of the fact that detonation pressures are in the region of hundreds of kbar, onset of initiation is very strongly affected by the ambient static pressure. Even static pressures as low as a few bars may prevent initiation.

For example, the falling weight tests of Bowden and Yoffe [9] in the case of NG show a 100% efficiency at ambient pressure, whereas this efficiency drops to zero at 20 to 30 bar ambient pressure. Gurton [14] has observed that by an increase of the static pressure to 68 bar, the frequency of onset of high velocity detonation (HVD) is reduced for NG as well as for crystalline powdered explosives. Even LVD initiation is progressively impeded if

the ambient pressurizing gas is methane. This is demonstrated by the reduction of the detonation velocity from 7690 m/s (1 bar, air) to 6670 m/s (14.3 bar, methane) down to 909 m/s (67.7 bar, methane) in the same assembly using the same initiation method.

In the case of tetryl (0.9 g/cm^3), flaked TNT (0.8 g/cm^3), and nitroguanidine (0.5 g/cm^3), the normal LVD velocities were exhibited at ambient pressures of air, ether, or pentane. In the case of pressurization by methane, LVD was prevented at 48 bar in tetryl, 41 bar in flaked TNT and 18 bar in nitroguanidine, whereas up to a pressure of 68 bar HVD was not influenced by the pressure. According to Eitz [15, 16] permitted explosives exhibit a strong influence of pressure on detonation: a closed-pore gelatinous permitted explosive (German class I) failed to detonate completely at 10 bar ambient pressure of methane, whereas an open-pore salt explosive of the same class detonated completely at 40 bar ambient methane pressure, and pressurization by nitrogen is more critical than pressurization by air or methane. There is also a strong influence from the ambient temperature, so for a German class III permitted explosive at 40°C full detonation occurs, whereas only 5% detonates at 0°C at 60 bar ambient methane pressure.

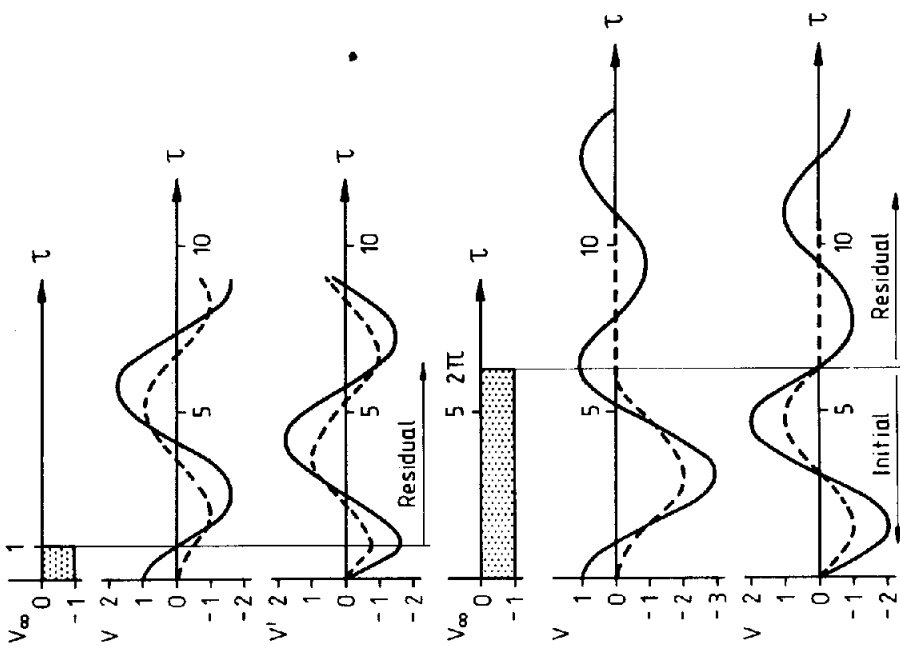
Chick [17] reports that the gap values to initiate a HVD are also reduced by ambient gas pressure for PETN and HMX. Gases of a complicated molecular structure seem to be more effective in preventing detonation than simple gases (like in the drop weight test, see Ref. [9]), but no differences between air and nitrogen have been found. Additionally the grain sizes are important. The transition to detonation is prolonged, but the HVD velocity is not influenced. Marshall [18] confirms this for HMX, except that up to 70 bar nitrogen or methane pressure no influence on detonation build-up was found. He concludes that the pressure-dependent initiation mechanism is different from the pressure-independent mechanism of HVD growth. This reflects long experience that the onset of detonation occurs via the route: any stimulation \rightarrow LVD \rightarrow HVD. Therefore it is quite possible, that the pressure dependence of the LVD initiation is reflected in HVD studies. As one example, according to Brochet [19] onset of HVD for isopropylnitrate (IPN) depends on temperature, pressure and as such LVD specific confinement. HVD can be obtained at

