NBS TECHNICAL NOTE 690

U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Is Hydrogen Safe?

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. The Bureau's overall goal is to strengthen and advance the Nation's science and technology and facilitate their effective application for public benefit. To this end, the Bureau conducts research and provides: (1) a basis for the Nation's physical measurement system, (2) scientific and technological services for industry and government, (3) a technical basis for equity in trade, and (4) technical services to promote public safety. The Bureau consists of the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, the Institute for Computer Sciences and Technology, and the Office for Information Programs.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement; coordinates that system with measurement systems of other nations; and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of the Office of Measurement Services, the Office of Radiation Measurement and the following Center and divisions:

Applied Mathematics — Electricity — Mechanics — Heat — Optical Physics — Center for Radiation Research: Nuclear Sciences; Applied Radiation — Laboratory Astrophysics[2] — Cryogenics[2] — Electromagnetics[2] — Time and Frequency[2].

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement, standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; provides advisory and research services to other Government agencies; and develops, produces, and distributes standard reference materials. The Institute consists of the Office of Standard Reference Materials, the Office of Air and Water Measurement, and the following divisions:

Analytical Chemistry — Polymers — Metallurgy — Inorganic Materials — Reactor Radiation — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations leading to the development of technological standards (including mandatory safety standards), codes and methods of test; and provides technical advice and services to Government agencies upon request. The Institute consists of the following divisions and Centers:

Standards Application and Analysis — Electronic Technology — Center for Consumer Product Technology: Product Systems Analysis; Product Engineering — Center for Building Technology: Structures, Materials, and Life Safety; Building Environment; Technical Evaluation and Application — Center for Fire Research: Fire Science; Fire Safety Engineering.

THE INSTITUTE FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in improving cost effectiveness in the conduct of their programs through the selection, acquisition, and effective utilization of automatic data processing equipment; and serves as the principal focus within the executive branch for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Institute consists of the following divisions:

Computer Services — Systems and Software — Computer Systems Engineering — Information Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal Government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System; provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

Office of Standard Reference Data — Office of Information Activities — Office of Technical Publications — Library — Office of International Relations — Office of International Standards.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Located at Boulder, Colorado 80302.

Is Hydrogen Safe?

J. Hord

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, Secretary

Edward O. Vetter, Under Secretary
Dr. Betsy Ancker-Johnson, Assistant Secretary for Science and Technology

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Acting Director

Issued October 1976

NATIONAL BUREAU OF STANDARDS TECHNICAL NOTE 690
Nat. Bur. Stand. (U.S.), Tech. Note 690, 38 pages (October 1976)

CODEN: NBTNAE

U.S. GOVERNMENT PRINTING OFFICE
WASHINGTON: 1976

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402
(Order by SD Catalog No. C13.46:690). Price 85 cents. (Add 25 percent additional for other than U.S. mailing)

CONTENTS

		Page
1.0	INTRODUCTION	1
2.0	GENERAL PHYSICAL AND CHEMICAL PROPERTIES	1
3.0	FIRE HAZARDS	7
4.0	FIRE DAMAGE	9
5.0	EXPLOSIVE HAZARD	11
6.0	EXPLOSIVE DAMAGE	12
7.0	COMPARISON OF FUEL STORAGE METHODS	15
8.0	FUTURE HYDROGEN APPLICATIONS	19
9.0	SUMMARY	20
10.0	REFERENCES	22
	Appendix: Hydrogen Safety Guidelines and Applicable Regulatory Codes	29
	Appendix References	31

LIST OF FIGURES

Figure 1. Quantity-distance relationships for the protection of personnel near liquid hydrogen storage and experimental areas (unbarricaded) 16

Figure 2. Quantity-distance relationships for liquid hydrogen dewar separation in storage and experimental areas (unbarricaded) 17

Figure 3. Industrial storage standards (quantity-distance) for hydrogen, liquefied natural gas (LNG) and gasoline 18

LIST OF TABLES

Table 1. Properties of Hydrogen, Methane and Gasoline 5-6

Table A1. Hydrogen Safety and Equipment Guidelines (nonmandatory) 29

Table A2. Regulations (mandatory) for Distribution of Hydrogen 30

IS HYDROGEN SAFE?

