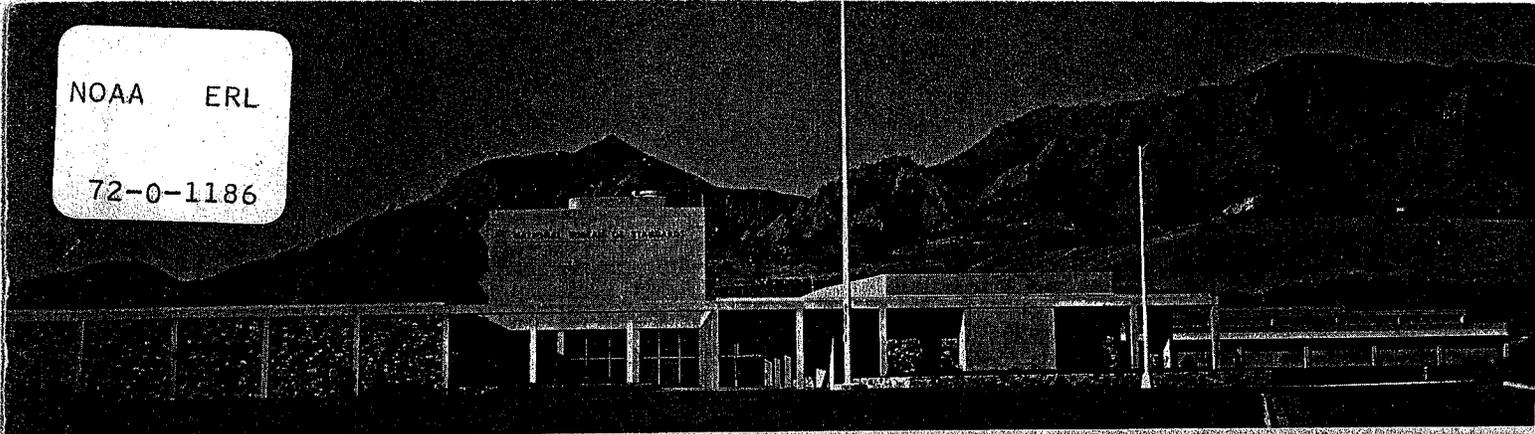


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NBS REPORT

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EXPLOSION CRITERIA FOR LIQUID HYDROGEN TEST FACILITIES

by

J. Hord

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**U. S. DEPARTMENT OF COMMERCE**  
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# NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

NBS REPORT

2754450

February 1972

10 734

## EXPLOSION CRITERIA FOR LIQUID HYDROGEN TEST FACILITIES

Prepared for

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Livermore, California  
Order No. SANL-903

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## Foreword

Because almost all available data concerning overpressure, fireballs and shrapnel are given in English units, this paper uses English units. Also, where metric units have been used by an author, they have been retained in this paper. Conversion to the SI System of units is easily accomplished with the following conversion factors:

pound  $\times$  0.4536 = kilogram

foot  $\times$  3.0480 = meter

gallon  $\times$   $3.7854 \times 10^{-3}$  = m<sup>3</sup>

liter  $\times 10^{-3}$  = m<sup>3</sup>

quart  $\times$   $9.4635 \times 10^{-4}$  = m<sup>3</sup>

PSI  $\times$  0.6895 = N/cm<sup>2</sup>

calorie  $\times$  4.1840 = joule

foot-pound  $\times$  1.3552 = joule.

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## Explosion Criteria for Liquid Hydrogen Test Facilities

J. Hord

### 1. Introduction

There are currently no guidelines for evaluating personnel safety hazards, due to overpressures, that may occur in liquid hydrogen (LH<sub>2</sub>) test facilities. Each facility and each experiment is individually reviewed to determine potential hazards, and normally these hazards are judged according to the conservatism of the reviewing panel or the safety committee. Whether establishing a new facility or modifying an old one, the procedure is the same -- a panel of knowledgeable persons, having considerable experience in the field but little numerical data on which to base their decision, pass judgement on the facility. Safety review boards, and most research laboratories, rely heavily on safety practices and procedures, i. e., training of personnel for safety-consciousness, safety policy of both management and personnel, operating procedures, adequate design, safety committee review and monitoring, and certain facility requirements. The facility requirements normally emphasize minimizing confinement, adequate ventilation for enclosed facilities, minimizing ignition sources, strict adherence to safety procedures, and limiting the quantity of H<sub>2</sub> that is permitted at a given facility.

It is this latter point to which we address our attention. The quantity of H<sub>2</sub> that is permitted in a given test facility varies from a few grams to over a million pounds, consequently the fire and explosion hazards also vary by orders of magnitude. Since personal judgement is involved, the protection afforded personnel varies widely from one facility to another. Because of stringent safety policy and procedures, some laboratories have successfully permitted the use of relatively large quantities of H<sub>2</sub> to be used adjacent to, or inside of,

inhabited buildings. Other organizations may require that these same experiments be conducted outdoors in remote areas. Review of each test facility and of each experiment at that test facility, on a continuing basis, will always be required to evaluate the potential safety hazards of each particular installation; however, some general guidelines would be a valuable asset to the reviewing panel and/or safety committee performing this review.

Some guidelines have been established for the protection of personnel against fire and shrapnel hazards. This information is supplied in the form of quantity - distance relationships applicable primarily to the storage of liquid or gaseous hydrogen. These quantity - distance tables vary widely, again reflecting the conservatism of the generating authority, and are generally not applicable to research or development test facilities. This point is stressed both in the CGA [1]\* pamphlet and in the NASA-LeRC [2] safety manual. The situation arises because most of the quantity - distance tables are based upon diked and built-to-code vessels. Such vessels are normally well designed and constructed of suitable materials so that failure is highly unlikely; if failure did occur, it most probably would be in a ductile manner. Ductile failures preclude large catastrophic spills. On the other hand, research experiments frequently use materials that can fail in a very brittle manner. Materials such as glass, beryllium, and plastics present difficult design problems and fail in a non-ductile manner at low temperatures. These failures can release large quantities of H<sub>2</sub> into the atmosphere in a very brief interval of time. Evaluation of the potential safety hazards associated

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\* Numbers in brackets indicate references at the end of this paper.

with equipment failure of this type, and the release of some known quantity of hydrogen into the atmosphere, is a formidable task. The quantity - distance tables are of little value because of the nature in which they are derived. The most conservative quantity - distance table is generated by the ASES<sup>1</sup> [3], and is based upon protection from fire and shrapnel for unprotected personnel. Less conservative quantity - distance guidelines have been supplied by the Bureau of Mines [4], and are based upon thermal radiation protection for personnel in inhabited buildings. Even smaller distances are permitted by ADL [5], NFPA [6], and the CGA [1]. The latter three are also derived from thermal radiation hazards and the fire resistance of materials, and the latter two<sup>2</sup> apply strictly to storage of liquid hydrogen at consumer sites. The Bureau of Mines [4], NFPA [6], and the CGA [1] also specify separation between storage dewars. The NASA-LeRC [2] has also modified the Bureau of Mines [4] values for dewar separation. Overpressure is appropriately neglected in these documents because 1) there is small probability of a major spillage, 2) confinement is minimized and ventilation is good, and 3) ignition sources are minimal.

Such is not the case with research test facilities, and we must admit to the possibility of spilling some quantity of LH<sub>2</sub> and attempt to estimate the associated hazards. It is this problem that is treated differently by each laboratory and by each safety review panel. The degree of hazard of each experiment is evaluated individually and the recommended quantity - distance tables may be enforced or may be waived [2]. Current policy is to neglect overpressure in open-air

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<sup>1</sup> Armed Services Explosive Safety Board.

<sup>2</sup> These tables are based upon a maximum credible spill of 50 gallons of LH<sub>2</sub> [59].

test facilities and provide protection for fire and shrapnel only. This policy stems from the ADL [5] and Bureau of Mines [4] experiments that concluded that LH<sub>2</sub> spills in open-air normally result in deflagrations, with accompanying low overpressures. Upon close examination of the results from these limited tests [4, 5], a known incident [7], and other data [8-10], it appears that the current policy may be ill-founded. Specifically, it is suggested that the blast hazard associated with open-air test facilities be assessed using a maximum of one pound of TNT equivalent per pound of LH<sub>2</sub> spilled. Abundant support for this statement will be given in this paper.

Blast potential of H<sub>2</sub> in enclosed spaces is well recognized, although few guidelines exist, in this case, for limiting the quantity of liquid that is permitted in a given space. Most laboratories rely heavily upon proper design, procedures, ventilation, etc. The Bureau of Mines [11] has conducted some experiments with LH<sub>2</sub> spills in confined spaces. As a result of these tests, some laboratories have restricted hydrogen quantities used in enclosed spaces so that the entire enclosure cannot be filled with a homogeneous detonable mixture of H<sub>2</sub>-air. There is no assurance that this procedure will prevent the occurrence of a detonation, but the likelihood is decreased. Even deflagrations in enclosed spaces can be devastating -- up to 8 atm overpressure -- and obviously avoidance of spillage and incidents is paramount. For this reason, all experiments of even slightly hazardous nature should be conducted outdoors, unconfined, whenever possible.

## 2. Definitions

The basic terms necessary for full understanding of this paper are given below:

flammable limits - range of concentrations of  $H_2$  in air where the mixture will burn, i. e., a homogeneous  $H_2$ -air mixture will propagate a flame freely within a limited range of compositions.

detonable limits - range of concentrations of  $H_2$  in air where the mixture will detonate, i. e., the flame front will propagate at supersonic speed.

mixture ratio (MR) - the mass of oxidizer (oxygen) divided by the mass of fuel (hydrogen).

stoichiometric mixture ratio - the mixture ratio (MR) at which maximum combustion energy is realized (MR = 8 for the  $H_2 - O_2$  or  $H_2 -$  air systems).

system yield factor (SYF) - the TNT equivalent of a combustible mixture or a bi-propellant combination, based upon the total mixture (or system) weight -- commonly referred to as "yield" and may be based upon overpressure or impulse.

hydrogen yield factor (HYF) - the TNT equivalent of a combustible mixture of  $H_2 - O_2$  or  $H_2 -$  air, based upon the  $H_2$  weight only, i. e.,  $HYF = (\text{grams of TNT})/(\text{gram of } H_2)$ .

explosion - the result of a sudden release of energy, ordinarily involving the rapid combustion of material, and accompanied by explosive blast waves and a loud noise. The energy release is dissipated in the formation of shock waves, acceleration of shrapnel, thermal radiation, etc.

deflagration - a low order explosion resulting from sub-sonic flame speed, relative to the unburned gas.

detonation - a high order explosion resulting from supersonic flame speed, relative to the unburned gas.

induction distance - the distance required for a deflagration to transit to a detonation -- dependent upon the flammable mixture constituents, concentration, temperature, pressure, enclosure geometry and strength of ignition source.

time delay - the time elapsed between the spillage of  $H_2$  into the air and ignition.

overpressure - the side-on or peak pressure rise accompanying the air blast waves resulting from an explosion.

impulse - the integral of the overpressure-force multiplied by time, over the time interval of explosive overpressure.

ignition source - thermal (weak) and shock-wave (strong) -- described more fully below.

Some brief comments regarding the foregoing definitions may be helpful. In order to have a fire or explosion there must exist in combination an oxidant, a fuel, and an ignition source. In our case the fuel and oxidizer are supplied by the release of  $H_2$  into air. The ignition source may be a mechanical or electrostatic spark, flame, impact, heat by kinetic effects, friction, chemical reaction, etc. In  $H_2$ -air mixtures the flame speed is the baseline used to measure the flammability and explosive potential of the mixture. A slow burning flammable mixture results in lower overpressures and less shrapnel hazard -- deflagration. A fast burning mixture causes higher overpressures and a greater shrapnel hazard -- detonation. The peak-to-initial pressure ratio ( $p_f/p_i$ ) of the latter may easily be an order of magnitude greater than that of a deflagration. For  $H_2$ -air, the  $p_f/p_i$  seldom exceeds 8 in a deflagration.

A deflagration may develop into a detonation in a closed system due to the influence of the confining walls. Geometrical changes in the confining walls that induce turbulence [12-14] enhance transition to detonation. The distance in a tunnel, pipeline, room, or test facility that it takes to progress from a deflagration to a detonation is called the induction distance. For gaseous  $H_2-O_2$  mixtures, this distance decreases [78] as the mixtures initial temperature is decreased. A flammable, but initially non-detonable, mixture of  $H_2$ -air may be detonated under certain conditions of confinement. A deflagration, propagating from one end of an elongated enclosure, may cause sufficient compression to effectively widen the detonable limits of the mixture, thus permitting transition to detonation in the initially non-detonable mixture [13-15]. Such a transition is particularly devastating because the deflagration may result in static pressure rise ratios of  $\approx 8:1$  before detonation sets in; the static pressure rise ratio<sup>3</sup> for detonation [15] is  $\approx 15:1$  and a peak reflected pressure rise ratio as high as 120:1 may be expected [14-17] where transition to detonation occurs. Reflected pressure rise ratios in excess of 300:1 are believed to be theoretically possible [14] where this transition occurs. The peak reflected pressure rise ratio for initially detonable mixtures of  $H_2-O_2$  varies from 40 to 120, see references [15, 17]. Transition to detonation occurs because compression of the  $H_2$ -air mixture by deflagration raises the mixture temperature and pressure, both of which increase the burning velocity [13, 14, 18] of this mixture. A detailed description of the transition mechanism is given in references [13, 14, 78]. Measured deflagration overpressures are in

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<sup>3</sup> Considerably higher pressure rise ratios are possible [72] with low initial temperatures and subatmospheric pressures.

reasonably good agreement with calculated values (see Appendix A and references [18, 19]).

A detonation may occur in open or closed systems if the ignition source has sufficient energy: matches, sparks, hot surfaces, and open flame are considered thermal (weak) ignition sources; shock-wave (strong) ignition sources are blasting caps, bursting vessels, TNT, high voltage-capacity shorts (exploding wires), lightning, and other explosive charges. For greater detail concerning combustion theory and definitions, the reader is referred to Zabetakis [15] or a standard text on the subject [19].