20 mm i. ϕ at $T > 310 \text{ K}$ and $p < 150 \text{ bar}$
 28 mm i. ϕ at $T > 300 \text{ K}$ and $p < 110\text{--}120 \text{ bar}$
 $T > 313\text{--}315 \text{ K}$ and $p < 230 \text{ bar}$

This pressure dependence of HVD initiation may be seen as a result of the pressure dependence of LVD initiation. Groothuizen, Pasman and Schilperoord [20] have observed a LVD for IPN.

In summary, as predicted, open-pore systems are less pressure sensitive than closed-pore systems, although experimental results are scarce and conflicting. It appears that HVD effects are governed by the prevailing pressure effects of LVD, if initiation occurs by a relatively weak stimulus via LVD \rightarrow HVD.

$\delta = 0$



$\delta = 0$

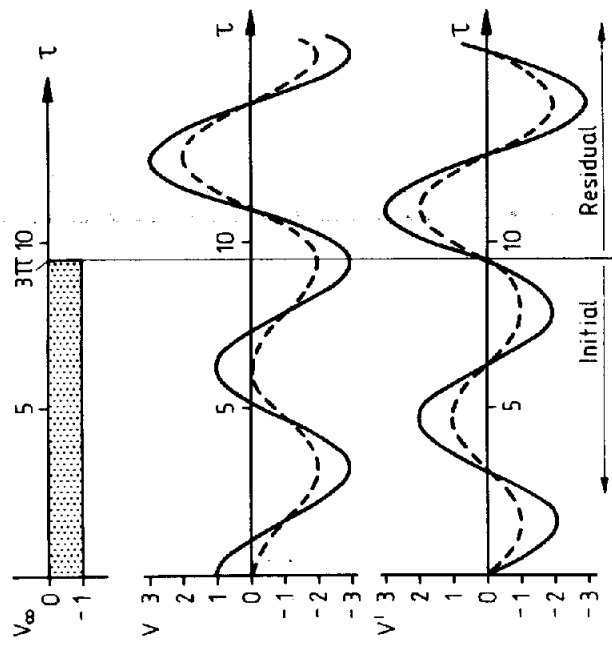


Fig. 5. Influence of the duration of excitation on the dynamics of low loss systems. The possibility of a residual initiation is to be envisaged (top left and right side), where the stimulating pulse has passed the system and then initiation occurs.

Complicated initiation modes

If a crude model of initiation is available, it is possible to speculate on complicated initiation modes.

In the preceding, the influence of a very short ($\tau = 0$), and a long excitation ($\tau \rightarrow \infty$) has been considered. Here we consider possible influences of the duration of excitation, denoted τ . In Fig. 5 the oscillator response in $|V|$ and $|V'|$ is considered for a low loss system ($\delta = 0$) for a stimulation shorter, equal to, and longer than the period of the oscillatory system. As may be seen, a chance exists that owing to larger V' values an initiation may occur in the residuum. This means initiation takes place as the exciting pulse has passed the system. It seems that sometimes such observations have been made. For systems of larger loss, such a chance is absent, see Fig. 6.