J. Hord

Cryogenics Division
Institute for Basic Standards
National Bureau of Standards
Boulder, Colorado 80302

The safety aspects of hydrogen are systematically examined and compared with those of methane and gasoline. Physical and chemical property data for all three fuels are compiled and used to provide a basis for comparing the various safety features of the three fuels. Each fuel is examined to evaluate its fire hazard, fire damage, explosive hazard and explosive damage characteristics. The fire characteristics of hydrogen, methane and gasoline, while different, do not largely favor the preferred use of any one of the three fuels; however, the threat of fuel-air explosions in confined spaces is greatest for hydrogen. Gasoline is believed to be the easiest and perhaps the safest fuel to store because of its lower volatility and narrower flammable and detonable limits. It is concluded that all three fuels can be safely stored and used; however, the level of safety risk for each fuel will vary from one application to another. Generalized safety comparisons are made herein but detailed safety analyses will be required to establish the relative safety of different fuels for each specific fuel application and stipulated accident. The technical data supplied in this paper will provide much of the framework for such analyses. Hydrogen safety guidelines, regulatory codes applicable to the distribution of hydrogen, and safety criteria for liquid hydrogen storage are compiled and presented.

Key words: Explosion, fire, fuel, gasoline, hydrogen, methane, safety.

1.0 INTRODUCTION

For many years now hydrogen has been considered a suitable, if not ideal, synthetic fuel for future generations. Its clean-burning, rapid-recycling characteristics are lauded by hydrogen advocates and its explosive characteristics are emphasized by hydrogen opponents. The safety aspects of hydrogen are the most common concern of the man-on-the-street when he is first introduced to the hydrogen fuel concept. This spontaneous fear reaction is probably attributable to the automatic association of hydrogen fuel with the 'hydrogen-bomb' and the Hindenburg fire. Subsequent to the Hindenburg incident this country has experienced more tragic and devastating fires involving natural gas, yet natural gas is a fuel that is commonly accepted by the general public. Also, there is no connection whatsoever between the chemical explosive potential of hydrogen fuel and the thermonuclear explosive potential of hydrogen as it is used in 'hydrogen-bombs.' Thus, even the novice will recognize that the wide-eyed fear of hydrogen is unjustified. Simultaneously we must realize that hydrogen is one of the most flammable and explosive fuels available to us and it must be handled with appropriate respect and safeguards.

Evaluation of the safety hazards of a particular fuel is a highly complex task requiring interpretation of specific technical data and intercomparisons with other fuels. Fire and explosion hazards must be carefully assessed to determine the relative safety of a fuel in each potential application. Therefore, hydrogen can be safer than conventional fuels in some applications and more hazardous in other applications. Because of the complexity and depth of this topic, it is treated rather superficially in page-limited technical articles dealing with hydrogen-energy concepts. The purpose of this paper is to systematically examine the safety aspects of hydrogen and to determine if hydrogen is sufficiently safe for use as a future fuel. It will be demonstrated herein that the answer is overwhelmingly, YES, although its use may be restricted in some future applications.

2.0 GENERAL PHYSICAL AND CHEMICAL PROPERTIES

To permit insight and provide perspective for the relative safety of hydrogen, comparative data are given in table 1 for methane and gasoline. Methane is the major constituent

of most compressed natural gases and of liquefied natural gas (LNG); therefore, methane and LNG are used interchangeably in this document. The significance of the technical data, listed in table 1, is discussed in considerable detail throughout the remainder of this paper. These data were obtained from numerous sources and are believed to be the best available. Some of the data given in table 1 were obtained by giving weighted consideration to several sources of data and by performing appropriate computations.

