

and of hydrocarbon–air mixtures, except acetylene, of the value

$$[17.2.41] \quad L_c \approx 15L_i$$

The induction length  $L_i$  increases as tube diameter increases. Nikuradse (1933) has shown that in pipe explosions the distance to the establishment of fully developed turbulence is about 60 diameters. A similar proportionality to diameter might be expected for the induction length. The question is discussed by Lewis and von Elbe (1987). The evidence is that the proportionality holds in some cases but not in others.

The cell width  $S$  is equivalent to the spacing of the transverse waves. For this spacing, Nettleton (1987) gives the following estimates for mixtures at atmospheric pressure: 1–10 mm for near stoichiometric fuel–oxygen mixtures; 10–100 mm for near stoichiometric fuel–air mixtures, and 0.1–1.0 m for lean fuel–air mixtures.

The cell length  $L_c$  is related to the critical diameter  $d_c$  for transmission of a detonation in a tube, and also across an abrupt expansion. Detonations do not develop in a tube of diameter less than  $d_c$ , where  $d_c$  depends on fuel composition. In a classic study, Zeldovich, Kogarko, and Semenov (1956) found that  $d_c/L_i = \text{constant}$  for all the gases which they tested.

Further work on this feature has been done by Gvozdeva (1961) and Mitrovanov and Soloukhin (1964). Using acetylene–oxygen mixtures, the latter obtained the relationships

$$[17.2.42a] \quad d_c = 13 S \quad \text{circular tubes}$$

$$[17.2.42b] \quad d_c = 10 S \quad \text{planar channels}$$

Additional work includes that of D.H. Edwards, Thomas, and Nettleton (1979), who have shown that the two results are equivalent and suggested that they are of general applicability to detonations.

D.C. Bull et al. (1982) have studied the cell length, and the factors influencing it, for a number of gases. For stoichiometric mixtures with air at atmospheric pressure they give the following values of  $L_c$ : methane 310 mm, ethane 54 mm, propane 46 mm, *n*-butane 54 mm, acetylene 9.2 mm, ethylene 24 mm, and hydrogen 10 mm.

These authors also discuss the relevance of cell size. A planar detonation wave cannot propagate in a channel of width substantially smaller than the half-width of a cell. This feature is relevant to the quenching of detonations.

In the transition from a planar to a spherical detonation wave at an abrupt expansion there is a critical number of cell widths in the planar front to sustain the detonation. For a circular tube this number is 13.

Equation 17.2.42a is a statement of this fact. This feature also is relevant to quenching.

There is a close connection between the cell size and the critical energy  $E_c$  for initiation of a spherical detonation. Thus, Zeldovich, Kogarko, and Semenov (1956) give the relation

$$[17.2.43] \quad E_c \propto \Delta^3$$

where  $\Delta$  is an induction length, which is related to the cell size.

In the transition from deflagration to detonation there is some indication that the critical turbulent length scales may be of the same order as detonation cell lengths and that systems of different reactivity have a rank order similar to that for cell sizes.

## 17.2.12. DETONABILITY CHARACTERISTICS

The detonability of fuel–air mixtures is characterized in terms of the detonation limits and ignition sources.

There has been some debate about the existence of detonation limits separate from flammability limits, as illustrated in the following comment by Burgess et al. (1968 BM RI 7196), 'A consensus has gradually developed that almost any gas mixture that is flammable is also detonable if initiated with a sufficiently strong ignition source.' However, the existence of separate detonation limits is now recognized.

Compilations of data on the flammability of fuels generally do not include detonation limits, although a considerable amount of data are available scattered in the literature.

There are certain features which cast a degree of uncertainty over detonation limits. One is the phenomenon of cool flames. Another is the existence of compounds which are capable of detonation in the absence of an oxidant. Further, a distinction is made in respect of detonation between confined and unconfined situations. Separate detonation limits are quoted for these two situations.