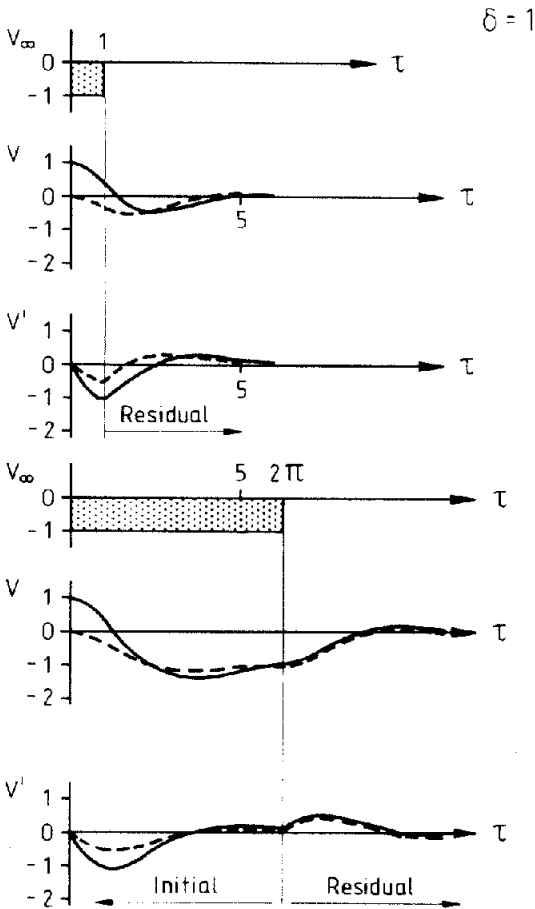


Fig. 6. Dynamic behavior of a higher loss vibratory system. Initial initiation only is possible.

Let us now consider the influence of the amplitude of excitation. From the theory of Fourier integrals, the low-frequency approximation of the frequency spectrum of a short exciting pressure pulse corresponds to $\int p \, dt$ for each shape, provided the duration of the exciting pulse is short compared with the period of the vibratory system. It is easy to verify this by integration of eqn. (I-1) or eqn. (I-40). This means that under given conditions it is not the amplitude but the value of $\int p \, dt$ that decides whether initiation takes place or not. It seems, in the case of crystalline explosives, that for very short pulses such behavior is present, but it is not clear that this is the case for liquid explosives.

Conclusions

A combination of old suggestions has been used to derive a rationale for the order of sensitivity of initiation, and for pressure effects on it. It appears that sensitivity depends more on bubble size and other circumstances than on the chemical properties of the liquid explosive by itself. In order to test this rationale a speculative extrapolation is made to more complicated initiation modes, which might be examined by experiment.

Acknowledgement

I would like to thank Prof. L. Huber and Dr. H. Dean Mallory for valuable suggestions.

References

- 1 W. Nernst, Diskussion zum Vortrag des Herrn Dr. R. Becker-Bergedorf (Zur Theorie der Detonation), *Z. Elektrochem.*, 23 (1917) 94 and R. Becker, Über die Fortleitung einer Detonation in flüssigen Sprengstoffen, *Z. Elektrochem.*, 23 (1917) 304–308.
- 2 R. Wild and J. Müller, Verhalten von Nitromethan bei Beaufschlagung mit einer Gasexplosion, BICT-Rept. 2.3–2/5799/82, 1982.
- 3 J.F. Roth, Personal communication, 1978.
- 4 J.F. Roth, Folgerungen aus der hydrodynamischen Theorie der Detonation — Neue Initiierungsmöglichkeiten durch Druckstoß und Hohlsoß, *Z. Gesamte Schieß- und Sprengstoffwes.*, 36 (1941) 160–163.
- 5 J. von Neumann, Theory of Detonation Waves, OSRD-Rept. No. 549, 1942.
- 6 J. Roth, Shock sensitivity and shock Hugoniot of high-density granular explosives, Proc. 5th Int. Symp. on Detonation ACR-184, Washington, DC, 1971, pp. 219–230.
- 7 R. Becker, Stoßwelle und Detonation, *Z. Phys.*, 8 (1922) 321–362 and R. Becker, Physikalische über feste und gasförmige Sprengstoffe, *Z. Tech. Phys.*, (1922) 253.
- 8 J.F. Roth, Prüfung der Empfindlichkeit von flüssigen und plastischen Sprengstoffen gegen die Implosion von Luftblasen, 36e Congrès International de Chimie Industrielle, Brussels, Belgium, 1966, pp. 20–22.
- 9 F.R. Bowden and A. Yoffe, Hot spots and the initiation of explosion, Proc. 3rd Symp. Combustion and Flame and Explosion Phenomena, Williams and Wilkins, Baltimore, MD, 1949, pp. 551–560.