Most of the properties listed in table 1 will be familiar to the average reader; however, each of the combustion properties will be briefly described because of their importance to this safety analysis and because some of them are not commonly used properties. The thermophysical properties conform with the conventionally accepted definitions; however, explanatory notes are provided at the bottom of table 1 to explain the bases for some of the "gasoline" properties. The heats of fusion and sublimation are taken at the triple point (at the freezing point for gasoline) and the heats of vaporization are taken at the normal boiling point. The combustion properties are defined in the following paragraphs.

Limits of flammability in air: The range of concentrations of gaseous fuel in air at which the mixture will burn, i.e., a homogeneous fuel-air mixture will propagate a flame within a limited range of compositions. These limits are determined experimentally [40] by visually observing upward propagation of flames through flammable mixtures in vertical tubes.

Limits of detonability in air: The range of concentrations of gaseous fuel in air at which the mixture will detonate, i.e., the flame front will propagate at supersonic speed. These limits are usually determined by measuring the rate of propagation [19,35,41] of combustion-supported pressure waves in long horizontal tubes filled with combustible mixtures of fuel in air.

Stoichiometric composition in air: The concentration of fuel in air at which all of the fuel and oxygen in the mixture are consumed by the reaction and maximum combustion energy is realized.

Minimum energy for ignition in air: The minimum spark energy required to ignite the most easily ignitable concentration of fuel in air. The most easily ignited mixture of fuel in air is usually not the stoichiometric composition. To determine the minimum ignition energy, a calibrated capacitor is charged to a specified voltage and discharged through an arc between parallel plate electrodes that are immersed in the combustible mixture of gases. Ignition energy is calculated from $(1/2)CV^2$, see references [42,43].

Autoignition temperature: The minimum temperature at which a combustible mixture of fuel and air can be ignited by a hot surface [8,18,44].

Hot air-jet ignition temperature: The temperature of a jet of hot air as it enters pure fuel vapors or a combustible fuel-air mixture at NTP and causes ignition to occur. The data given in table 1 represent the jet temperature of hot air as it enters pure fuel vapors at NTP. The jet diameter for these data is 0.4 cm. This ignition temperature decreases with increasing jet diameter [22,45,46] and for a given jet diameter the hot gas jet ignition temperature increases if hot jets of nitrogen gas (rather than air) are squirted into combustible fuel-air mixtures [45]. The hot gas jet ignition temperature is dependent upon the composition of the combustible mixture and the velocity of the jet of hot gas.

Flame temperature in air: The temperature within the flame as determined by burning premixed stoichiometric fuel-air mixtures in the open air. Fires at the scenes of fuel spills or leaks more closely simulate stationary gaseous diffusion flames which burn at lower temperatures. Detailed discussions on this topic and experimental techniques are reviewed by Lewis and von Elbe [47].

Percentage of thermal energy radiated from flame to surroundings: The percentage of the heat of combustion (high) that is radiated from the combustion zone to its surroundings. The higher heating value of every flame is eventually dissipated by radiative processes. The data given in table 1 are for flames fueled by vaporization of pools of liquid fuels in an air environment. These data are similar to those obtained in laboratory experiments with stationary gaseous diffusion flames [25,26]. Atmospheric moisture absorbs thermal

energy radiated from a fire and can reduce the values recorded in table 1. Hydrogen fires benefit most from this absorption effect [25], e.g., it is estimated that 45 percent of radiant hydrogen flame energy is absorbed within a distance of 8 m in 25°C air containing water vapor at 15 mmHg partial pressure.

Burning velocity in NTP air: The subsonic velocity at which a flame propagates through a flammable fuel-air mixture. This velocity is usually determined in the laboratory by measuring the velocity of gas flow to a bunsen burner [27].

Detonation velocity in NTP air: The supersonic velocity at which a flame (and accompanying pressure wave) propagates through a detonable fuel-air mixture.

Diffusion coefficient in NTP air: The diffusivity or coefficient of diffusion is a parameter used in Fick's equation to describe the rate at which a gaseous fuel diffuses through air. For a given fuel concentration gradient the mass diffusion flow rate is proportional to the diffusion coefficient. This coefficient can be computed from an empirical expression [48] that is based on the kinetic theory of gases.