### 2.1 TNT Equivalent

Explosions that create shrapnel and overpressure hazards are rated in terms of the amount of energy that is released. The energy release may be given directly in energy units such as the BTU (Joules); it is commonly expressed as an equivalent quantity of TNT (symmetrical trinitrotoluene). Because the explosive strength of TNT is well-known and reproducible, it is a good standard for rating explosive hazards and the explosive potential of various substances. Extensive data are available for ground-level explosions of TNT in open air -- figure 1 is an overpressure nomograph prepared from such data. To use figure 1, simply enter the chart with 2 of the 3 variables (overpressure, distance, TNT equivalent) and with a straight-edge estimate the third variable. It is common procedure to relate all types of explosions to an equivalent mass of TNT -- at great distances from the explosion this is a good technique for evaluating damage potential; however, at distances inside or near the reaction zone, this procedure is less accurate. This situation arises because of the difference in shape and peak magnitude of the impulse (pressure x time) diagram. A bursting vessel may deliver a considerably lower

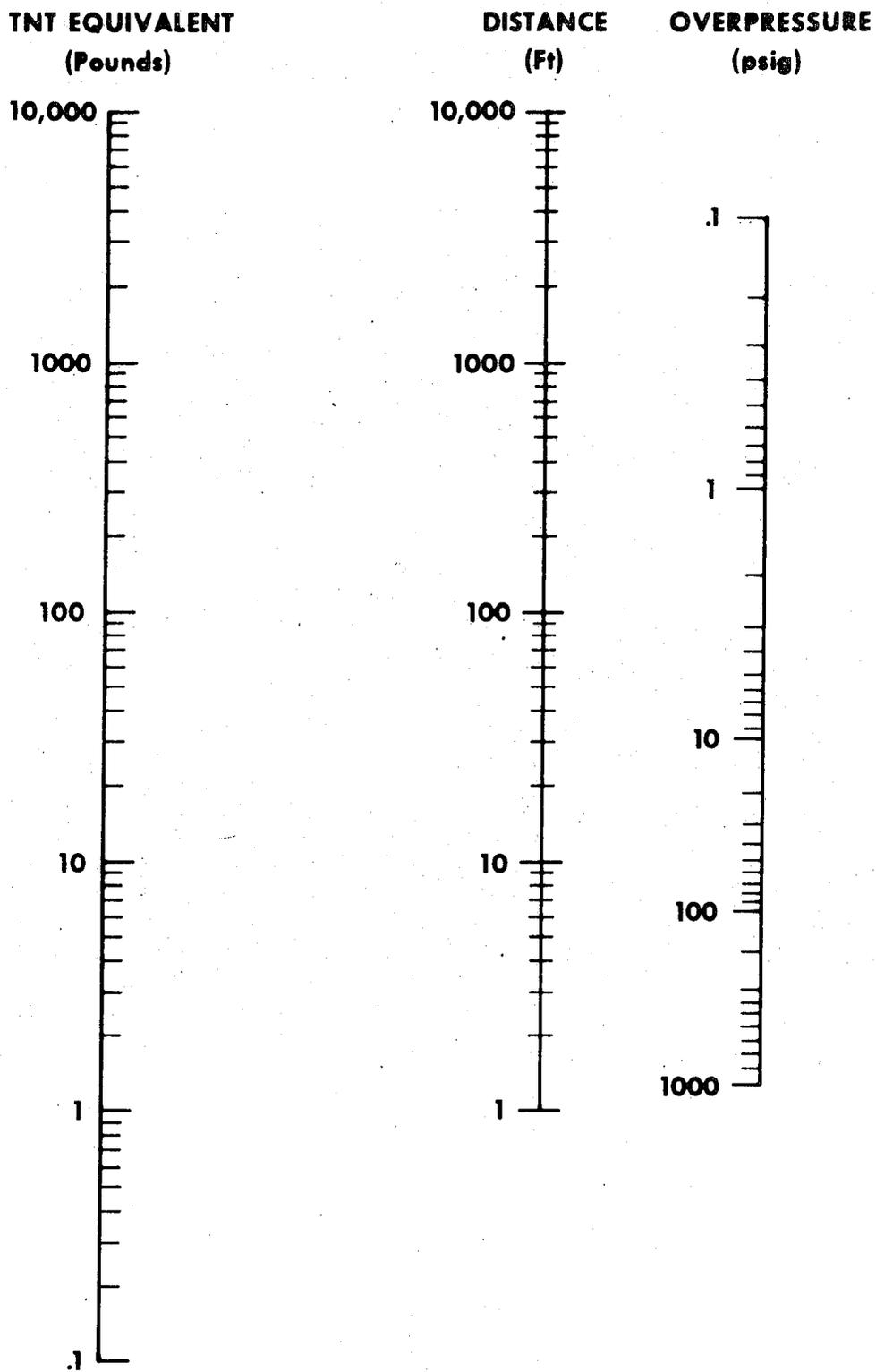


Figure 1. Nomograph for estimating overpressures resulting from open-air surface explosion of TNT.

overpressure, relative to TNT, over a longer time interval and thus have less crushing effect on some structures, but a greater overturning moment. Propellant (or fuel-air mixtures) explosions have similar characteristics [20-22], and consequently equivalent TNT yields are normally used to assess shock effects at distances well removed from the source. Fletcher [20] states that "to avoid exceeding human and structural tolerances, when sufficient data are not available, it is recommended that the near region equivalent yield be based upon impulse". Fletcher describes a propellant explosion as a low-order detonation followed by deflagration, and provides an excellent comparison of TNT and propellant explosions. Of course, in the absence of detonation, the unconfined fuel-air explosion is simply a deflagration and thermal radiation (fireball) is the main hazard. Thus, the TNT equivalent concept can be used to evaluate impulse and overpressure effects at distances well-removed from the explosion source, and to evaluate impulse effects in the near-combustion zone. For propellant explosions the impulse yield normally exceeds the overpressure yield in and near the combustion zone, see Fletcher [20] and Gunther and Andersen [22].

The theoretical TNT equivalent, of various explosive materials, is not so readily calculable because of the scarcity of requisite data. Kinney [23] carefully discusses the appropriate methods for computing TNT equivalents -- the decrease in Helmholtz free energy is used to compute the maximum energy available for explosive yield. The theoretical TNT equivalent for  $H_2$ , as reported in the literature, varies from five [24] to thirty-five [25]. Other values [5, 26] have also been reported. This confusion obviously arises from the technique employed to compute the theoretical HYF, i. e., whether the heat of explosion,

heat of combustion, heat of detonation, or heat of formation is used to perform the calculation. Undoubtedly, the source of data for these computations also has some influence on the varied results. Kinney [23] computes explosive yield as the sum of the 'heat of explosion' and an 'entropy of explosion' term. Following this procedure we obtain the theoretical limiting value of HYF  $\approx 28$ .

### 3. Open-Air (Unconfined) Facilities

In this section we shall discuss in detail available experimental data. To view these data in the proper perspective, we must first prescribe or specify the maximum credible accident (MCA) in an open-air test facility. This is no small task because we know that a deflagration, with accompanying fire and negligible overpressure, is the very least hazard that may occur. Total spillage and vaporization, accompanied by stoichiometric mixing with air, and ignition by a shock-wave initiator is the very worst case that we face. Somewhere between these extremes is the credible situation that we seek. In the case of total spillage, stoichiometric mixing and detonation, we may achieve TNT equivalents of approximately 28 pounds of TNT per pound of  $H_2$ . For our maximum credible accident we will specify:

- 1) We can suffer a brittle failure of equipment that spills the entire  $LH_2$  contents onto the ground.
- 2) Thermal ignition sources are omnipresent in the form of electrostatic or friction sparks, hot fragments, and/or electrical short circuits resulting from the equipment failure. Relatively strong initiators may also be present in the form of bursting vessels and/or high energy electrical shorts (see discussion below).
- 3) At least one protective, vertical wall is provided for the protection of personnel and/or equipment.

4) All ignition sources will be eliminated within a few seconds after spillage, i. e., emergency procedures will be enacted and all systems will be restored to a safe operating condition -- all electrical power will be deenergized, plumbing systems will be restored to a fail-safe condition, etc.

All of these conditions appear perfectly reasonable to the author and, as we shall soon see, can get us into some rather nasty situations. Items 2) and 3) are very crucial points and deserve some additional comment. For example, it is commonly assumed that most ignition sources in test facilities are of the thermal (low energy) variety. It appears that a relatively strong initiator could be provided in at least two separate ways, both associated with the sudden failure of a vessel. One involves the short circuiting of electrical wiring due to shrapnel, or tearing, as a result of the equipment failure. Such failures could easily generate melting-wire initiators and with sufficient electrical energy, even exploding-wire initiators. Failure of the equipment itself, under sufficiently high pressure, could easily provide another source of shock-wave ignition. Experimental apparatus commonly employs more than one vessel, or more than one compartment filled with  $\text{LH}_2$  so that staged failure may occur, e. g., equipment malfunction -- such as the failure of a valve pneumatic cylinder, a pressure regulator, and/or the failure of relief devices to operate properly -- and the resultant partial (or total) failure of one vessel -- may release  $\text{H}_2$  into the air and simultaneously cause the violent failure of the second vessel. The second vessel may fail directly as a result of inflicted shrapnel damage, or as a result of excessive pressure rise due to cryogenic phase change. There are many cases, and many ways, that the latter situation can develop. Because pressure vessels can fail with great violence, and are commonly rated in terms of their

TNT equivalent (see Appendix B) upon failure, it is apparent that one strong initiating source has been overlooked in the design of outdoor test facilities. An exploding wire, of course, is readily conceded to be a strong initiating source.

Our other concern (item 3) is that partial confinement may occur in outdoor test facilities, sufficient to sustain the transition from deflagration to detonation, when ordinary (thermal) ignition sources are present. ADL [5] found in their tests, that three walls plus the ground comprised sufficient confinement to support 'significant' overpressures using thermal ignition sources. It is not clear from this report whether these overpressures were attributed to high-order deflagrations or low-order detonations, but in any case they were considered 'strong'. Also, it is not clear what extent of confinement is required, to promote significant overpressures in an outdoor test facility, where thermal ignition sources are present. It is clear from this report that strong shock-wave initiators can propagate detonations of  $H_2$ -air mixtures in the open air. In theory, all that is required to promote transition to detonation is two appropriately spaced, opposed planar surfaces. In such configurations, reflected waves initiate pressure-piling which promotes transition to detonation from an ordinary (thermal) ignition source. Even in open air test facilities it is sometimes difficult to avoid two opposed surfaces, e. g., an apparatus, and the protective barrier, can easily provide at least two walls that may be sufficient confinement to permit transition to detonation. Even the apparatus itself can provide two opposing surfaces, and in some cases a great deal of effort is required to avoid this situation. Shed roofs, sight-screens and temporary weather-closures are also popular and frequently essential.

Thus, it appears that we have admitted to all of the ingredients necessary to sustain a significant overpressure should our maximum credible accident occur. We may well have sufficient confinement to sustain a significant overpressure in the event of thermal ignition, and we have potential shock-wave initiators in the form of bursting vessels and electrical short circuits. With sufficient energy, the latter can initiate detonation of  $H_2$ -air mixtures directly, even in unconfined spaces. Accordingly, a method for assessing blast hazards in open-air  $LH_2$  test facilities is needed.

### 3.1 Discussion of Experimental Data

Only two main sources [4, 5] of experimental data concerning liquid hydrogen spill hazards exist. ADL [5] performed a variety of tests, including spill tests (5 liter to 5,000 gal), gaseous mixture detonation tests, pipe-line ruptures, liquid hydrogen-solid air reaction tests, dewar ruptures and fireball tests. On the basis of these tests it was concluded that:

- 1) Detonation of an unconfined stoichiometric mixture of  $H_2$ -air could be accomplished only with shock-wave initiators (blasting caps or 2 gm of pentolite). The blasting cap produced a HYF  $\approx 1$  and the pentolite a HYF  $\approx 21$ . Thermal ignition sources produced deflagrations and negligible pressure waves.
  - 2) Spill and rupture tests resulted in deflagrations only, using both thermal and shock wave initiators.
  - 3) Oxygen enriched solid air in liquid hydrogen is a potential hazard.
  - 4) Partial confinement (U-shaped enclosure plus ground surface) caused a 'significant increase' in the deflagration pressure waves.
- These tests were performed by spilling one quart of  $LH_2$  into a 2 ft x 2 ft test bay, and igniting the vaporized gases with a spark.

It is reported that combustion resulted in a 'strong pressure pulse'. It is also reported that 'tests with larger quantities ignited in a semi-confined space established the fact that even partial confinement can add substantially to the magnitude of the pressure wave generated by the combustion of gases in free space'.

It is not clear what the magnitude of the pressure pulses were in the partial-confinement tests. It is implied that a higher order deflagration occurred. Of the conclusions set forth in the ADL report, items 1) and 4) appear defensible. The detonation tests were carefully controlled and we can hardly take issue with these results. The partial confinement tests provide a stimulus to our curiosity -- what degree of confinement is required to constitute a significant overpressure hazard (whether it be higher order deflagration or transition to detonation)? The spill and rupture tests (item 2) appear marginal at best. It is doubtful that any statistician would place significant confidence in these test results. Because of the numerous parameters (variables) pertinent to these tests, and the limited number of tests conducted, the results are subject to debate, e. g., 48 spill tests were conducted with 5 liter quantities but only a total of 22 tests with larger quantities (up to 5,000 gal). The two 5,000 gal tests are inconsequential due to pre-ignition prior to spill. Most of these tests were ignited by spark initiator (only 5 tests using 32 gal quantities were shock wave initiated). It hardly seems proper to conclude from these 5 tests that explosive igniters will not initiate detonations in  $\text{LH}_2$ -air spills. Even liquid oxygen compatibility experiments, that are carefully controlled, require 20 tests without reaction to draw such conclusions. Allan [27], in a later article, reflected that 'in all probability, the mixtures at the point of ignition were not within the detonable range'. With regard to transition to detonation, Allan also states that 'the effect of partial

confinement and the turbulent inducing parts of the system, such as piping complex, are not known'.

From these tests we may conclude that 'partial confinement' may cause 'significant' overpressure and may permit transition to detonation -- we know that a U-shaped test bay is unacceptable, but otherwise have no idea what degree of confinement is tolerable. Also, detonation of  $H_2$ -air mixtures requires strong initiators. It is highly unlikely that a  $LH_2$  spill could produce an appreciable fraction of the spilled mass in stoichiometric proportions with air -- it is more probable that a small region of nearly ideal  $H_2$ -air mixture could be ignited by a relatively strong initiator (e. g., high voltage electrical short or bursting vessel). Because of the difficulty of achieving an ideal homogeneous  $H_2$ -air mixture and because of the scarcity, in most test facilities, of initiators with greater energy than blasting caps, it appears that we can conservatively select a  $H Y F \approx 1$ . To provide greater insight into the significance of this value, we note that a  $H Y F$  of 1 requires a  $H_2$ -air  $S Y F \approx 0.11$ . This eleven percent system yield factor is obtained as follows: By definition,  $(W_o + W_f) S Y F = \text{TNT equivalent} = (W_f) H Y F$ , where  $W_o =$  oxidizer weight and  $W_f =$  fuel weight. Rearranging these terms and recalling that  $M R = W_o / W_f$ , we obtain

$$(1 + M R) S Y F = H Y F. \quad (1)$$

For a stoichiometric mixture, the  $M R = 8$ , and the  $S Y F \approx 0.11$  for  $H Y F \approx 1$ . The  $H Y F \approx 1$  was deduced from the low-order detonation data of ADL using their definitions of "yield". The significance of  $S Y F$  will be discussed more fully in the following pages, but it is apparent that a low  $S Y F$  reflects 'mixing limitations'.

Subsequent tests [28, 29] have clarified item 3) of the ADL results. Also, the experimental program on H<sub>2</sub>-air detonation characteristics is summarized in reference [79].

The second major source of experimental spill data originates from the Bureau of Mines [4]. Again it appears that relatively few tests were conducted and although the data are not overwhelming, the primary variables were controlled and/or documented -- i. e., vaporization rates, mixture concentrations and flammable regions, delay times, spill quantities, ignition source location and strength, flame volumes and thermal radiation were considered and noted. LH<sub>2</sub> quantities up to 90 liters were spilled and the vapor-air mixtures ignited in open-air with thermal ignition sources -- delay times were varied from 0 to 15.8 seconds. From these tests it was concluded [4] that fire is the chief hazard in open-air H<sub>2</sub> spills with thermal ignition sources -- only negligible deflagration overpressures were measured. This result reinforces the findings of ADL [5] and has been accepted throughout the industry.

As a result of their work, Zabetakis and Burgess [4] also recommended some quantity-distance relationships for LH<sub>2</sub> storage. These relationships were based on thermal radiation characteristics, and recommend safe distances for inhabited buildings and companion storage dewars. Because these distances are believed to be conservative (on the safe side), they are probably the most widely accepted guidelines at research and development laboratories. Consumer (storage)site guidelines [1, 6] are less stringent.