For detonation limits for confined situations measurements are made in tubes. Accounts of such work include those of Michels, Munday, and Ubbelohde (1970) and Borisov and Loban (1977). The measurement of detonation limits in unconfined gas clouds is more difficult.

Features of such work have included the use of containment such as a balloon, a very high energy ignition source, and oxygen-enriched mixtures, the results being extrapolated back to the composition of air. Work in this area has been described by Benedick, Kennedy, and Morosin (1970) and D. C. Bull, Elsworth, and Hooper (1979a,b).

Table 17.8 from Nettleton (1980b) gives detonation limits for a number of fuels in air for confined and unconfined situations. The author's original table gives limits for a large number of compounds and also the limits for mixtures with oxygen. In general, the detonation limits of a particular fuel are narrower than its flammability limits, with the exception of compounds which can detonate in the absence of an oxidant.

There are a number of compounds which can detonate in the absence of an oxidant. One such substance is gaseous acetylene, and extensive precautions are necessary when handling it industrially. Other self-decomposing chemicals include ethylene at pressures in excess of 7 MPa, hydrogen peroxide, and ozone. Information on such compounds is given by Bretherick (1985).

Nettleton suggests that any self-decomposing compound should be considered as possibly capable of detonation, but also adds that there is no well-established example of unconfined detonation of a self-decomposing substance.

**TABLE 17.8** Some Data on Detonation Limits in Mixtures with Air for Confined and Unconfined Situations

Compound	Detonation Limits (%)				Flammability Limits (%)	
	Confined Tube		Unconfined		Lower	Upper
	Lower	Upper	Lower	Upper		
C <sub>2</sub> H <sub>6</sub>	2.87	12.20	4.0	9.2	3.0	12.4
C <sub>3</sub> H <sub>8</sub>	2.57	7.37	3.0	7.0	2.1	9.5
C <sub>4</sub> H <sub>10</sub>	1.98	6.18	2.5	5.2	1.8	8.4
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	1.45	2.85			0.95	
C <sub>2</sub> H <sub>4</sub>	3.32	14.70			2.70	36.0
C <sub>3</sub> H <sub>6</sub>	3.55	10.40	3.5	8.5	2.4	11.0
C <sub>2</sub> H <sub>2</sub>	4.20	50.0			2.5	80.0
C <sub>6</sub> H <sub>6</sub>	1.60	5.55			1.3	7.9
C <sub>2</sub> H <sub>5</sub> OH	5.1	9.8			3.3	19.0
H <sub>2</sub>	18.3	58.9			4.0	75.0

Source: Courtesy of Fire Prevention Science and Technology; after Nettleton (1980b).

In view of the relative paucity of data on detonation limits, it is attractive to be able to derive them from the flammability limits. Some correlations have been given by Nettleton (1987, p. 77) for both confined and unconfined detonations. For a number of fuels, which include alkanes and alkenes, he gives the following relations for the lower and upper limits of detonation in a confined situation: defines  $\phi$  as the fuel–air ratio and the subscripts l, st, and u to denote the lower limit, stoichiometric, and upper limit, respectively. For mixtures with air

$$[17.2.44] \quad \log_{10} \phi_l = 1.08 \log_{10} \phi_{st} - 0.84$$

$$[17.2.45] \quad \log_{10} \phi_u = 1.06 \log_{10} \phi_{st} + 0.64$$

and for mixtures with oxygen

$$[17.2.46] \quad \log_{10} \phi_l = 0.60 \log_{10} \phi_{st} - 0.78$$

$$[17.2.47] \quad \log_{10} \phi_u = 1.13 \log_{10} \phi_{st} - 0.56$$

The stoichiometric mixture is defined in terms of water and carbon dioxide as the products. For unconfined situations there is a single correlation for mixtures with air or with oxygen. This is