Diffusion velocity in NTP air: The velocity at which a gaseous fuel diffuses through air. For a specified fuel concentration gradient the diffusion velocity is proportional to the diffusion coefficient and can be estimated from Stefan's equation [49]. Diffusion velocity varies with temperature according to $T^{3/2}$ and consequently low temperature gases produced by cryogenic liquid fuel spills will diffuse more slowly than NTP fuel gases. The values recorded in table 1 are based on NTP fuel gas and NTP air densities and fuel concentrations that vary from 99.99 percent to 0.0 percent over path lengths of 3 cm to 30 m.

Buoyant velocity in NTP air: The velocity at which gaseous fuels rise in air under the influence of buoyant forces. This velocity cannot be determined in a direct manner as it is dependent upon drag and friction forces that oppose buoyant forces acting on the rising volume of gaseous fuel. Atmospheric turbulence as well as shape and size of the rising volume of gas can affect the terminal velocity of the buoyant gas. Buoyant forces are related to the difference in air and fuel densities; therefore, cold, dense fuel gases produced by cryogenic fuel spills will rise more slowly than NTP fuel gases. The buoyant velocities recorded in table 1 were estimated from fundamental principles of dynamics and with the aid of empirical data [50,51]; it was assumed that the radii of the buoyant masses of NTP fuel gas varied from 3 cm to 1.5 m.

Maximum experimental safe gap (MESG) in NTP air: The maximum permissible clearance, between flat parallel steel surfaces, that prevents the propagation of dangerous flames or sparks through the gap. The MESG is measured by igniting a combustible fuel-air mixture inside of a test enclosure and observing a similar combustible mixture surrounding the enclosure to detect its ignition. The MESG is the largest gap size that does not permit ignition outside of the test enclosure. The MESG is dependent upon the test gap flange width, composition of combustible mixtures inside of and surrounding the test enclosure, the initial pressure and temperature of the mixture, location of the ignition source and enclosure geometry [31,52]. The hydrogen and gasoline MESG data recorded in table 1 were obtained using parallel steel flanges that were 1.905 cm wide and 10.16 cm long. The methane MESG data were obtained using an 8 liter chamber with equatorial flanges that were 2.54 cm wide. MESG data are of vital importance to the design and manufacture of explosion-proof equipment.

Quenching gap in NTP air: The spark gap between two flat parallel plate electrodes at which ignition of combustible fuel-air mixtures is suppressed, i.e., smaller gaps have the effect of totally suppressing spark ignition [16,33]. Other types of electrode geometries are also used in laboratory measurements [16,33] of quenching distance. The experimental data [16,33,53] are dependent upon the temperature, pressure and composition of the combustible gas mixture and electrode configuration. Experiments have shown that the quenching distance is relatively independent of the mode of ignition. The quenching distance is sometimes determined by measuring the smallest diameter tube through which flame will propagate in a flammable NTP mixture of fuel-air that fills the tube. Similarly, quenching distances can be obtained by measuring the gap required to quench propagation of flame between flanges or plates that form a narrow channel and are filled with a flammable fuel-air mixture at NTP. In the latter two experiments the explosive gas mixture is ignited at one end of a long tube or channel by a pilot flame.

Detonation induction distance in NTP air: The distance required for a deflagration to transit to a detonation in a detonable fuel-air mixture. This distance is usually experimentally determined in a long cylindrical tube with a spark or hot wire ignitor on one end of the tube. The tube is instrumented along its length to sense the velocity of the flame front as it propagates through the detonable mixture of gases. The distance from the ignitor to the axial position in the tube where the flame front first attains the detonation velocity is reported as the induction distance. This distance is dependent upon the combustible mixture constituents, the pressure, temperature and concentration of the gaseous mixture, the enclosure geometry [54] and strength of the ignition source [18]. A deflagration is a low order explosion resulting from subsonic flame speed, relative to the unburned gas. It is conventionally defined as a propagating reaction in which the energy transfer from the reaction zone to the unreacted zone is achieved through ordinary rate-limiting transport processes such as heat and mass transfer. A detonation is a high order explosion resulting from supersonic flame speed, relative to the unburned gas. It may be defined as a propagating reaction in which energy is transferred from the reaction zone to the unreacted zone on a reactive shock wave.