One of the most interesting results of Zabetakis and Burgess [4] was the development of a mathematical expression for the maximum width or height of the H<sub>2</sub>-air fireball,

$$\widehat{D} = \widehat{H} \text{ (ft)} = 17.8 \sqrt{W_f \text{ (pounds)}}. \quad (2)$$

They also developed an expression for maximum flame volume

$$\text{MAX. Vol. (ft}^3) \approx 750 V_{\text{LH}_2} \text{ (liters)}, \quad (3)$$

where  $V_{\text{LH}_2} = \text{LH}_2$  volume in liters. Van Dolah [30] has compared (2) with an empirical formula derived by Gayle and Bransford [31] for the diameter of spherical explosion-fireballs. The latter is based on an extensive compilation of data for bipropellants and solid explosives and a single  $\text{H}_2$ -air reaction,

$$D \approx 10 (W_o + W_f)^{1/3}. \quad (4)$$

Van Dolah [30] found that (2) and (4) did not agree too well for the  $\text{H}_2$ -air system, even when he used  $\text{MR} = 8$  in (4), i. e., (2) generally overpredicted, relative to (4). That (4) does not agree too well with (2) is not so surprising, because (4) was derived by computing the equivalent spherical fireball diameter from a large quantity of flame-volume data. Now, if we use (3) and compute the equivalent spherical diameter and convert  $V_{\text{LH}_2}$  into  $W_f$ , we obtain

$$D \approx 20.8 W_f^{1/3}. \quad (5)$$

To obtain good agreement with the single  $\text{H}_2$ -air fireball data [31] it is necessary to select  $\text{MR} = 5$  for use in (4). This is the  $\text{MR}$  common to most  $\text{H}_2 - \text{O}_2$  fueled rockets. Substituting  $\text{MR} = 5$  into (4) we obtain

$$D \approx 18.2 W_f^{1/3}. \quad (6)$$

The agreement between (5) and (6) is exceptionally good considering the nature of the data from which they originate. Equations (5)

and (6) are identical when  $MR = 8$  is used in (4). This interesting comparison, showing correlation of results for a wide variety of explosives, suggests that examination of the extensive bipropellant explosive data [8-10] may be profitable.

Extensive and relatively recent bipropellant explosion tests have been conducted on Project Pyro [8]. Preliminary bipropellant blast hazard data were supplied by Gayle et al. [9]. The latter performed tests using two propellant combinations, including liquid hydrogen-liquid oxygen ( $LH_2-LO_2$ ), and the Pyro tests used three combinations, including  $LH_2-LO_2$ . Gayle et al. [9] spilled 200 pounds total weight ( $MR = 5$ ) of  $LH_2-LO_2$ , obtaining an average SYF  $\approx 0.6$ .  $LH_2$ -filled vessels were also allowed to burst into  $LO_2$ -filled vessels and an average SYF  $\approx 0.06$  was obtained. All of these tests [9] were plagued by self-ignition; ignition was spontaneous in all of the tank tests when the separation-diaphragm (aluminum) was ruptured, and self-ignition prevented scheduled delay times in excess of 2.5 sec in the spill tests. Pyro [8] was also troubled by self-ignition in their larger scale spill tests. The relatively low yields [9] are attributed to mixing limitations in both the vapor and condensed phases. The low SYF obtained in the tank tests [9] agreed reasonably well with the 1 percent yield estimated from a Saturn IV incident [32].

Pyro [8] was an exhaustive follow-up on the preliminary tests of Gayle et al. [9]. Spill, tank, and sled-impact tests were conducted using bipropellant weights of 200 to 100,000 pounds. Delay times were varied and ignition was accomplished by squib or detonator, when self-ignition did not occur. The results of these tests indicate that the SYF varies widely as a function of failure mode, ignition delay time, etc. -- for  $LH_2-LO_2$  ( $MR = 5$ ) the delay time (mixing limitations) was most critical. In these tests the  $LH_2-LO_2$  SYF varied

from near zero to over 100 percent, with the yield decreasing with increasing bipropellant weight. The small scale (200 pound) tests agreed reasonably well with the work of Gayle et al. [9], i. e.,  $SYF \approx 0.6$ .

Gunther and Andersen [22] have since taken issue with many of the Pyro conclusions. They performed a statistical analysis of Pyro's results, combining the small scale primarily controlled ignition tests with the large scale primarily self-ignition tests. Pyro's  $LH_2-LO_2$  tank tests were dismissed as unmeaningful -- too much data scatter -- although they concluded in a qualitative sense that yield decreased with increasing propellant weights. Gunther and Andersen [22] did derive some meaningful results from the  $LH_2-LO_2$  spill tests (most tests were in the 200 to 1000 pound category), although they concluded that in general the extensive Pyro tests were inadequate. It is somewhat alarming to consider what a statistical review of our meager  $H_2$ -air data may reveal. The Bellcomm analysis [22] indicates that a  $SYF \approx 0.6$  is about the maximum to be expected for bipropellant weights of 200 pounds, and the  $SYF$  decreases with increasing weights. The drop-off in  $SYF$ , with increasing weight, is approximately proportional to the inverse of the cube root of the bipropellant weight. As a result of the Pyro [8] and Bellcomm [22] work, NASA-ASESB [33] are considering revising their facility siting criteria by using a  $SYF \approx 0.2$  (rather than the current 0.6); however, the most recent joint-authority document [80] indicates that  $SYF = 0.6$  is still being used. For very large quantities of  $LH_2-LO_2$ , as common to missile launch complexes, it appears that a  $SYF \approx 0.10$  may be adequate.

Now, how does all of this  $LH_2-LO_2$  data relate to the  $H_2$ -air problem? Because of the exceptional agreement between the  $H_2$ -air

fireball data [4] and the bipropellant and solid explosive fireball data [31], it was felt that we could establish an upper limit for the explosive hazards of the  $H_2$ -air system by studying the  $LH_2$ - $LO_2$  system -- recall, that we are only considering nearly instantaneous ignition. We must recognize that gaseous  $H_2$ -air and  $H_2$ - $O_2$  contribute to the  $LH_2$ - $LO_2$  explosion data. The contribution of gaseous vs condensed phase is not known, and would obviously vary with delay time. The data of Pesante et al. [10] suggest that a large portion of the yield may come from the condensed phases. In this experiment  $LH_2$  and  $LO_2$  were mixed and detonated by placing  $LO_2$ -filled glass dewars in a  $LH_2$ -filled pan, and transmitting an explosively generated shock wave into the bottom of the pan. The cryogenic propellants reacted spontaneously on contact, and the  $LH_2$ - $LO_2$  contact area was carefully controlled in these tests<sup>4</sup> -- a rather difficult task in spill tests. Little time was available for vaporization, so that the major portion of yield in these tests must be attributed to reaction in the condensed phases. These experiments used  $LH_2$ - $LO_2$  quantities (MR = 5) of 100 to 225 pounds, and the SYF compared favorably with those of Pyro [8] and Gayle et al. [9]. Thus, it appears that we can attribute a significant portion of the SYF in  $LH_2$ - $LO_2$  explosions to reaction of the condensed phases -- just how much of the SYF is attributable to reaction in the condensed phases is unknown, because the bipropellant contact area can vary widely from one spill incident to another.

Because there are no condensed phases available for reaction in the  $LH_2$ -air system -- at least for delay times of a few seconds to tens of seconds -- we can conservatively estimate that the maximum

<sup>4</sup> See also reference [73].

SYF for the  $\text{LH}_2$ -air system cannot exceed that of the  $\text{LH}_2$ - $\text{LO}_2$  system. To assign the entire SYF of the  $\text{LH}_2$ - $\text{LO}_2$  system to a  $\text{H}_2$  -  $\text{O}_2$  gas phase reaction is obviously overconservative; however, if we make allowances in the gaseous  $\text{H}_2$  -  $\text{O}_2$  system for replacement of  $\text{O}_2$  with air we will have a more reasonable SYF for the gaseous  $\text{H}_2$ -air system. Summarily, we are suggesting that 1) the entire SYF of the  $\text{LH}_2$ - $\text{LO}_2$  system be assigned to a gaseous  $\text{H}_2$  -  $\text{O}_2$  reaction and 2) that the  $\text{O}_2$  in this reaction be replaced by air to estimate the SYF for the  $\text{H}_2$ -air (or  $\text{LH}_2$ -air) system.

For a typical unconfined, but diked,  $\text{LH}_2$ - $\text{LO}_2$  spill with  $\text{MR} = 5$  we could expect the  $\text{LO}_2$  vaporization rate to exceed that of  $\text{LH}_2$  by 100 percent, i. e., 2 grams of  $\text{LO}_2$  could vaporize for each gram of  $\text{LH}_2$  ( $\text{MR} \approx 2$  in  $\text{H}_2$  -  $\text{O}_2$  gas phases). These estimates are obtained by taking into account the latent heats of vaporization, and film pool boiling coefficients [34] for  $\text{LH}_2$  and  $\text{LO}_2$ . The low SYF of the  $\text{LH}_2$ - $\text{LO}_2$  system is good evidence that only a small fraction of the spilled  $\text{LH}_2$  takes part in the initial reaction. Because a  $\text{MR} \leq 2$  will support a detonation in the  $\text{H}_2$  -  $\text{O}_2$  system, it is apparent that the evaporation rates estimated above will supply an abundance of gaseous  $\text{O}_2$  in the near vicinity of the potential ignition sources. In fact, for short delay times, it is difficult to visualize how a  $\text{H}_2$ -air reaction could contribute appreciably to the initial reaction in such a  $\text{H}_2$  -  $\text{O}_2$  system. Then, if we replace the  $\text{O}_2$  in the  $\text{H}_2$  -  $\text{O}_2$  system with air and use the SYF for the  $\text{LH}_2$ - $\text{LO}_2$  system, we should have a conservative (safe) SYF for the  $\text{LH}_2$ -air system -- for short delay times. The Bureau of Mines spill tests [4] indicated that 2 to 3 seconds is sufficient to obtain  $\text{H}_2$ -air mixtures that will support detonation. Then for a  $\text{LH}_2$ -air spill, with reasonably short ignition delay times (not more than a few seconds), we may proceed with the understanding that we are  $\text{H}_2$ -air

'mixing-limited.' With air containing about 20 percent  $O_2$  we will supply only 1/5 of the  $O_2$  available in the  $H_2 - O_2$  system. By comparison with the  $LH_2 - LO_2$  spill tests where  $MR = 5$ , the  $LH_2$ -air system will have a  $MR \approx 1$ , i. e., 1 gram of  $O_2$  per gram of  $H_2$  on a bulk spill basis. Obviously, in local regions near the ignition source the  $MR$  can be any value and a portion of the spilled  $H_2$  can react in a detonation or deflagration.

Using eq (1),  $MR = 5$ , and  $SYF \approx 0.6$ , we obtain  $HYF \approx 3.6$  for the  $LH_2 - LO_2$  system. Retaining  $SYF \approx 0.6$  and using  $MR \approx 1$  for the  $LH_2$ -air system, we obtain  $HYF \approx 1.2$  for  $LH_2$ -air. If we adhere to the vaporization-limited gas phase  $H_2 - O_2$  system with  $MR \approx 2$ , and replace the  $O_2$  with air, we obtain a  $HYF \approx 0.8$  for the  $LH_2$ -air system. Another way to compute the  $HYF$  for  $LH_2$ -air is to compare the available explosive energy of a  $H_2 - O_2$  mixture ( $MR = 5$ ), and a  $H_2$ -air mixture ( $MR = 1$ ) -- note that, on a bulk basis,  $MR = 1$  is slightly below the  $H_2$ -air lower flammable limit, see Appendix A. From a gross viewpoint, we can merely state that the  $LH_2$ -air system, being restricted to 0.2 of the  $O_2$  available in the  $H_2 - O_2$  system, can only consume 0.2 as much  $H_2$  in the initial reaction. Then, roughly 1/5 of the explosive energy of the  $H_2 - O_2$  system is available and  $HYF \approx 3.6/5 \approx 0.7$  for the  $LH_2$ -air system. So, from the available  $LH_2 - LO_2$  data [8-10] we have deduced that the  $HYF$  for  $LH_2$ -air may vary from 0.7 to 1.2. If we were to simply accept the potential candidate [33]  $SYF^5 \approx 0.1$  to 0.2 for  $LH_2 - LO_2$  systems ( $MR = 5$ ), and consider this criterion as the upper limit for  $LH_2$ -air systems, we obtain  $HYF \approx 0.6$  to 1.2 -- in good agreement with the deduced values.

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<sup>5</sup> For bipropellant weights in excess of 25,000 pounds.

The  $\text{LH}_2$ - $\text{LO}_2$  blast data suggest that the blast hazard of 'mixing-limited'  $\text{LH}_2$ -air spills may conservatively be assessed with  $\text{HYF} \approx 1$ .

Next, we resort to data furnished by a report on an incident. This incident involved release of room temperature  $\text{H}_2$  gas into the air, self-ignition, and assessment of resultant structural damage. An unconfined, large-volume  $\text{H}_2$ -air explosion has been described by Reider et al.[7]. This experiment was performed to obtain acoustic data associated with the release of gaseous  $\text{H}_2$  at high flow rates. The unscheduled ignition occurred about 26 seconds after the  $\text{H}_2$  gas flow was started.  $\text{H}_2$  gas flow at the time of ignition was estimated at 35 pounds per second, and was preceded by flow rates of 120 pounds per second over a 10 second interval. Assessment of structural damage in the test area complex, examination of infra-red film, and some analysis led the authors [7] to three basic conclusions: 1) the deflagration overpressure was  $\leq 0.5$  psi at a 120 to 170 ft radius, 2) of the 2000 pounds of  $\text{H}_2$  released into the air, only about 200 pounds was involved in the explosion, and 3) the fireball dimensions, as determined from film, corresponded to a cloud about 150 ft high and 30 ft in diameter.

It is quite enlightening to examine these bits of information one at a time. First, if the 0.5 psi overpressure, as determined by structural damage, is reasonably accurate, we can estimate the mass of TNT required to produce 0.5 psi at a distance of 120 to 170 ft. Referring to figure 1 we find that the required equivalent TNT is 4 to 12 pounds -- the latter figure is for 170 ft separation and the 4 pound requirement is for 120 ft separation. Because ignition followed a long delay time, most of the  $\text{H}_2$  gas had sufficient time to become diluted below the lower flammable limits -- in this case normal dilution by diffusion and buoyant

dispersion was assisted by wind and high exhaust velocities. Our second piece of information estimates that only 200 pounds of  $H_2$  was involved in the explosion. Then, for blast hazard analysis, let us assume a case where 200 pounds of  $H_2$  is released into the air and ignited almost instantly. Assigning  $HYF \approx 1$  and referring to figure 1, we find that 200 pounds of TNT produces overpressures of  $\sim 2$  to 3 psi at 120 to 170 ft. This overpressure does not agree well with the 0.5 psi overpressure estimated from structural damage. Of course, we must remember that the fireball in this incident was quite large, and propellant explosions do not resemble TNT explosions in the near-combustion region -- particularly, for low-order deflagrations of propellants. The fireball dimensions are probably the firmest data from this incident. If we use the given dimensions (cylindrical) and compute an equivalent spherical diameter, we obtain  $D \approx 60$  ft. From eqs (5) and (6) we have  $D \approx 20 W_f^{1/3}$ , and the  $W_f$  required is 27 pounds of  $H_2$ . Again, assigning  $HYF \approx 1$  and entering figure 1 we obtain overpressures of 0.8 to 1.2 psi -- not too unreasonable in comparison with the estimated 0.5 psi value and taking into consideration the deflagrative nature of the  $H_2$  explosion.