- 10 Wissenschaftliche Tabellen Geigy, 8. Aufl., Ciba-Geigy AG, Basel, 1980.
- 11 Messerschmitt-Bölkow-Blohm, Technische Zuverlässigkeit, 2. Aufl., Springer, Berlin, 1977.
- 12 M.G. Ribaud, Constantes thermodynamiques des gaz aux températures élevées, Publ. Scientifiques du Ministère de l'Air, No. 266a, Paris, 1961.
- 13 E. Kuss, The viscosity of gas/oil solutions at high pressure, High Temp. — High Pressures, 15 (1983) 93–105.
- 14 O.A.J. Gurton, The role of gas pockets in the propagation of low velocity detonation, Proc. 2nd ONR Symp. on Detonation, 1955, pp. 464–482.
- 15 E. Eitz, Über das Verhalten von Wettersprengstoffen bei Initiierung im anstehenden Gasdruck, Nobel Hefte, 28 (1962) 62–78.
- 16 E. Eitz, Untersuchungen über Fragen der Schußbeeinflussung bei Wettersprengstoffen, Nobel Hefte, 31 (1965) 1–21.
- 17 M.C. Chick, The effect of interstitial gas on the shock sensitivity of low density explosive compacts, Proc. 4th Int. Symp. on Detonation, ACR-126 Office of Naval Research, Washington, 1965, pp. 349–358.
- 18 W.W. Marshall, The role of interstitial gas in the detonation build-up. Characteristics of low-density granular HMX, Proc. 5th Int. Symp. on Detonation, ACR-184, Office of Naval Research, Arlington, VA, 1970, pp. 247–249.
- 19 C. Brochet, Monopropellants detonation: Isopropyl nitrate, Astronautica Acta, 15 (1970) 419–425.
- 20 Th.M. Groothuizen, H.J. Pasman and A.A. Schilperoord, LVD in some liquids, Int. Jahrestagung des ICT (Sprengstoffe, Grundlagen, Technologie und Anwendungen), 1976, pp. 371–386.

Appendix

Pressure dependence of the specific heat

There are different pressure dependences of the specific heats at constant volume C_V or constant pressure C_p

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p \quad (\text{A.1})$$

$$\left(\frac{\partial C_V}{\partial p}\right)_T = \left(\frac{\partial C_V}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V \left(\frac{\partial V}{\partial p}\right)_T \quad (\text{A.2})$$

where p , T and V are the pressure, absolute temperature and volume, respectively. Accordingly, the specific heat ratio, $\gamma = C_p/C_V$, is a function of pressure.

For static pressures of the order below 50 bar, one may use Berthelot's equation of state. Ribaud [12] obtained

$$C_p(\text{real}) = C_p(\text{ideal}) + \Delta C_p \quad (\text{A.3})$$

$$C_V(\text{real}) = C_V(\text{ideal}) + \Delta C_p/3 \quad (\text{A.4})$$

TABLE A1

Differences of the specific heats in the real and ideal state

Gas	Mol. weight	Critical pressure, P_c (bar)	Critical temperature, T_c (K)	$(\Delta C_p)_{273\text{ K}}^{1\text{ bar}}$ (cal/mol K)	$(\Delta c_p)_{273\text{ K}}^{1\text{ bar}}$ (J/g K)
He	4	2.3	5.3	1.59×10^{-5}	1.6×10^{-5}
Ar	39.9	4.8	151	0.176	0.0185
H ₂	2.0	12.8	33.1	0.0007	0.0014
O ₂	32	49.7	154.2	0.0181	0.0024
N ₂	28	33.5	125.9	0.0146	0.0022
CH ₄	16	45.8	190.5	0.0371	0.0097
C ₃ H ₈	44.1	43	368.6	0.2862	0.0272
NO	30	65	179	0.0217	0.0030
CO	28	35	134	0.0169	0.0025
H ₂ O	18	217.7	647	0.3057	0.0710
CO ₂	44	72.85	304	0.0948	0.0090
NO ₂	46	100	431	0.1967	0.0179

where

$$\Delta C_p = 5.0 \frac{p}{p_c} \left(\frac{T_c}{T} \right)^3 \quad \text{cal/mol K} \quad (\text{A.5})$$

is expressed in terms of the critical pressure, p_c , and temperature, T_c .

For practical purposes one uses the expression

$$\Delta C_p = (\Delta C_p)_{273 \text{ K}}^{1 \text{ bar}} p \left(\frac{273}{T} \right)^3 \quad (\text{A.6})$$

and values of $(\Delta C_p)_{273 \text{ K}}^{1 \text{ bar}}$ are given in Table A1.

From these values a pressure dependence of the specific heat ratio γ may be calculated. For Ar at 273 K and 50 bar ambient pressure we have $\gamma = 1.445/0.620 \approx 2.33$, which may be the reason for the exaggerated high luminosity of discharges in pressurized Ar.