Limiting oxygen index: The minimum concentration of oxygen that will support flame propagation in an unknown mixture of fuel, air and nitrogen, e.g., no mixture of hydrogen, air and nitrogen at NTP conditions will propagate flame if the mixture contains less than 5.0 volume percent oxygen [14]. Use of diluents other than nitrogen results in different values for the limiting oxygen index of each fuel [14,34].

Vaporization rates of liquid pools without burning: The rate at which the liquid level decreases after a pool of liquid fuel has been formed by spilling fuel onto a warm surface such as sand or soil. These evaporation rates are measured after subsidence of the violent boiling that accompanies the initial liquid spill. Vaporization rates of the cryogenic fuels can be expected to vary widely with the conductivity and heat capacity of the soil or other material confining the spilled liquid fuel. In the case of gasoline, vaporization rates will vary with the volatility of constituents (blend), age, fuel temperature, ground surface texture and temperature, etc. Wind velocity influences the vaporization rate of all fuels considered herein.

Burning rates of spilled liquid pools: The rate at which the liquid level decreases after a pool of liquid fuel has been formed by spilling fuel onto a warm surface and the resultant vapor-air mixture has been ignited. Again, these burning rates are measured after the initial-spill violent boiling has subsided and the vapor is mixing and burning in air above the pool of spilled fuel. These burning rates may also be obtained by adding the vaporization rate (without burning) and the liquid level regression rate attributable to the burning of vapors in the open air over liquid fuels that are contained in open-mouthed insulated vessels. Steady state burning rates increase with liquid pool diameter while vaporization rates continuously decrease with time, irrespective of pool size. Burning rates can be expected to vary with pool diameter and wind velocity [25,26,118].

Flash point: The minimum liquid fuel temperature required to provide a fuel vapor-air mixture above the surface of the liquid that will propagate a flame. The liquid fuel is heated in an open or closed cup [55] until the vaporization rate is sufficient to form a mixture of fuel vapor and air that is within the flammable limits near the liquid surface. Ignition is accomplished with an open flame near the surface of the liquid.

Toxicity: The quality or condition of being harmful, destructive, deadly or poisonous to living organisms. The toxicity of a fuel can only be described in terms of its effects on living organisms and specifically in terms of its effects on humans [56]. Toxicity ratings [56] are (of necessity) relative values and threshold limit values for exposure to toxic substances are published annually -- see reference [57].

Energy of explosion: The theoretical maximum energy available from a chemical explosion. This maximum energy release is determined by computing the isothermal decrease in the Helmholtz free-energy function. Explosive energies listed in table 1 are expressed in terms of equivalent quantities of TNT (symmetrical trinitrotoluene) and may be converted directly to energy units by multiplying by 4602 J/(g TNT).

Table 1. Properties of Hydrogen*, Methane and Gasoline**.