Using only the basic data from this incident, i. e., the 0.5 psi overpressure and the fireball dimensions, we would estimate that 27 pounds of  $H_2$  was involved in the initial reaction; only 4 to 12 pounds of TNT is required to cause the same overpressure. By definition the  $HYF \approx 4/27$  or  $12/27$  and is well below one. For the 200 pound involvement estimated by Reider et al. [7], the  $HYF$  is even smaller. Although the fireball formula has not been experimentally proven for release and subsequent explosion of  $H_2$  gas in air, it appears that it may be useful in post-incident analysis. As previously noted, it is also useful in predicting thermal radiation hazards. If we were

to use eq (2) to compute the  $W_f$  required to develop a maximum flame dimension of 150 ft, we would predict that 71 pounds of  $H_2$  was needed. The purpose of belaboring these data is to demonstrate that all criteria predict a HYF considerably less than one -- another testimonial to the 'mixing-limited' argument. Even with long delay times and conditions conducive to mixing, only a small fraction of the released  $H_2$  was involved in the initial reaction. Also, release of  $H_2$  gas with attendant hazards<sup>6</sup> is as important to us as  $LH_2$  spills.

Having reviewed pertinent incident and experimental  $H_2$  release data, it appears that a  $HYF \approx 1$  will provide conservative estimates of the blast hazards associated with our proposed MCA.

The remaining task is to determine the rate at which the HYF decreases with increasing  $H_2$  weight. Recall that the  $LH_2-LO_2$  test results reported in Pyro [8], and evaluated by Bellcomm [22], can be fairly well approximated by a  $W_f^{-1/3}$  relationship. This regression of yield on weight only applies when  $W_f \geq 33.3$  pounds (smallest  $LH_2-LO_2$  test was 200 pounds). Then, we will take  $HYF \approx 1$  when  $W_f < 33.3$  pounds and apply the regression rate when  $W_f \geq 33.3$  pounds. Using eq (1) we can determine the regression expression for HYF in the  $LH_2$ -air system as follows:  $HYF = (1+MR) SYF = 6SYF$  for  $MR = 5$  as in the  $LH_2-LO_2$  system; at  $W_f = 33.3$ , the  $HYF = 1 = c/(33.3)^{1/3}$  and  $c = 3.22$ . Then for  $W_f \geq 33.3$  the  $HYF = 3.22 W_f^{-1/3}$ . The overpressure scaling law is given by  $D_2/D_1 = (W_2/W_1)^{1/3}$ , where  $D_1$  = the distance from a one pound charge of TNT,  $W_1$ ;  $D_2$  is the distance at which the overpressure for  $W_2$  pounds of TNT will be identical to that for  $D_1$  and  $W_1$ . For our problem  $W_2 = HYF (W_f)$ , and using the values of HYF derived above

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<sup>6</sup> See reference [74].

$$\frac{D_2}{D_1} = \left( \frac{W_f}{W_1} \right)^{1/3}, \quad 0 \leq W_f \leq 33.3 \text{ pounds, and}$$

$$\frac{D_2}{D_1} = \left( \frac{1.5}{W_f^{0.11}} \right) \left( \frac{W_f}{W_1} \right)^{1/3}, \quad W_f > 33.3 \text{ pounds.}$$

Now, by prescribing maximum allowable overpressures on structures, dewars, etc., we may derive quantity-distance guidelines to satisfy this criterion. TNT overpressure-distance data, along with the above scaling expressions, have been used to compute the quantity-distance data shown on figures 2 and 3. Note that the data on these figures is separated into two categories, storage areas and experimental areas. The 'experimental area' data are superimposed on the 'storage area' data for comparative purposes only. Reference to figure 2 indicates that neither the fireball nor the overpressure requirements are excessive in comparison with the 'storage area' data. The overpressure thresholds plotted on figure 2 were chosen to conform with breakage of ordinary window glass (0.5 to 1.0 psig). These values are also well below human tolerances (eardrums rupture at about 5 psig). Convergence of the fireball and overpressure criteria, for extremely large quantities of  $H_2$ , implies that in this case fire and overpressure may be of equal importance; for smaller quantities, common to research test facilities, the overpressure hazard is dominant.

Unbarricaded distances required for the protection of personnel [71, 80], in inhabited buildings that are exposed to shrapnel from TNT explosions, are indicated by curve 6 on figure 2. These data also pre-

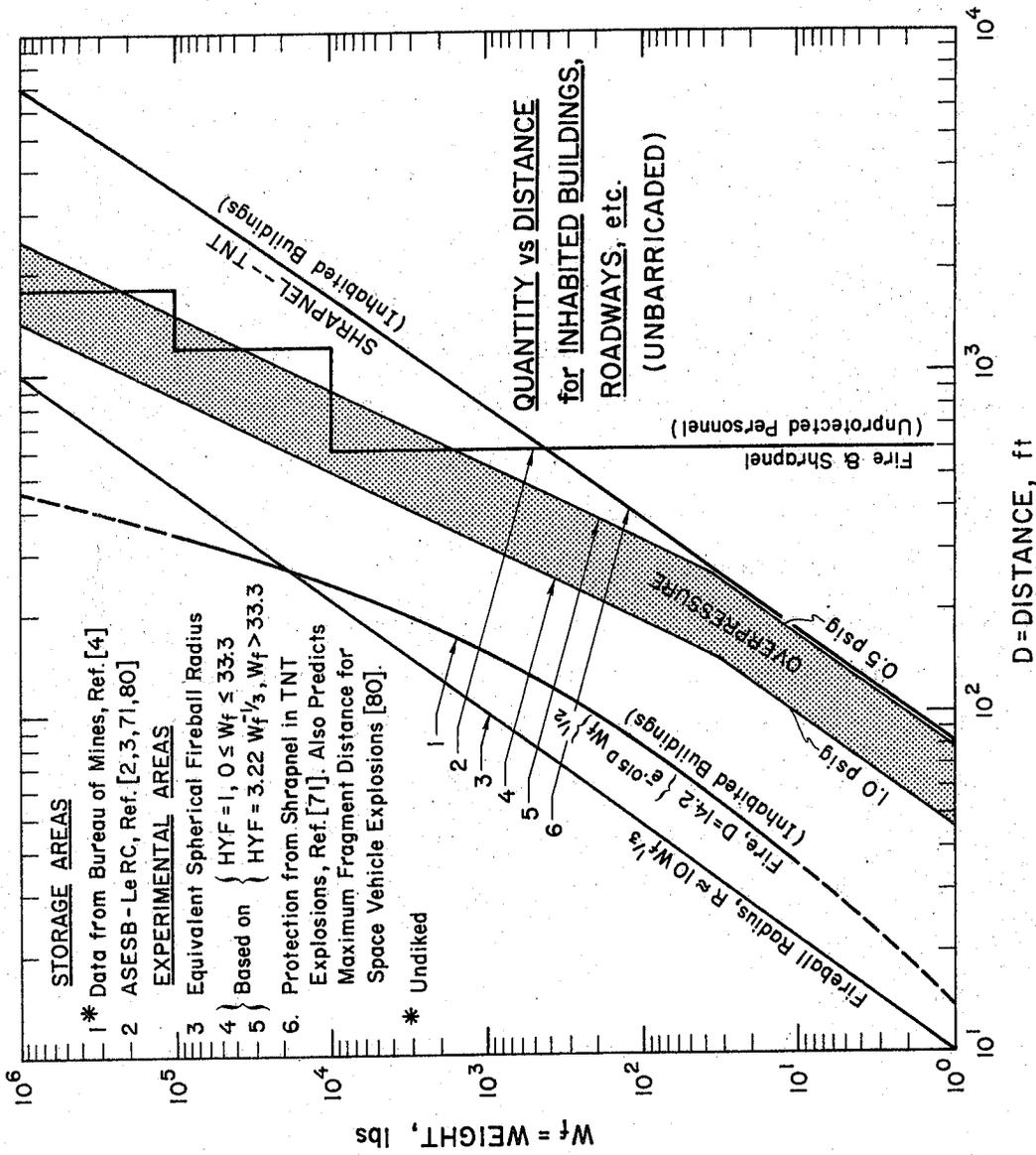


Figure 2. Quantity-distance relationships for the protection of personnel near liquid hydrogen storage and experimental areas (unbarricaded).

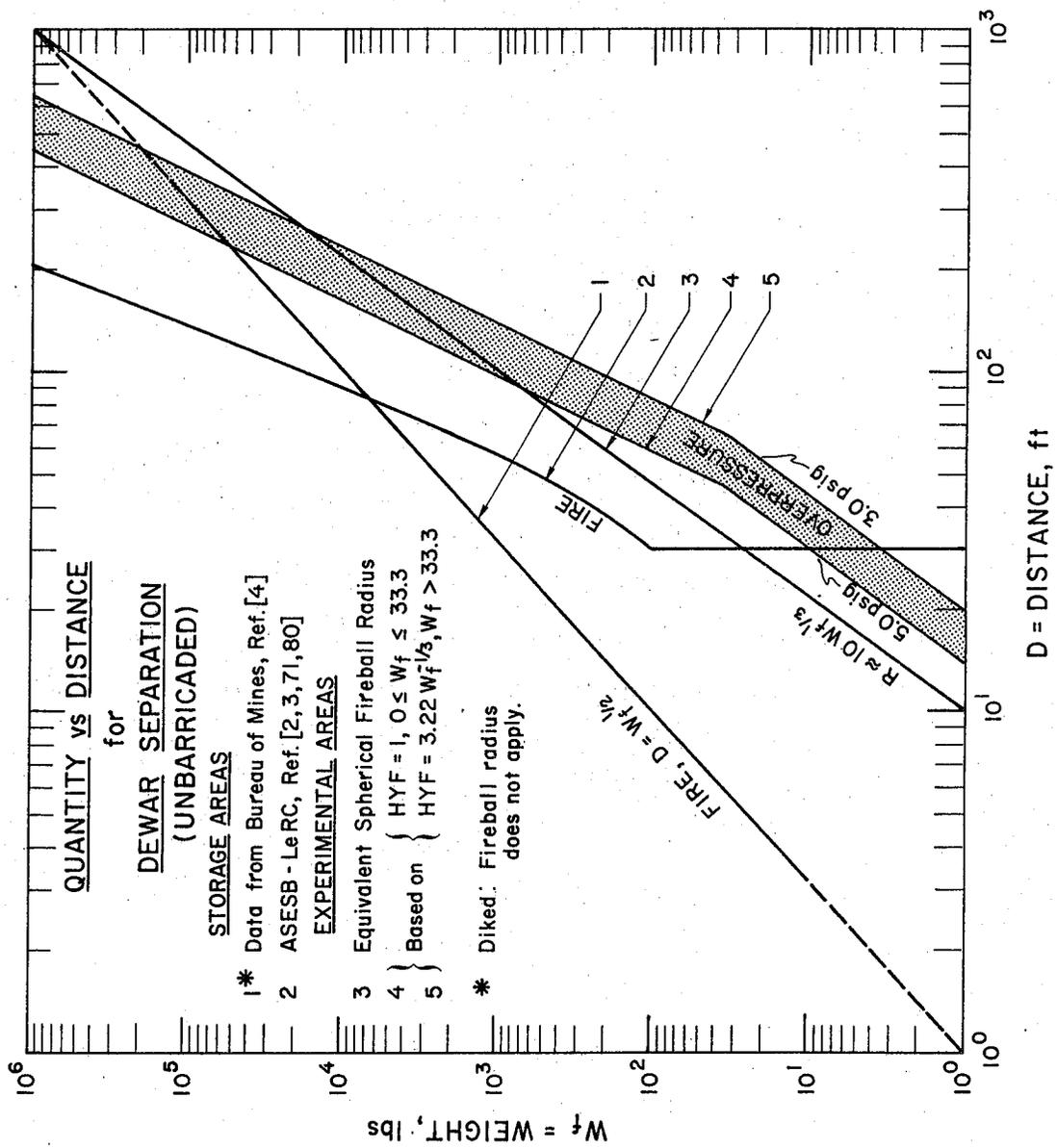


Figure 3. Quantity-distance relationships for liquid hydrogen dewar separation in storage and experimental areas (unbarricaded).

dict the maximum observed fragment distances for space vehicle explosions [80], and are more restrictive than the unbarricaded distances required [71, 80] for shrapnel protection of personnel on roadways. Fletcher has suggested [21] that TNT shrapnel hazard data may be used to estimate propellant-explosion shrapnel hazards--assuming that the appropriate TNT equivalent is used. There is evidence [21] that large, low-velocity fragments emitted from propellant explosions may exceed the TNT shrapnel scatter limits. This situation results because propellant explosions endure longer and can impart more impulse to the projectile; however, the range of high population-density projectile scatter is normally greatest [21] for an equivalent quantity of TNT.

Recently, a joint DOD-NASA document [80] adopted the TNT shrapnel hazard data for propellant explosives at range launch pads and rocket engine test stands. It is shown [80] that these TNT data adequately predict maximum fragment distances for known incidents involving propellant explosions. Similarly, we may extrapolate these TNT shrapnel hazard data to  $H_2$  experimental areas, using an appropriate value for HYF. For  $HYF = 1$ , we would simply use curve 6 of figure 2 and not allow for regression of yield with increasing hydrogen weight; however, we can easily account for regression of yield as we did with overpressure. Note that curve 6 nearly coincides with that portion of curve 5 where  $HYF = 1$ . Then, curve 5 may be considered as a guide for estimating shrapnel scatter distances for  $H_2$ -air explosions; if one is not willing to concede to the regression concept, curve 6 should be used. Reference to curve 6 indicates that the latter approach would make the shrapnel hazard the most restrictive of the explosive criteria for experimental areas, indicating the need, in certain cases, for shrapnel barricades.

Guidelines for estimating safe barricaded distances for TNT (and propellant) explosions are also available [71, 80]. Interestingly enough, the latter data are nearly coincident with that portion of curve 4, figure 2, where HYF = 1. Thus, it appears that curve 4 may be used to estimate safe barricaded distances --for inhabited buildings--for H<sub>2</sub>-air explosions. Again, if one is not willing to accept the regression concept, a straight-line extrapolation of the lower portion of curve 4 should be used. Such an extrapolation adequately represents the tabulated data [71, 80] where  $W_f < 10^5$  pounds.

The overpressure curves on figure 3 result from the assumption that a neighboring storage dewar can withstand about 3 psi overpressure -- allowance for 5 psig as a maximum case is also shown. Most coded storage vessels have powder-filled vacuum insulation, and are designed with sufficient safety factor [35, 36] to avoid collapse under external pressure. cursory calculations indicate that most storage vessels could easily withstand 3 psi overpressure, but may be translated (moved) or overturned by the overpressure pulse. Because well-constructed heavy masonry buildings will withstand ~ 4 psi overpressure without significant damage, it appears reasonable that most storage vessels would survive similar loads. Figure 3 indicates that the fireball and overpressure hazards may well be of equal importance, particularly for large quantities of H<sub>2</sub>. In general the overpressure and fireball hazard data for experimental areas, indicated on figure 3, are more stringent than the storage area data. This seems quite reasonable because the storage area data are based upon the sustained fire-resistance of storage dewars; therefore, the fireball and overpressure criteria do not apply. Note also that curve 1 of figure 3 applies to diked storage dewars.

Because of their double wall construction, most storage dewars are relatively shrapnel-resistant and shrapnel shields are not normally provided between storage dewars--such shields introduce some confinement and may increase explosive hazards. When storage dewars are located in close proximity to experimental areas, suitable shrapnel barriers are usually provided between the storage dewars and the experimental areas--with proper attention to confinement features. Separation distances between unshielded storage dewars and experimental areas may be conservatively estimated from curve 6 (or curve 5) of figure 2, i. e., the storage dewars would be located beyond the maximum shrapnel scatter range of the experimental area.