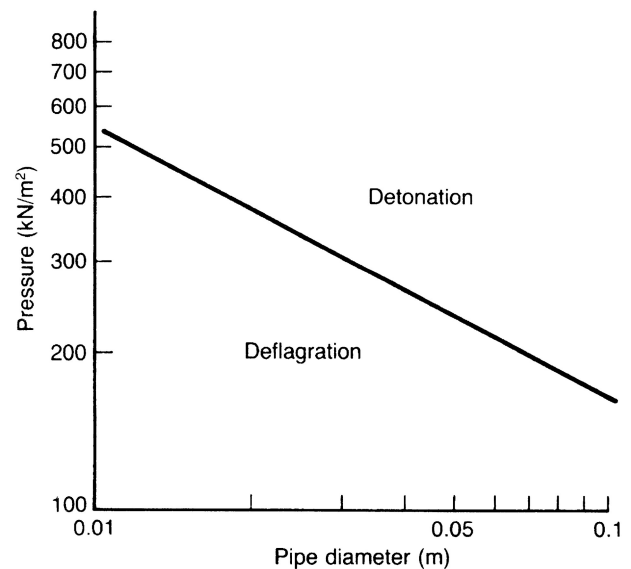
$$[17.2.48] \quad \log_{10} \phi_l = 0.51 \log_{10} \phi_{st} - 0.81$$

$$[17.2.49] \quad \log_{10} \phi_u = 1.17 \log_{10} \phi_{st} + 0.60$$

These correlations do not apply to acetylene, for which the detonation limits are wider. Another approach to the prediction of detonation limits is in terms of homologous series.

There is relatively little information available on the influence of initial pressure and initial temperature on detonation limits, in confined situations. The general effect of an increase in initial pressure is to widen the detonation limits, and the same applies to an increase in initial temperature. The widening is more marked for the upper limit.

For acetylene, however, there exists a good deal of information on the effect of initial pressure. For this gas there is a pipe diameter below which only deflagration occurs, but above which detonation is possible, and this



**FIGURE 17.3** Effect of pipe diameter and pressure on detonability of pure acetylene. Source: After Sargent (1957).

diameter is a function of the initial pressure. The correlation for this, which has been widely used in plant design, is shown in Figure 17.3. There is less information on the effect of initial temperature on acetylene, but at temperatures much in excess of 100°C there are likely to be present decomposition products which will affect the detonation limits.

The influence of additives, whether they are inert gases such as nitrogen or chemically active additives such as halohydrocarbons, presents a complex picture. The general effect of a diluent such as nitrogen is to narrow the detonation limits, particularly the upper limit. The amount of diluent required to suppress detonation tends to be large, but falls off sharply for mixtures close to the detonation limits. With regard to chemically active additives, the action of such additives may be rather specific, and there is some evidence, for example, that an additive

effective as a fire extinguishant may not suppress a detonation.

The foregoing account has been concerned with the limits of detonation. However, whereas a mixture close to stoichiometric is, comparatively, readily detonable, one at the limits of detonation is only marginally detonable.

### 17.2.13. INITIATION OF DETONATION WAVES

The modes of initiation of a detonation differ somewhat from the modes of initiation of a deflagration. In both cases the process may be initiated by a suitable ignition source, but in the case of detonation other important mechanisms to be considered are initiation of a detonation by shock waves and acceleration of a deflagrative combustion into a detonation. It is also necessary to consider the distinction already made between confined and unconfined situations.

A further relevant distinction is that between readily detonable and marginally detonable mixtures. It is by no means clear that the mechanisms of detonation in readily detonable media are those operating in marginally detonable media.

In addition, there is some evidence that detonation may be a stochastic process (Terao, 1977).

In treating detonation by an ignition source, it is usual to speak of strong and weak sources. The terms are convenient but often not well defined. Nettleton (1987) treats as strong those ignition sources which produce a shock or blast wave of velocity greater than the CJ velocity, associated particularly with marginally detonable media and with unconfined systems. These strong ignition sources can range in strength from <10 J from sparks up to some 50 kJ from high explosives.