Property	Hydrogen	Methane	Gasoline
Molecular weight	2.016 [1]	16.043 [5]	~107.0 [7]
Triple point pressure, atm	0.0695 [1]	0.1159 [5]	---
Triple point temperature, K	13.803 [1]	90.680 [5]	180 to 220[1] [7]
Normal boiling point (NBP) temperature, K	20.268 [1]	111.632 [1]	310 to 478 [7,8]
Critical pressure, atm	12.759 [1]	45.387 [5]	24.5 to 27 [7]
Critical temperature, K	32.976 [1]	190.56 [5]	540 to 569 [7]
Density at critical point, g/cm^3	0.0314 [1]	0.1604 [5]	0.23 [9]
Density of liquid at triple point, g/cm^3	0.0770 [1]	0.4516 [5]	---
Density of solid at triple point, g/cm^3	0.0865 [1]	0.4872 [1]	---
Density of vapor at triple point, g/m^3	125.597 [1]	251.53 [5]	---
Density of liquid at NBP, g/cm^3	0.0708 [1]	0.4226 [1]	~.70[2] [7]
Density of vapor at NBP, g/cm^3	0.00134 [1]	0.00182 [1]	~0.0045[2] [9]
Density of gas at NTP, g/m^3	83.764 [1]	651.19 [1]	~4400 [9]
Density ratio: NBP liquid-to-NTP gas	845 [1]	649 [1]	156[3] [7,9]
Heat of fusion, J/g	58.23 [1]	58.47 [1]	161 [12]
Heat of vaporization, J/g	445.59 [1]	509.88 [1]	309 [7,9]
Heat of sublimation, J/g	507.39 [1]	602.44 [1]	---
Heat of combustion (low), kJ/g	119.93 [2]	50.02 [2]	44.5 [2,4,9]
Heat of combustion (high), kJ/g	141.86 [2]	55.53 [2]	48 [2,4,9]
Specific heat (C_p) of NTP gas, J/g-K	14.89 [1]	2.22 [1]	1.62[2] [9]
Specific heat (C_p) of NBP liquid, J/g-K	9.69 [1]	3.50 [1]	2.20[2] [9]
Specific heat ratio (C_p/C_v) of NTP gas	1.383 [1]	1.308 [1]	1.05[2] [7]
Specific heat ratio (C_p/C_v) of NBP liquid	1.668 [1]	1.676 [1]	---
Viscosity of NTP gas, g/cm-s	0.0000875 [1]	0.000110 [1]	0.000052 [9]
Viscosity of NBP liquid, g/cm-s	0.000133 [1]	0.001130 [1]	0.002 [9]
Thermal conductivity of NTP gas, mW/cm-K	1.897 [1]	0.330 [1]	0.112 [9]
Thermal conductivity of NBP liquid, mW/cm-K	1.00 [1]	1.86 [1]	1.31 [9]
Surface tension of NBP liquid, N/m	0.00193 [1]	0.01294 [1]	0.0122 [9]
Dielectric constant of NTP gas	1.00026 [3]	1.00079 [1]	1.0035[3] [10]
Dielectric constant of NBP liquid	1.233 [3]	1.6227 [1]	1.93[4] [9]
Index of refraction of NTP gas	1.00012 [1]	1.0004 [1]	1.0017[3] [10]
Index of refraction of NBP liquid	1.110	1.2739 [1]	1.39[4] [9]
Adiabatic sound velocity in NTP gas, m/s	1294 [1]	448 [1]	154
Adiabatic sound velocity in NBP liquid, m/s	1093 [1]	1331 [1]	1155[5] [12]
Compressibility factor (Z) in NTP gas	1.0006 [1]	1.0243 [1]	1.0069
Compressibility factor (Z) in NBP liquid	0.01712 [1]	0.004145 [1]	0.00643[2]
Gas constant (R), cm^3-atm/g-K	40.7037 [1]	5.11477 [1]	0.77
Isothermal bulk modulus (a) of NBP liquid, MN/m^2	50.13 [3]	436.16 [6]	763[6] [11]
Volume expansivity (B) of NBP liquid, K^{-1}	0.01658 [3]	0.00346 [6]	0.0012[2] [9]

Table 1. Properties of Hydrogen*, Methane and Gasoline** (continued).