Figures 2 and 3, as presented, provide guidelines for all aspects of  $\text{LH}_2$  facility hazards, i. e., for the safety of equipment and personnel (protected and unprotected) against fire, shrapnel and overpressure.

It was previously indicated that overpressure and impulse, from propellant explosions, are difficult to estimate in the near-combustion zone; however, such data are needed to design protective barriers, buildings, etc. Fletcher [20] indicates that the near-region impulse yield from a propellant explosion may exceed that of an equivalent quantity of TNT by as much as 50 percent. On the other hand, near-region overpressure yield from the propellant explosion may be only 20 percent of that expected for TNT. Thus, for the near-combustion zone, use of TNT blast data will provide conservative results for overpressure and perhaps non-conservative results for impulse; however, it hardly seems prudent to account for the larger impulse of propellant explosions, when evaluation of the HYF is so uncertain. A structural design, based on TNT blast characteristics, will be adequate if the HYF is sufficiently

conservative--our goal. Thus, it is suggested that the extensive design data [71, 80] for TNT explosions be used until more definitive data for H<sub>2</sub>-air explosions are available.

Although self-ignition occurs in many instances with tank burst and spill tests involving the release of H<sub>2</sub> into the air, it cannot be guaranteed. In addition to the data previously discussed, the tank burst data of ADL [5] and the plastic window rupture data of Soini and Hoenig [37] indicate that spontaneous ignition occurs randomly. Thus, the possibility of accumulating combustible H<sub>2</sub>-air mixtures always exists when H<sub>2</sub> is released into the atmosphere, irrespective of whether the release is planned or unexpected. For this reason, considerable effort [38] has been devoted to safe disposal (venting) of H<sub>2</sub> gas under controlled conditions.

Finally, having been somewhat critical of the work of others, the extrapolations, interpretations, and deducements presented herein should be subjected to the same scrutiny. Certainly, the results can be faulted and are not likely to favorably impress a statistician; however, in the absence of definitive experimental data, it is believed that this review provides a reasonable and conservative estimate of the blast hazards associated with open-air LH<sub>2</sub> test facilities. Carefully planned well-controlled experiments are needed to establish more meaningful criteria, and strengthen our ability to predict H<sub>2</sub>-air blast hazards.

### 3.2 Fireballs, Shrapnel and Barricades

All of the available fireball data for LH<sub>2</sub>-air [4, 31], and LH<sub>2</sub>-LO<sub>2</sub> [8, 10, 31], are adequately correlated with the expression

$$D \approx 20 W_f^{1/3}, \quad (7)$$

where  $D$  = diameter of the spherical fireball in ft, and  $W_f$  = weight in pounds of  $H_2$  released into the air. In the case of  $LH_2$  spills,  $W_f$  is the total weight of  $LH_2$  spilled, but in a gaseous  $H_2$  release  $W_f$  is only a portion of the  $H_2$  released. If the gaseous release is sufficiently rapid, and the ignition time delay is sufficiently short, the entire weight of  $H_2$  released may be taken as  $W_f$ . Otherwise, it will be necessary to estimate what fraction of the total weight released may react in the fireball. Equation (7) is useful for estimating the weight of  $H_2$  associated with an explosion (fireball) when the physical dimensions of the fireball are known. The maximum dimension (width or height) of a deflagration fireball for spills of  $LH_2$  up to  $\sim 100$  l may be estimated [4] from

$$\hat{H} = \hat{D} = 17.8 \sqrt{W_f}, \quad (8)$$

where  $\hat{H}$  and  $\hat{D}$  are in ft and  $W_f$  is in pounds. The fireball duration may be estimated [31, 8] from

$$t \approx 0.36 W_f^{1/3}, \quad (9)$$

where  $t$  is in seconds and  $W_f$  is in pounds.

It is not the intention, in this paper, to elaborate upon the design of barricades for shrapnel and overpressure protection. Design of structures to withstand dynamic loads imposed by explosions<sup>7</sup> is a rather popular subject [15, 18, 23, 39-42], while definition of shrapnel hazard is still somewhat arbitrary [21]. Design for shrapnel protection is difficult because it is necessary to estimate the size, mass, and velocity of fragments emitted from

<sup>7</sup> Response of structural elements to  $H_2$ - $O_2$  detonations are treated in reference [75].

explosions of varied type, strength, and location. Some guidance on this subject may be found in references [2, 8, 11, 21, 32, 40, 43, 44]. TNT shrapnel hazard distances are also given in reference [71]. A single document that summarizes much of this information is now available [80]; this document is an extensive treatise on overpressure, impulse, fireballs, shrapnel, barricades, structural response and physiological effects, as they relate to propellant explosions. Facility site planning is discussed in references [40, 80].

### 3.3 Recommendations

As an interim measure, it is recommended that figures 2 and 3 be used to assess fire (thermal radiation), fireball, shrapnel and overpressure hazards at liquid hydrogen open-air test facilities. Also, carefully-controlled experiments should be performed to provide more definitive data for estimating H<sub>2</sub>-air blast hazards.

## 4. Enclosed Facilities

The hazards of using H<sub>2</sub> in enclosed spaces has already been discussed. Under favorable conditions, any ignition source can initiate a detonation. Spillage or release of any quantity of H<sub>2</sub> is to be avoided, and experiments of even slightly hazardous nature should be conducted outdoors. Proper design, safety review and monitoring, well-trained safety-conscious personnel, good procedures, and adequate facilities are essential.

### 4.1 Discussion of Experimental Data

Considerable effort has been devoted to the study of H<sub>2</sub>-O<sub>2</sub> [12, 13, 16, 17, 45-48] and H<sub>2</sub>-air [13, 29, 49-51] explosions in tubes and closed vessels. Low pressure experiments, to simulate spaceship

environments, using both condensed [52-54] and gas phase mixtures [72, 76, 77] of  $H_2-O_2$  have been performed. Condensed phase mixtures of  $H_2-O_2$  and ( $O_2$  - enriched air) -  $H_2$  mixtures are especially potent [5, 26, 28, 29]. Only one major piece of work, involving  $LH_2$  spills in an enclosed space, has been reported [11]. Zabetakis et al. [11] performed several interesting experiments in enclosed spaces. Typical glass bubble chamber windows were broken, permitting 10 l of  $LH_2$  to spill into a room temperature vacuum enclosure; pressure rise rates due to vaporization were noted in vented and unvented vacuum vessels. Similar experiments were performed using  $H_2$  gas in the inner tank, and some fragment velocity and penetration data are given. Mixing data were obtained by releasing both gaseous and liquid hydrogen in buildings or simulated buildings. Detonable mixtures formed in less than 2 seconds following spillage of 65 l of  $LH_2$  in an enclosed blockhouse (3800 ft<sup>3</sup>). Up to 40 l of  $LH_2$  were spilled in this blockhouse and the  $H_2$ -air vapors ignited by electric match and M-36 military detonator. Ignition time delays were varied from 2 to 30 seconds. With quantities of  $LH_2$  less than 30 l, ignition with match or detonator resulted in deflagrations and overpressures  $\leq$  4 psi. A 35 l spill ignited by detonator produced 40 psig and a 40 l spill ignited by electric match produced a detonation pressure  $\geq$  200 psig. This blockhouse was equipped with a 1/8-in thick masonite wall (180 ft<sup>2</sup>) and a 3 ft<sup>2</sup> beam-port opening. Inability of this 'weak' wall to relieve the detonation overpressure is evident. The 'weak' wall is credited with relieving, to some extent, the deflagration overpressures.

An interesting comparison may be drawn between this blockhouse data, and the  $H_2$ -air explosion data of Cousins and Cotton [49]. The latter performed experiments with near stoichiometric (40 vol %  $H_2$  in air) gaseous mixtures in vented cylindrical containers. The

length-to-diameter ratio of these cylinders varied from 1.44 to 22.10. We cannot make a direct comparison between these two sets of data because of 1) the differences in geometry of the enclosures, 2) Zabetakis et al.[11] data probably did not involve either homogeneous or stoichiometric room temperature mixtures, and 3) some of the vaporized  $H_2$  gas in the latter tests undoubtedly escaped through the beamport. All of these differences tend to reduce<sup>8</sup> the overpressures in the Zabetakis et al tests below those expected from Cousins and Cotton's results. The stubby geometry of the blockhouse would enhance more rapid pressure relief and of course items 2) and 3) result in less explosive yield. Using the blockhouse vent ratio (vent area divided by room volume) the data of Cousins and Cotton predict an overpressure of about 21 psi. For 15 to 30 l spills, Zabetakis et al.[11] obtained overpressures of  $\sim 3$  psi; however some adjustments in these differences can be made. Let us consider first the 15 l spill -- the entire 15 l of  $LH_2$  weighs approximately 2.3 pounds and the blockhouse holds about 300 pounds of air. Assuming no  $H_2$  or air escapes from the blockhouse the  $MR \approx 27$  or the mixture is  $\approx 11$  volume percent  $H_2$  (at room temperature). If we allow the warming  $H_2$  gas to purge air from the blockhouse we obtain a 12 volume percent  $H_2$ -air mixture (at room temperature). The latter procedure requires  $\approx 22$  l of  $LH_2$  to form a uniformly detonable  $H_2$ -air mixture in the 3800 ft<sup>3</sup> blockhouse. Just 22 l were required to form a homogeneous detonable  $H_2$ -air mixture, but 35-40 l spills were required to obtain a detonation. Now, referring to figure 1 of Appendix A we note that the  $p_f/p_i$  for  $MR = 8$

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<sup>8</sup> With the exception that a uniform mixture of lower initial temperature produces a greater pressure rise ratio, see reference [18].

is about double the  $p_f/p_i$  when  $MR = 27$ . For the same initial (atmospheric) pressure, the  $p_f$  is about twice as large for  $MR = 8$ . Then Cousins and Cotton's data ( $p_f \approx 36$  psia) may reasonably be reduced by a factor of about two on the basis of combustion energy alone. Reduction of Cousins and Cotton's data by this method predicts an overpressure of  $\sim 3$  psi -- in good agreement with the Zabetakis et al. data. Using the 30 l spill quantity and following the same procedure we would predict an overpressure of  $\sim 14$  psi -- considerably larger than that measured by Zabetakis et al. [11]; however, the Cousins and Cotton data overpredicts as expected.

It appears as though the data of Cousins and Cotton could be used to estimate deflagration overpressures in most buildings equipped with low pressure relief walls. There is not sufficient data to pursue this matter further. Certainly 'weak' walls are of great advantage in relieving deflagration overpressures and are of little or no advantage in relieving detonation overpressures. It also appears that weak but pressure-wave reflecting walls will permit transition to detonation, although in some instances they may prevent, or lessen the effects of detonation [11, 14, 42]. Soft, non-wave-reflecting (plastic curtain) walls are a possible solution to this problem. Browne et al. [42] has proposed such a test cell complex. Wherever sight-screens and/or temporary closures may be required, serious consideration should be given the soft, non-reflecting, but 'weak' closure principle. Figure 1 in Appendix A indicates the maximum deflagration overpressure to be expected in room temperature  $H_2$ -air or  $H_2$ - $O_2$  confined explosions. Experimental data [19, 29, 49] do not normally exceed 70 to 80 percent of the values indicated on this figure. The initial temperature [18] and pressure [52] of the combustible mixture can drastically alter these

data. Detonation overpressures can easily be an order of magnitude higher [14-17, 52].

#### 4.2 Summary and Recommendations

Release of  $H_2$ , in any quantity, in an enclosed space represents a serious blast hazard. It is impractical to design structures to withstand detonations; therefore, personnel safety becomes primarily a matter of thorough knowledge and good practices, i. e., release of  $H_2$  is avoided. Strong safety policy usually emanates from, and must be enforced by, management. Safety-consciousness and thorough training of operating personnel are required. High quality safety review panels, and/or safety committees, with management-backed authority should critically review apparatus design and assure compliance with established procedures. Heavy reliance is placed upon proper design, good practices, preconceived emergency procedures and attention to facility details. Most laboratories optimize ventilation (20 to 30 room air changes per hour) and try to minimize ignition sources. The latter is accomplished by using explosion proof electrical equipment where possible; electrical equipment that is not explosion proof is inert-gas purged. Electrostatic ignition sources are minimized, and the quantity of  $H_2$  permitted in the laboratory is usually limited. Several [2, 55-58] excellent safety reviews and manuals cover these procedures in great detail.

The data of Zabetakis et al.[11] indicate that quantities of  $H_2$ , permitted in enclosed spaces, should be restricted so that homogeneous detonable mixtures of  $H_2$ -air cannot be formed; however, there is no assurance that detonations cannot occur in local detonable regions in the room, or even that transition to detonation cannot occur in  $H_2$ -air mixtures that are not initially detonable. In most cases deflagrations

will occur in initially non-detonable mixtures, and 'blow-out' walls will materially relieve deflagration overpressures. Weak walls will not respond rapidly enough to relieve detonation overpressures, but may help prevent transition to detonation. Low inertia, soft, non-reflecting weak walls are especially effective in relieving deflagration overpressures and should not contribute to transition to detonation. Such soft walls are very attractive for sight-screens and temporary closures. Large vent ratios [42], as provided by properly designed weak walls, are the most effective way of minimizing deflagration overpressures. The data of Cousins and Cotton [49] may be used to estimate potential deflagration overpressures for test enclosures with prescribed vent ratios and known quantities of  $H_2$ . More experimental data are needed to establish the effects of vent ratio, and soft weak walls, on deflagration overpressures in enclosures of varied geometry (such as laboratory rooms). Experiments to evaluate the influence of various soft, weak walls on transition to detonation would also be of value. Regulation of the quantity of  $H_2$  permitted in a given room is probably the best precaution at our disposal. Where possible,  $H_2$  quantities permitted in enclosed spaces should be restricted in the following priority:

- 1) The quantity of  $H_2$  should be an absolute minimum and should be less than that quantity required to form a homogeneous flammable mixture of  $H_2$ -air at room temperature.
- 2) The quantity of  $H_2$  should be less than that quantity required to form a homogeneous detonable mixture of  $H_2$ -air at room temperature.
- 3) Larger quantities of  $H_2$  should not be permitted unless it is absolutely necessary and it can be demonstrated that the experiment is inherently safe. Several classes of experiments fall into this category.

The quantities described above do not include source quantities, i. e., portable LH<sub>2</sub> dewars, etc. It is almost always impractical to apply the quantity limitations to source dewars. Often, these dewars can be removed from the enclosure during the experiment, or can be located outside of the enclosure and valved off.

From the foregoing guidelines, it is apparent that judgment will be required on almost all occasions -- such is the function of safety panels. Experiments that are judged to be even slightly hazardous should be performed outdoors.

## 5. Future Work

Additional experimental data are needed to provide firm blast criteria for the design and operation of liquid hydrogen test facilities. Candidate H<sub>2</sub>-air experiments are listed below; both gas and liquid phase experiments are desirable.

### 5.1 Open-Air Facilities

- 1) Perform systematic studies of the ignition energy of potential ignition sources at test facilities.
- 2) Study the effects of piping complex and turbulence inducing apparatus on transition to detonation.
- 3) Study the effects of partial confinement on explosion overpressure and transition to detonation.
- 4) Evaluate the effects of various spill quantities, spill configurations, facility configurations, atmospheric conditions, ignition energy, and time delays on resultant blast hazards.
- 5) Determine the effects of low inertia (elastic and inelastic) surfaces, that are used as sight-screens and temporary closures, on deflagration overpressures in partially-confined outdoor test facilities.