There is a considerable literature on the initiation of detonations in confined systems, but a large variety of methods have been used, and the interpretation of the findings is not straightforward. A greater degree of uniformity is now obtained by the adoption of standard methods, notably that of Zeldovitch and Kompaneets (1960). In this method a readily detonable mixture and a driving mixture are held in a tube separated by a diaphragm, which is removed seconds before detonation is initiated in the driving mixture. This technique allows the parameters of the driving mixture such as composition and initial pressure to be varied and the effect of the strength of the triggering wave to be investigated. The technique has been adapted to the study of unconfined detonations using an expansion nozzle.

Dealing first with initiation by ignition sources, for confined systems the quantity of interest is the minimum ignition energy for detonation. In principle, this is measured as spark energy. However, data on this parameter are sparse and generally there is no alternative but to resort to the value of the regular minimum ignition energy (MIE), that for ignition of a flammable mixture.

A large amount of work has been done on initiation of detonation in unconfined vapor clouds by ignition sources such as sparks and high explosives. Here, the ignition energy for detonation is generally expressed as the critical energy  $E_c$  for a spherical detonation.

The critical energy  $E_c$  varies with the concentration of the fuel and has a minimum value  $E_c^*$ .

Work on spark initiation of detonation of unconfined clouds has shown that, as in similar work on ignition of flammable mixtures, the results obtained depend on factors such as the spark gap width and efficiency and the rate of energy deposition.

With regard to the strength of the explosive ignition source necessary to induce detonation, work by Bach, Knystautas, and Lee (1971) has shown that for direct initiation of spherical detonation waves the rate of deposition of energy into the gas is critical. Reviewing this work, Strehlow (1973b) suggests that charge geometry is probably very important and that this factor may account for the apparent discrepancies in the quantities of explosive required to initiate detonation in the work which he quotes.

In considering the initiation of detonation in an unconfined cloud, the mechanism by which this occurs is of some relevance. It is now believed that when initiation occurs by a source with relatively low energy such as an electrical spark or 10 g of high explosive, the velocity of the initial blast wave decays below the CJ value before significant chemical reaction occurs in the flow, and there may be a propagation as quasi-steady-state velocity before acceleration sets in again and leads to detonation. For the size of charge quoted, the distance over which this overall process occurs is of the order of 10 cm. For larger charges the distance is correspondingly greater, and may thus be appreciable.

Critical energies for initiation of spherical detonation have been obtained by a number of workers. Reviewing these, Nettleton (1987) quotes in particular data given by Carlson (1973) for mixtures of fuel and oxygen. The fuel concentrations in the most readily detonable mixtures lie in the range 20–40% and the values of the critical energy  $E_c$  obtained range over two orders of magnitude from <0.11 J for acetylene to 12.5 J for acetaldehyde. He comments that the chemical nature of the fuel strongly influences detonability but that the effect is more complex than one of simple bond strength.

The critical energy  $E_c$  for detonation in a spherical cloud is related to the critical diameter  $d_c$  for transmission of a detonation from a tube across an abrupt enlargement of area as described below. The determination of  $d_c$  therefore provides a means of estimating  $E_c$ . Matsui and Lee (1979) use the relation

$$[17.2.50] \quad E_c = \frac{\pi p_D u_D}{24 C_D} d_c^3$$

where  $a$  is the velocity of sound,  $p$  is the absolute pressure, and  $u$  is the particle velocity and the subscript D denotes the detonation, or CJ, state.

These authors also give a detonation hazard parameter  $D_H$ , which they define as

$$[17.2.51] \quad D_H = \frac{E_c^*(\text{fuel})}{E_c^*(\text{acetylene})}$$

where  $E_c^*$  is the minimum critical energy determined.

Work on the critical energy for detonation of fuel–air mixtures using high explosives has been described by