Property	Hydrogen	Methane	Gasoline
Limits of flammability in air, vol. %	4.0 to 75.0 [13,14]	5.3 to 15.0 [13,14]	1.0 to 7.6 [8,18]
Limits of detonability in air, vol. %	18.3 to 59.0 [15]	6.3 to 13.5 [19]	1.1 to 3.3 [20]
Stoichiometric composition in air, vol. %	29.53	9.48	1.76
Minimum energy for ignition in air, mJ	0.02 [16]	0.29 [16]	0.24 [16,21]
Autoignition temperature, K	858 [17]	813 [8]	501 to 744 [8,18]
Hot air-jet ignition temperature, K	943 [22]	1493 [22]	1313[7] [22]
Flame temperature in air, K	2318 [23]	2148 [23]	2470 [24]
Percentage of thermal energy radiated from flame to surroundings, %	17 to 25 [25,26]	23 to 33 [25,26]	30 to 42 [25,26]
Burning velocity in NTP air, cm/s	265 to 325 [27,28]	37 to 45 [18,19]	37 to 43 [18,24]
Detonation velocity in NTP air, km/s	1.48 to 2.15 [29,35]	1.39 to 1.84 [19]	1.4 to 1.7[8] [30]
Diffusion coefficient in NTP air, cm^2/s	0.61	0.16	0.05
Diffusion velocity in NTP air, cm/s	$\leq$2.00	$\leq$0.51	$\leq$0.17
Buoyant velocity in NTP air, m/s	1.2 to 9	0.8 to 6	nonbuoyant
Maximum experimental safe gap in NTP air, cm	0.088 [31]	0.12 [32]	0.07 [31]
Quenching gap in NTP air, cm	0.064 [16,33]	0.203 [16,33]	0.2 [33]
Detonation induction distance in NTP air	L/D$\approx$100 [35,36]	----	----
Limiting oxygen index, vol. %	5.0 [34]	12.1 [34]	11.6[9] [34]
Vaporization rates (steady state) of liquid pools without burning, cm/min	2.5 to 5.0 [26]	0.05 to 0.5 [26]	0.005 to 0.02
Burning rates of spilled liquid pools, cm/min	3.0 to 6.6 [25,26]	0.3 to 1.2 [25,26]	0.2 to 0.9 [25,26
Flash point, K	gaseous	gaseous	~230 [8]
Toxicity	nontoxic [37] (asphyxiant)	nontoxic [38] (asphyxiant)	slight [39] (asphyxiant)
Energy[10] of explosion, (g TNT)/(g fuel)	~24	~11	~10
Energy[10] of explosion, (g TNT)/(cm^3 NBP liquid fuel)	1.71	4.56	7.04
Energy[10] of explosion, (kg TNT)/(m^3 NTP gaseous fuel)	2.02	7.03	44.22

NBP = Normal boiling point.

NTP = 1 atm and 20 C (293.15 K).

* Thermophysical properties listed are those of parahydrogen.

** Property values are the arithmetic average of normal heptane and octane in those cases where "gasoline" values could not be found (unless otherwise noted).

[1] Freezing temperatures for gasoline @ 1 atm.

[2] @ 1 atm and 15.5 C.

[3] Density ratio @ 1 atm and 15.5 C.

[4] @ 1 atm and 20 C.

[5] @ 1 atm and 100 C.

[6] @ 1 atm and 25 C.

[7] Based on the properties of butane.

[8] Based on the properties of n-pentane and benzene.

[9] Average value for a mixture of methane, ethane, propane, benzene, butane and higher hydrocarbons.

[10] Theoretical explosive yields.

3.0 FIRE HAZARDS

By considering fire hazards, fire damage, explosive hazards and explosive damage attributable to each fuel we can expose the relative safety merits of each fuel for potential fuel applications. By definition, a hazard identifies a pending risk or peril. Of course, the existence of a hazard does not assure the occurrence of a fire or explosion or that damage will be sustained if a fire or explosion does occur. Thus, the safety hazards and damage potential of candidate fuels must be compared to provide the requisite safety criteria for fuel selection. The degree or extent of hazard and damage potential are frequently difficult to express in indisputable scientific terms. Consequently, scientific data are usually tempered with experienced judgment to formulate safety evaluations for different fuels. Hence, the perpetual controversy over the relative safety of fuels.