## 5.2 Enclosed Facilities

- 1) Perform deflagration overpressure experiments in vented containers with various geometries and vent ratios.
- 2) Evaluate various weak-wall materials and configurations with various vent ratios in the experiments described in 1).
- 3) Evaluate the ability of elastic weak-walls to inhibit or prevent transition to detonation.
- 4) Basic studies to determine maximum pressures attainable on transition to detonation would be of academic interest.

## 6. Summary

The rudiments of combustion, TNT equivalency, and characteristics of TNT and propellant explosions are reviewed to provide background data for the combustible  $H_2$ -air system--our problem. A nomograph for estimating overpressure from TNT (propellant) explosions is given. Data are also provided for estimating the pressure rise in closed vessels due to the adiabatic combustion of  $H_2$ - $O_2$  and  $H_2$ -air mixtures. The burst energy (TNT equivalency) of bursting vessels--filled with water, gas, or liquid-vapor mixtures--may also be determined from appropriate formulae and/or graphs. Bursting vessels are considered strong ignition sources, and the effects of ignitor strength on potential explosion overpressure are discussed in considerable detail.

A state-of-the-art review indicates that explosion criteria, for the design and operation of  $LH_2$  test facilities, are inadequate. The current practice, based on limited experimental data, of neglecting overpressure hazard and providing only fire protection appears ill-founded. Normal test facility operations are taken into consideration to propose a maximum credible accident (MCA) for an open-air  $LH_2$  test facility. Available experimental  $H_2$ -air explosion data are reviewed, giving full consideration to the specified MCA. These data indicate that current practices are nonconservative.

Potential yields for  $H_2$ -air explosions are deduced from existing  $H_2$ -air data and from extensive  $H_2$ - $O_2$  explosive data. Use of the  $H_2$ - $O_2$  data was prompted by the successful correlation of fireball data for  $H_2$ -air, bipropellants, and solid explosives. Empirical formulae are given for estimating the size and duration of  $H_2$ -air explosion fireballs; these formulae were obtained from the literature, and were initially derived to fit bipropellant and solid explosive data. Overpressure hazard data, for experimental areas, are superimposed on

existing 'storage area' quantity-distance graphs. These graphs provide a handy reference for all aspects of H<sub>2</sub>-air explosive hazards, i. e., thermal radiation, fireball radius, shrapnel, and overpressure.

As a result of this study, it is tentatively recommended that each gram of H<sub>2</sub> be treated as a gram of TNT in assessing fire, fireball, shrapnel, impulse, and overpressure hazards at open-air LH<sub>2</sub> test facilities. Carefully controlled experiments are needed to provide more definitive data for estimating H<sub>2</sub>-air blast hazards--candidate experiments are outlined.

The hazards of using H<sub>2</sub> in enclosed spaces are reviewed, and emphasis is placed upon proper safety procedures, personnel training, etc. A method is suggested for estimating deflagration overpressures in buildings equipped with 'blow-out' walls. Where possible, the use of elastic curtains for sight-screens, temporary closures, etc., appears attractive. Recommendations concerning permissible quantities of H<sub>2</sub> in enclosed test facilities are provided.

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## Appendix A

### Pressure Rise in Closed Vessels Due to the Adiabatic Combustion of $H_2 - O_2$ , $H_2 - Air$ Mixtures.

#### Conversion to SI System of Units:

Calorie  $\times$  4.1840 = joule

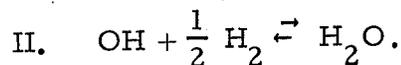
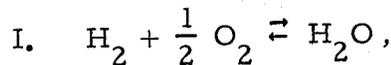
When hydrogen gas burns in a closed container, there is a marked increase in gas pressure. The pressure rise is dependent upon initial quantities of oxidizer and fuel gases present. Safe design of vessels and laboratory structures frequently requires calculation of this pressure rise.

A feasible approach to the problem is to assume an adiabatic combustion process. Lewis and von Elbe [1] have treated the  $H_2-O_2$  combustion in great detail over a limited range of mixture ratios. Mixture ratio (M.R.) is defined as the mass of oxidizer divided by the mass of fuel. The calculation scheme outlined in Lewis and von Elbe will be used herein with some simplifying modifications. The energy balance for the combustion process is written as follows:

$$\sum M_c (\Delta U)_c = \sum M_D (\Delta U)_D + \sum M_f (\Delta U) \quad , \quad (1)$$

where  $M_c$  = moles of combustible gases  
 $M_D$  = moles of dissociated gases  
 $M_f$  = moles of gases at the final or elevated temperature  
 $(\Delta U)_c$  = energy of reaction per mole of combustible gas  
 $(\Delta U)_D$  = energy required to dissociate dissociable products at the initial (pre-combustion) temperature  
 $\Delta U$  = change in internal energy of the post-combustion gases due to temperature rise.

Equation (1) states that the reaction occurs in three steps: First, the combustible gases burn to completion at the initial temperature ( $T_i$ ) until all of the oxygen or all of the combustible gases are consumed; second, part of this combustion energy is used to dissociate dissociable products at  $T_i$ ; third, the remainder of the combustion energy is used to raise the temperature of the post-combustion gases to the final temperature ( $T_f$ ). The dissociation energy term is quite complicated and involves equilibrium constants and knowledge of dissociation temperatures of various gases. Lewis and von Elbe show that water dissociates in two ways:



Both kinds of dissociation should be considered when making refined calculations. It is also necessary to consider whether excess hydrogen or oxygen is present in the combustible mixture. Excess hydrogen exists for M.R. less than 8, and excess oxygen exists for M.R. greater than 8. The maximum combustion energy is realized at M.R. = 8, which is defined as the stoichiometric M.R.

In order to calculate the pressure increase in a closed vessel due to an adiabatic explosion, it is necessary to choose a final gas temperature ( $T_f$ ). Equation (1) is then iterated until a balance is achieved. Each term on the right hand side of equation (1) is rather lengthy and temperature dependent and thus the calculations are laborious. Once  $T_f$  is established, the pressure rise may be calculated by the perfect gas law. In order to simplify the calculations, the dissociation energy term was neglected. Therefore, all combustion energy is used to elevate the temperature of the gases, and a conservative value is obtained for the pressure rise. Dissociation of water vapor is assumed to occur as per I. The initial temperature of the dry combustible mixture is taken as 300 K. The results of these calculations compare favorably (slightly higher) with those of Lewis and von Elbe for identical mixture ratios. This would indicate that the dissociation energy term is of second-order importance. The quantity of moisture and diluent gases present in the combustible mixture also affects the final pressure. Dissociation of these diluents absorbs some combustion energy and still more energy is required to increase the gas temperature. The effect of nitrogen in  $H_2$ -air explosions is shown on figure 1. The final pressure ( $p_f$ ) attainable for a given M.R. is considerably less with air than with oxygen. In order to clarify the data plotted on figure 1 it is necessary to define the mixture ratio in terms of volume for air and oxygen.

$$(M.R.)_{O_2/H_2} = \frac{\text{mass oxygen}}{\text{mass hydrogen}} = \frac{M_{O_2}^{(32)}}{M_{H_2}^{(2)}} = 16 \frac{M_{O_2}}{M_{H_2}}, \quad (2a)$$

$$(M.R.)_{air/H_2} = \frac{.21 M_{air}^{(32)}}{M_{H_2}^{(2)}} = 3.36 \frac{M_{air}}{M_{H_2}}. \quad (2b)$$

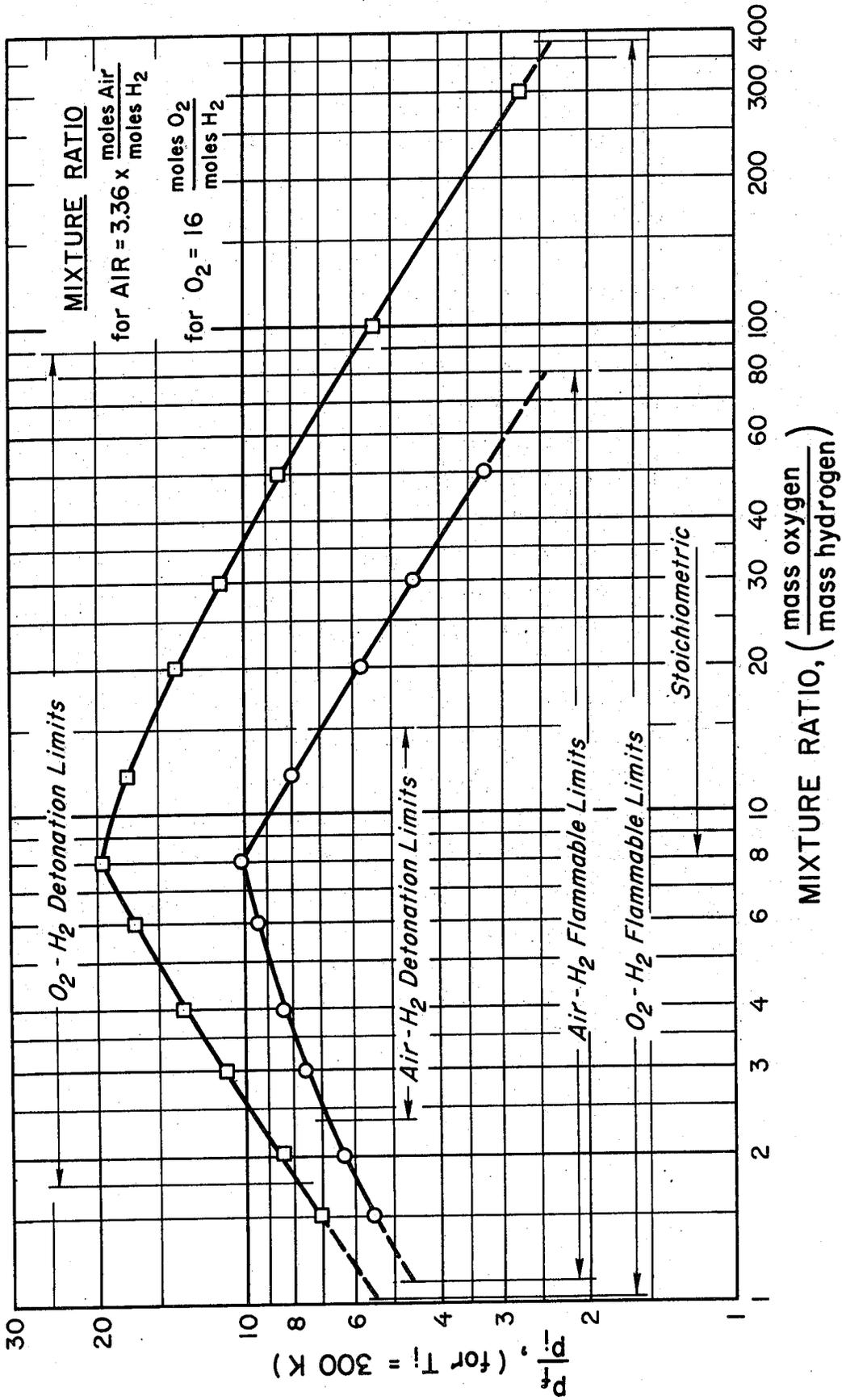


Figure 1. Adiabatic pressure rise in closed container due to combustion of hydrogen gas:  
(pre-combustion gas temperature = 300 K)

Using equations (2a) and (2b) the M.R. for  $H_2-O_2$  or  $H_2$ -air is easily computed and the pressure ratio ( $p_f/p_i$ ) may be read directly from figure 1. The combustion process in the closed vessel is considered an adiabatic constant volume process so that  $p_f/p_i = T_f/T_i$ .

The flammable and detonation limits for  $H_2-O_2$  and  $H_2$ -air are also shown on figure 1; presence of nitrogen in the  $H_2$ -air mixture strongly influences these limits. The flammable and detonation limits are given in Table I in terms of per cent hydrogen by volume and M. R.

TABLE I. Flammable and Detonation Limits for  $H_2-O_2$  and  $H_2$ -Air

	% $H_2$ in $O_2$ by volume	% $H_2$ in Air by volume	M. R. $H_2-O_2$	M. R. $H_2$ -Air
Flammable Limits	4 to 94	4 to 75	1.02 to 384	1.12 to 80.6
Detonation Limits	15 to 90	18.3 to 59	1.78 to 90.7	2.34 to 15

Excess  $H_2$  in  $H_2-O_2$  Mixture:

For type I dissociation of water  $2H_2 + O_2 \rightleftharpoons 2H_2O$ . It is assumed that all of the  $O_2$  is consumed and that for each initial mole of  $O_2$  there are two moles of water vapor formed. The energy of formation of one mole of water at 300 K is about 57,500 calories. Therefore for M. R.  $\leq 8$  the combustion energy may be written  $\sum M_c(\Delta U)_c = 2M_{i-O_2}(57,500)$ , where  $M_{i-O_2}$  = initial moles of  $O_2$ . This combustion energy is then used to heat the post-combustion gases; therefore,  $\sum M_f(\Delta U) = M_{f-H_2O}(\Delta U)_{H_2O} + M_{f-H_2}(\Delta U)_{H_2}$ , where the subscripts refer to the final (post-combustion) gas conditions.

$$\text{Since } M_{f-H_2} = M_{i-H_2} - M_{c-H_2},$$

$$M_{c-H_2} = 2M_{c-O_2} = 2M_{i-O_2},$$

$$M_{f-H_2O} = 2M_{i-O_2},$$

$$\text{and } (M. R.)_{O_2/H_2} = \frac{16M_{i-O_2}}{M_{i-H_2}},$$

the energy balance of equation (1) may be written

$$57,500 = (\Delta U)_{\text{H}_2\text{O}} + \left\{ \frac{8}{\text{M.R.}} - 1 \right\} (\Delta U)_{\text{H}_2}, \quad (3)$$

for  $\text{H}_2\text{-O}_2$ ,  $\text{M.R.} \leq 8$ .

Excess  $\text{O}_2$  in  $\text{H}_2\text{-O}_2$  Mixture:

It is assumed that all of the hydrogen gas is consumed and that a mole of water vapor is formed for each initial mole of hydrogen. By the same method used to determine equation (3) we obtain,

$$57,500 = (\Delta U)_{\text{H}_2\text{O}} + \left\{ \frac{\text{M.R.}}{16} - \frac{1}{2} \right\} (\Delta U)_{\text{O}_2}, \quad (4)$$

for  $\text{H}_2\text{-O}_2$ ,  $\text{M.R.} \geq 8$ .

Equations (3) and (4) are identical at the stoichiometric M.R.

Excess  $\text{H}_2$  in  $\text{H}_2\text{-Air}$  Mixture:

The energy balance of equation (1) becomes

$$2M_{\text{i-O}_2} (57,500) = M_{\text{f-H}_2\text{O}} (\Delta U)_{\text{H}_2\text{O}} + M_{\text{f-H}_2} (\Delta U)_{\text{H}_2} + M_{\text{i-N}_2} (\Delta U)_{\text{N}_2}. \quad (5a)$$

Again  $M_{\text{f-H}_2\text{O}} = 2M_{\text{i-O}_2}$ ,

$$M_{\text{f-H}_2} = M_{\text{i-H}_2} - M_{\text{c-H}_2},$$

$$M_{\text{c-H}_2} = 2M_{\text{i-O}_2} \text{ or } M_{\text{f-H}_2} = M_{\text{i-H}_2} - 2M_{\text{i-O}_2},$$

$$M_{\text{i-N}_2} = 0.79 M_{\text{i-air}}, \quad M_{\text{i-O}_2} = 0.21 M_{\text{i-air}},$$

$$(\text{M.R.})_{\text{air/H}_2} = 3.36 \frac{M_{\text{i-air}}}{M_{\text{i-H}_2}},$$

and equation (5a) is written

$$57,500 = (\Delta U)_{\text{H}_2\text{O}} + \left\{ \frac{8}{\text{M.R.}} - 1 \right\} (\Delta U)_{\text{H}_2} + 1.88 (\Delta U)_{\text{N}_2}, \quad (5b)$$

for  $\text{H}_2$  - air,  $\text{M.R.} \leq 8$ .

Excess  $\text{O}_2$  in  $\text{H}_2$ -Air Mixture:

Following the procedure outlined in obtaining equation (5b) we get

$$57,500 = (\Delta U)_{\text{H}_2\text{O}} + \left\{ \frac{\text{M.R.}}{16} - \frac{1}{2} \right\} (\Delta U)_{\text{O}_2} + 0.235 \text{M.R.} (\Delta U)_{\text{N}_2}, \quad (6)$$

for  $\text{H}_2$ -air,  $\text{M.R.} \geq 8$ .

Equations (3), (4), (5b), and (6) were used to compute the data points plotted on figure 1.

References:

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Appendix B  
Energy Release of Bursting Vessels

Conversion to SI System of Units:

atmosphere x 10.1325 = N/cm<sup>2</sup>

foot x 3.0480 = meter

foot-pound x 1.3552 = joule

pound x 0.4536 = kilogram

PSI x 0.6895 = N/cm<sup>2</sup>

## Appendix B

### Energy Release of Bursting Vessels

The evaluation of potential hazards associated with apparatus and test cells requires estimation of the burst energy of high pressure storage and transport vessels. Rupture of high-pressure vessels used to store gases, low-temperature liquefied gases, and ambient-temperature liquids can be considered dangerous under certain conditions; consequently, the question of whether an experimental test item should be pneumostatically or hydrostatically proof-tested frequently arises. Pneumostatic tests should never be substituted for hydrostatic tests where personnel safety is concerned because the stored energy in gas-filled systems is much greater than that of liquid-filled systems (see figures 1 and 2). If one views an energy release from a distance or inspects the damage incurred, it is sometimes difficult to differentiate between various types of energy release, such as: 1) high-explosive ignition (e. g., TNT or other solid explosive), 2) detonation of confined combustible gases, 3) rupture of a pressure vessel. Thus, it is apparent that knowledge of the potential energy of high pressure containers is essential to personnel safety.

Ordnance personnel frequently use the "TNT equivalent"[1]<sup>†</sup> as a convenient index to indicate the energy level of an explosion; the energy equivalent[1] of one pound of TNT is  $1.54 \times 10^6$  ft-lb. Thus, the potential energy of fluids stored under high pressures is calculated and reported herein in terms of equivalent pounds of TNT. The computed mass of TNT may then be used to determine explosion overpressure and safe distances for personnel and buildings.

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<sup>†</sup> Numbers in brackets indicate references at the end of this Appendix.

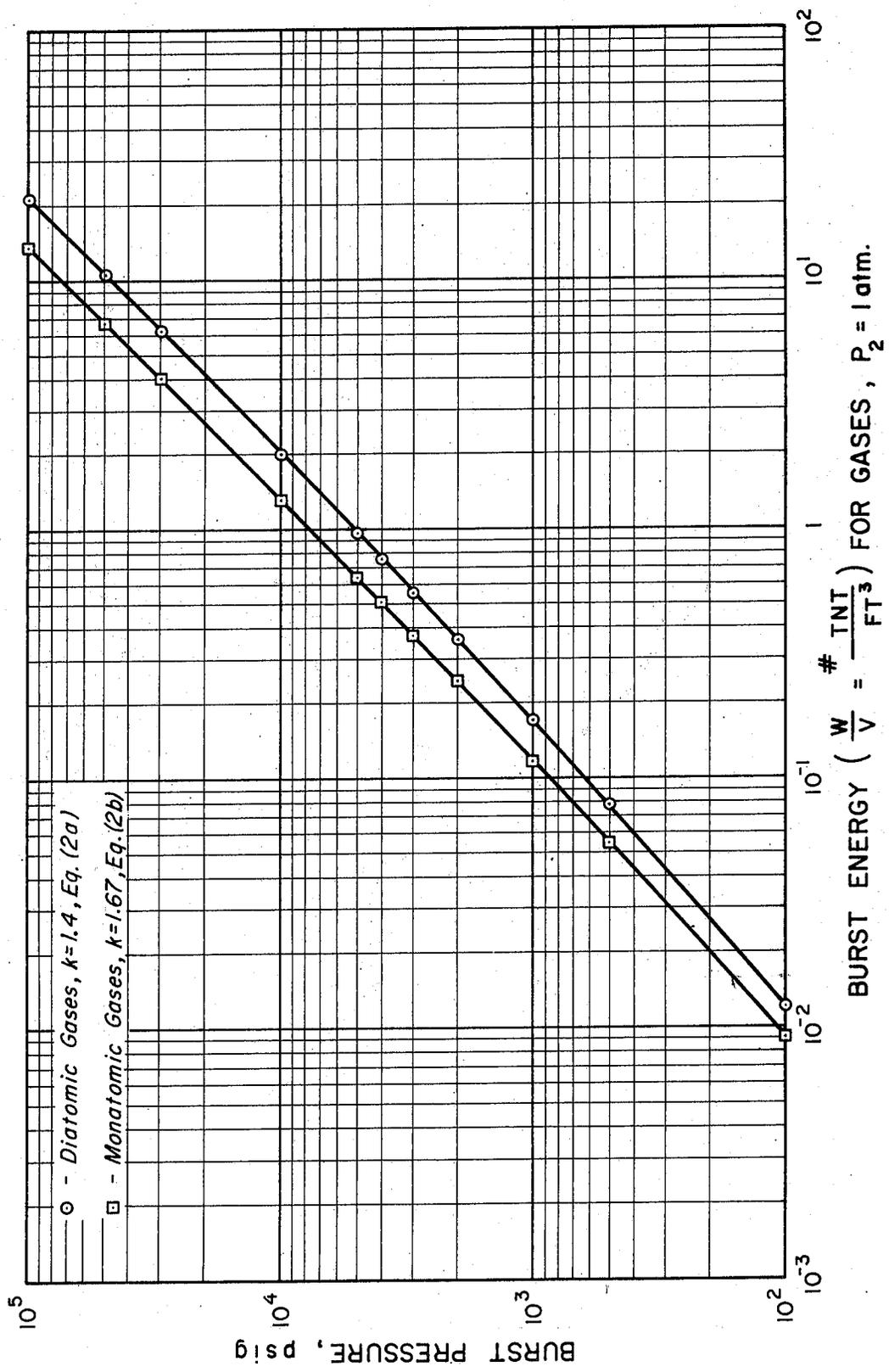


Figure 1. Burst energy of gas-filled vessels.

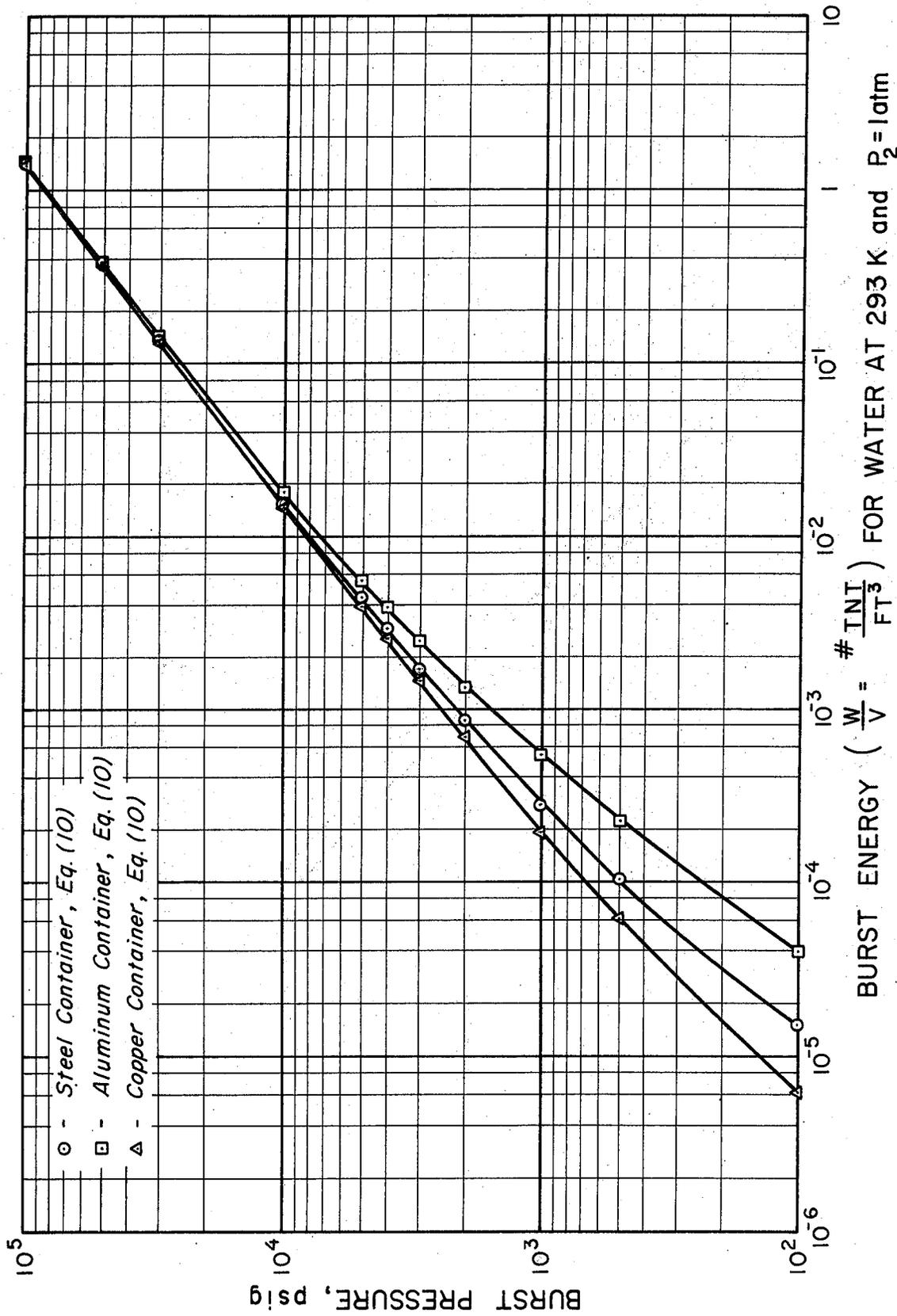


Figure 2. Burst energy of water-filled vessels.

### Storage of Gases:

The total energy stored in a gas-filled system is that of the gas and the energy required to elastically deform the container. The latter is usually small compared to the internal energy of the gas and will be neglected. We will assume the tank rupture is followed by a frictionless adiabatic<sup>1</sup> expansion of the gas. Practically, the process cannot be adiabatic; however, most of the tank failures occur rapidly[2] and, hence, little time is available for transfer of heat. Application of the non-flow energy equation results in an expression for the work performed by the expanding gas,

$$U_2 - U_1 = -W; \quad (1a)$$

the symbols are identified in the notation section of this Appendix. Tabulated thermodynamic data may be used to evaluate the change in internal energy over a limited pressure range; however, it is expedient to utilize the ideal gas law and the expression for adiabatic work,

$$W = \frac{p_1 V}{k - 1} \left\{ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right\}. \quad (1b)$$

For near-atmospheric temperatures the ratio of specific heats is 1.4 for diatomic gases and 1.67 for monatomic gases. In English units,  $p$  is in psia and eq. (1b) may be written

$$\left( \frac{W}{V} \right)_{\text{Diatomic}} = 234 p_1 \left\{ 1 - \left( \frac{p_2}{p_1} \right)^{0.286} \right\} 10^{-6}, \quad (2a)$$

<sup>1</sup> - Kinney[1] illustrates the computation of burst energies based on isothermal gas expansion.

and

$$\left(\frac{W}{V}\right)_{\text{Monatomic}} = 140 p_1 \left\{ 1 - \left(\frac{p_2}{p_1}\right)^{0.401} \right\} 10^{-6}. \quad (2b)$$

The units of  $\frac{W}{V} = \frac{\text{lbs of TNT}}{\text{ft}^3}$ . Equations (2a) and (2b) represent the

equivalent energy release per cubic foot of tankage as a function of initial and final pressure. If the ambient pressure,  $p_2$ , is one atmosphere, the results shown on figure 1 are obtained, and are valid at those temperatures and pressures where  $k \approx 1.4$  for diatomic gases and 1.67 for monatomic gases. If  $k$  differs appreciably from these values, eq. (1b) must be used.

#### Storage of Non-Flashing Liquids:

In non-flashing liquid-filled systems, the potential energy is the sum of the energy of compression of the liquid plus the elastic strain energy stored in the container. The container elastic deformation energy is not negligible in these systems except at very high pressures. The work done by the expanding liquid is simply  $\int p dV$ . Assuming the liquid is relatively incompressible and  $p_2 \ll p_1$ , the work term may be approximated by

$$W = \frac{p_1}{2} \Delta V. \quad (3a)$$

By definition the bulk modulus is written  $K = V \Delta p / \Delta V$ . When  $p_1 \gg p_2$ , substitution for  $\Delta V$  in eq. (3a) gives

$$W = p_1^2 V / 2K. \quad (3b)$$

The bulk modulus may be either the isothermal or the adiabatic value, depending upon which state path is assumed applicable to vessel failure.

It will be shown later that  $W$  may be expressed in terms of the thermodynamic properties of the liquid.

The expression for the strain energy of the container is not so easily obtained. We start with the assumption that the maximum-strain-energy failure theory is applicable and the energy expended in deforming the shell is entirely recoverable, i. e., the principal stresses in the shell at failure do not exceed the proportional limit<sup>2</sup> of the material. This is a reasonably good assumption for materials with yield and ultimate strengths which are nearly identical. With materials such as mild steel, which have considerable post-yield strength, the assumption is not so good but still gives a rough approximation to the stored energy. In effect, these assumptions state that the energy expended in plastic deformation is not recoverable. At pressures above 30,000 psi, the energy stored in the shell is small compared to the liquid compression energy and the validity of the assumption is irrelevant (see figure 2). The uniaxial internal strain energy ( $U^*$ ) per unit volume of container material may be written

$$\Delta U^* = (1/2) \sigma_m \epsilon_m. \quad (4a)$$

For triaxial stress, such as that encountered in pressure vessel walls, the unit strain energy is written

$$\Delta U^* = (1/2) \{ \sigma_\theta \epsilon_\theta + \sigma_\phi \epsilon_\phi + \sigma_r \epsilon_r \}; \quad (4b)$$

the subscripts refer to an orthogonal system of rectilinear coordinates in the vessel wall. If, for the sake of simplicity, we assume that thin-shell theory is applicable ( $\bar{D} > 10t$ ), it is easily shown that the radial energy

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2 - Proportional limit and yield strength are used interchangeably in this discussion and the critical uniaxial-failure stress is taken as  $\sigma_m$ , where  $\sigma_m > \sigma_y$ .

component  $\sigma_r \epsilon_r$  is small compared to  $\sigma_\theta \epsilon_\theta$  and  $\sigma_\phi \epsilon_\phi$  and eq. (4b) degenerates to a biaxial state of stress. Under these assumptions, Hooke's generalized laws may be written

$$\epsilon_\theta = \frac{1}{E} \{ \sigma_\theta - \mu \sigma_\phi \}, \quad (5a)$$

$$\epsilon_\phi = \frac{1}{E} \{ \sigma_\phi - \mu \sigma_\theta \}. \quad (5b)$$

Combining eq. 's (4b), (5a), and (5b), the incremental strain energy is

$$\Delta U^* = \frac{1}{2E} \{ \sigma_\theta^2 - 2\mu \sigma_\theta \sigma_\phi + \sigma_\phi^2 \}. \quad (6a)$$

For cylindrical vessels,  $\sigma_\phi = (1/2)\sigma_\theta$  and

$$\Delta U^* = \frac{\sigma_\theta^2}{2E} (1.25 - \mu). \quad (6b)$$

For spherical shaped vessels,  $\sigma_\theta = \sigma_\phi$  and eq. (6a) becomes

$$\Delta U^* = \frac{\sigma_\theta^2}{E} (1 - \mu). \quad (6c)$$

The total strain energy ( $U^*$ ) stored in the vessel walls is

$$U^* = V_M \Delta U^*, \quad (7)$$

where  $V_M$  is the volume of metal comprising the vessel walls.

Assuming reasonably large diameter tanks (diameter is at least ten times the wall thickness), the metal volume,  $V_M$ , for spheres and long cylinders is approximated by

$$\text{Cylinders:} \quad V_M \approx \pi \bar{D} L t. \quad (8a)$$

$$\text{Spheres:} \quad V_M = \pi \bar{D}^2 t. \quad (8b)$$

Consistent with the assumptions being used are the expressions for average hoop stress,  $\sigma_\theta$ , in spheres and cylinders;

$$\left(\sigma_\theta\right)_{\text{cyl.}} = p_1 \bar{D} / 2t, \quad (8c)$$

$$\left(\sigma_\theta\right)_{\text{sph.}} = p_1 \bar{D} / 4t. \quad (8d)$$

To facilitate evaluation of  $U^*$ ,  $\sigma_\theta$  is also equated to the yield stress in the following derivation. If we write the simple expressions for the liquid volume,  $V$ , of a cylinder and sphere and combine them with eq. 's (6b), (6c), (7), (8c), and (8d), we obtain

$$\text{Cylinders:} \quad U^* = \frac{p_1 V}{E} \sigma_y (1.25 - \mu). \quad (9a)$$

$$\text{Spheres:} \quad U^* = \frac{3}{2} \frac{p_1 V}{E} \sigma_y (1 - \mu). \quad (9b)$$

For ordinary values of  $\mu$  ( $\sim 0.3$ ), eq. 's (9a) and (9b) agree within about 10 percent; eq. (9b) produces the largest numbers and is selected for the calculations herein.

The total potential energy of a liquid-filled system is the sum of eq. 's (3b) and (9b). Again, using English units and expressing the potential energy in TNT equivalent, we obtain

$$\frac{W}{V} = \left\{ 46.8 \frac{p_1^2}{K} + 140 \frac{p_1}{E} \sigma_y (1 - \mu) \right\} 10^{-6}. \quad (10)$$

Table I lists typical material properties for various metals at room temperatures.

TABLE I. MATERIAL PROPERTIES

Material	E (psi)	$\sigma_y$ (psi)	$\mu$
Stainless Steel (Type 321)	$29 \times 10^6$	40,000	0.30
Carbon Steel (Structural)	$29 \times 10^6$	40,000	0.30
Aluminum (6061-T6)	$10 \times 10^6$	40,000	0.33
Copper (Annealed)	$20 \times 10^6$	10,000	0.33

The bulk modulus of water at 293 K is  $\approx 3.16 \times 10^5$  psi. The energy equivalent for liquid-filled metal containers, per unit liquid volume of the container, may then be computed and typical results are plotted on figure 2. The shell energy is shown to be insignificant at the higher pressures.

The Hencky-von Mises (shear-distortion) failure theory is considered[3] to be superior in applications involving hydrostatic pressure: for this failure theory and the condition of biaxial stress, eq.'s (6a), (6b), and (6c) would become

$$\Delta U^* = \frac{1 + \mu}{3E} (\sigma_\theta^2 - \sigma_\theta \sigma_\phi + \sigma_\phi^2). \quad (11a)$$

$$\text{Cylinders:} \quad \Delta U^* = \left( \frac{1 + \mu}{4E} \right) \sigma_\theta^2. \quad (11b)$$

$$\text{Spheres:} \quad \Delta U^* = \left( \frac{1 + \mu}{3E} \right) \sigma_\theta^2. \quad (11c)$$

Comparison of eq. (6b) with (11b) and (6c) with (11c) indicates that the strain-energy theory provides larger values of  $\Delta U^*$ , and thus is more conservative for the problem being considered.

#### Liquid-Vapor Systems:

Low temperature liquefied gases, as well as steam boilers, fall into this category. In low-temperature liquefied gases, the potential energy is the sum of the energy of liquid compression, gas internal energy, and shell strain energy. If the liquid temperature exceeds the saturation temperature at  $p_2$ , additional energy release may be provided by spontaneous flashing upon failure of the container. In low temperature liquids such as helium, hydrogen, nitrogen, and oxygen, there is little difference in gas and liquid densities at temperatures near critical so that the effects of rapid vaporization would not be too large. If these liquids are near their normal boiling point when failure occurs, it is unlikely that sufficient heat could be absorbed by the liquid in the brief failure interval to cause significant vaporization<sup>3</sup>. The liquid-to-gas density ratio for these and other liquids is largest at the lower and intermediate saturation pressures; this is the region where vaporization could contribute significantly to the energy release. The internal energy of the cold pressurizing gas is considerably less than that of 293 K gas at the same pressure. In steam boilers, the vapor has high internal energy and the liquid/gas density ratio is usually large (well below the critical point). Vessels of this type, under seemingly low pressures, should be treated in detail because the sudden reduction in pressure accompanying failure permits the energy stored in the form of superheated liquid to be realized. It is convenient to analyze these liquid-vapor systems from the thermody-

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3 - Sufficient heat could be gained in a cryogenic liquid system if the liquid-containing inner shell of a dewar failed somehow, spilling cryogen into the warm, uninsulated outer shell.

dynamic viewpoint and certain pertinent assumptions are in order if one is to obtain an estimate of their destructive potential. Most cryogenic vessels and steam boilers have some sort of insulating jacket or protective covering. It is assumed that this shell or jacket does not absorb any of the burst energy or otherwise alter the energy release of the bursting vessel. Secondary energy releases attributable to chemical or combustion reactions are also excluded; e. g., oxygen or fluorine may react with portions of the tank walls and hydrogen may mix with air and be detonated.

Figure 3 indicates typical expansions which may take place isentropically between the initial (burst) state-point and the final (environmental or ambient) pressure.

The general non-flow energy equation may be written

$$(\Delta U)_f = u_1 m_1 - (u_{f2} m_{f2} + u_{v2} m_{v2}). \quad (12a)$$

Conservation of mass requires

$$m_1 = m_2 = m_{f2} + m_{v2}, \quad (12b)$$

and the assumption that the expansion takes place isentropically provides

$$m_1 s_1 = m_{f2} s_{f2} + m_{v2} s_{v2}. \quad (12c)$$

Combining eq. 's (12a), (12b), and (12c) we obtain the desired expression

$$(\Delta U)_f = m_1 \left\{ u_1 - \left[ u_{f2}(1-x) + u_{v2}x \right] \right\}, \quad (13a)$$

where  $x = (s_1 - s_{f2}) / (s_{v2} - s_{f2})$ . Since  $m_1 = V_1 / v_1$  and  $(\Delta U)_f = W$ ,

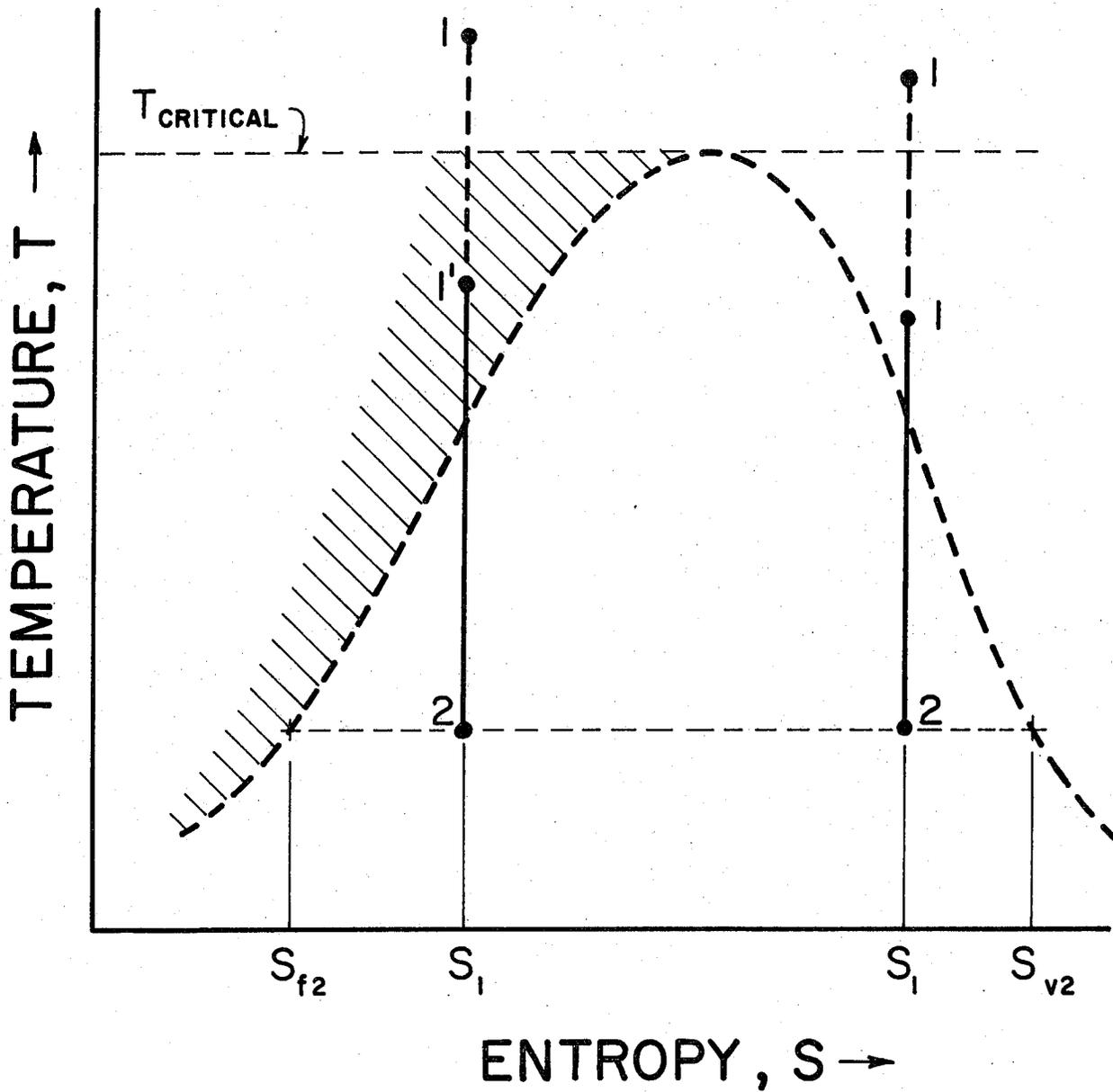


Figure 3. Typical isentropic fluid expansions that may occur on failure of liquid-vapor filled vessels.

eq. (13a) may also be written in terms of  $W/V_1$  for numerical comparison with the expressions previously obtained for gas-filled and liquid-filled systems. Equation (13a) degenerates into the basic relationship used for both gas and liquid systems as follows:

$$\text{Gases:} \quad x = 1 \text{ and } u_{v2}x = u_2.$$

$$\text{Liquids} \quad x = 0 \text{ and } u_{f2} = u_2.$$

Equation (13a) is totally valid for the fluid in any initially-stable state except for a saturated or subcooled liquid (e. g., see statepoint 1' and shaded region on figure 3). We account for these initial fluid states by adding the change in internal energy of the ullage gas<sup>4</sup>,

$$(\Delta U)_{ug} = m_{ug1} \left\{ u_{ug1} - \left[ u_{f2}(1 - x_{ug}) + u_{v2}x_{ug} \right] \right\}, \quad (13b)$$

The bracketed term containing  $x_{ug}$  accounts for condensation of some of the ullage gas. Combining eq. 's (13a), (13b), and (7) we obtain the general expression for energy release of a bursting vessel,

$$\begin{aligned} \Delta U = & m_1 \left\{ u_1 - \left[ u_{f2}(1 - x) + u_{v2}x \right] \right\} \\ & + m_{ug1} \left\{ u_{ug1} - \left[ u_{f2}(1 - x_{ug}) + u_{v2}x_{ug} \right] \right\} + V_M \Delta U^*, \end{aligned} \quad (13c)$$

where  $V_M \Delta U^*$  is evaluated by combining eq. 's (6) and (8) to obtain

$$\text{Long Cylinders: } V_M \Delta U^* = \frac{\pi \bar{D} L t \sigma^2 (1.25 - \mu)}{2JE}.$$

<sup>4</sup> - This process is shown on the vapor-side of the dome in figure 3; note that  $x_{ug} = (s_{ug1} - s_{f2}) / (s_{v2} - s_{f2})$ .

$$\text{Spheres: } V_M \Delta U^* = \frac{\pi \bar{D}^2 t \sigma^2 (1 - \mu)}{JE}$$

In the use of eq. (13c), it is emphasized that the second bracketed term disappears for all cases except those where two distinct fluid phases (i. e., liquid-vapor) exist at state-point 1.

Application of eq. (13c) requires the use of thermodynamic tables or charts such as those given in references [4-10].

#### Use of Computed Burst-Energy Values:

Having obtained the equivalent energy release for a bursting vessel, the overpressure, impulse, and shrapnel hazards may be assessed as indicated in the main text of this paper.

#### Nomenclature

$\bar{D}$	=	arithmetic mean diameter of cylinder or sphere
$E$	=	Young's modulus of elasticity
$J$	=	mechanical equivalent of heat
$k$	=	ratio of specific heats
$K$	=	bulk modulus of elasticity [ $\equiv V \Delta p / \Delta V$ ]
$L$	=	length of cylindrical vessel
$m$	=	mass of fluid
$p$	=	pressure in fluid
$s$	=	specific entropy of fluid
$t$	=	thickness of vessel wall
TNT	=	symmetrical trinitrotoluene, high explosive
$u$	=	specific internal energy of fluid
$U$	=	internal energy of fluid
$U^*$	=	internal strain energy in vessel walls

$v$  = specific volume of fluid  
 $V$  = liquid capacity or volume of vessel  
 $V_1$  = volume of fluid at the initial state-point  
 $V_M$  = volume of metal in the container walls  
 $W$  = work done by the expanding fluid  
 $x$  = quality of fluid

#### Greek

$\epsilon$  = unit strain in vessel walls  
 $\mu$  = Poisson's ratio  
 $\sigma$  = unit stress in vessel walls

#### Subscripts

1 = denotes initial (bursting) condition or state-point  
2 = denotes final (environmental) condition or state-point  
f = denotes fluid  
f2 = denotes saturated liquid condition at  $p_2$   
m = denotes failure condition in uniaxial tension  
r = denotes radial component  
ug = denotes ullage gas  
ug1 = denotes ullage gas at initial conditions  
v2 = denotes saturated vapor condition at  $p_2$   
y = denotes yield point (usually 0.2 percent offset on stress-strain curve)  
 $\theta$  = denotes circumferential component or direction  
 $\phi$  = denotes longitudinal component or direction orthogonal to  $\theta$  and  $r$  coordinates

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