By referring to the combustion properties listed in table 1 we can systematically step through the fire hazards of hydrogen, methane and gasoline. First we will consider the accidental or inadvertent means of obtaining flammable mixtures of fuel in air. Usually, such mixtures are the result of fuel leakage or spillage which may be attributable to mechanical failure of equipment, material failure, erosion, physical abuse, improper maintenance, collision, etc.

The rate at which the fuel vapors mix with air is indicated by their diffusion velocities and their buoyant velocities. The buoyant effect is dominant for hydrogen and methane and from the data listed in table 1 it is apparent that hydrogen can be expected to mix with air more rapidly than methane or gasoline -- the latter is obviously the slowest mixing fuel of the three fuels considered. In the event of a fuel spill, one could expect hydrogen to form combustible mixtures more rapidly than methane because hydrogen has a higher buoyant velocity and a slightly lower flammable limit. Again, gasoline would be orders of magnitude slower than hydrogen or methane in forming combustible mixtures in air. In some fuel applications these relative mixing times may be important while in others they are meaningless, e.g., an instantaneous fire hazard exists for the impact rupture of an auto fuel tank irrespective of the type of fuel carried.

Because of their higher buoyant velocities, hydrogen and methane can also be expected to disperse more rapidly than gasoline and thus shorten the duration of the flammable hazard. Even though the upper flammable limit (UFL) of hydrogen is much higher than that of methane the higher buoyant velocity of hydrogen permits it to disperse to concentrations below the lower flammable limit (LFL) more rapidly [58] than methane. Thus, one could expect a fire hazard to exist most readily with hydrogen, methane and gasoline respectively, and to persist in the inverse order.

We must exercise some caution in analyzing fuel mixing and dispersion rates by comparing relative buoyant and diffusion velocities of the NTP fuel gases. In large cryogenic liquid fuel spills, the vaporization of liquid and warming of the vapor can cool large masses of air. In addition, NBP hydrogen vapor density approaches that of NTP air while NBP methane vapor density is greater than the density of NTP air. Consequently, for some finite period of time these cold vapor-air mixtures are nonbuoyant and may extend to appreciable distances from the spill. Therefore, both the range and duration of the fire hazard may be extended somewhat when cryogenic liquid fuels are spilled. More definitive experimental data are needed in this area to supplement existing knowledge [25,26,96]. Some experimental data and analyses for LNG spills on land are available [118]; these data treat the dispersion and drift characteristics of vapor clouds that form over LNG spills.

The low value of limiting oxygen index reflects the high value of the UFL for hydrogen-air mixtures. The wide flammability limits of hydrogen are of practical significance only when fuel leakage into enclosed spaces is a major concern. In this case the flammable limits of hydrogen are sufficiently wide to enhance the probability of combustion from a random ignition source. This flammability characteristic should not preclude the use of hydrogen because the LFL is the vital one in most applications. The LFL is important because ignition sources are nearly always present when a leaking fuel first reaches combustible proportions in air.

The rate of vapor generation and burning over spilled liquid pools is of interest for the various fuels. As indicated in table 1 the volumetric vaporization rates and burning rates are highest for hydrogen, methane, and gasoline, respectively. Consequently, for a

given liquid spillage volume, gasoline fires will last the longest and hydrogen fires the shortest while all of the fuels burn at about the same flame temperature. The thermal energy radiated from these pool-fed fires may be computed by multiplying the appropriate (burning rate) X (NBP liquid density) X (high heat of combustion) X (percentage of thermal energy radiated from the flame to its surroundings). The radiated thermal energy should not exceed 276 W/cm^2 of pool liquid-vapor surface area for hydrogen, 155 W/cm^2 for methane or 212 W/cm^2 for gasoline. Then, the scene of a hydrogen fire may be hotter than that of a hydrocarbon fire, but the hydrocarbon fires will last five to ten times longer than hydrogen fires (for equivalent fuel spillage volumes). Additional data for LNG vaporization and burning rates and for radiant heat flux emitted from fires over LNG pools are presented in reference [118].

Another matter of concern in evaluating fire hazards is the rate of leakage flow of liquids or gases through leakage paths of varying geometries, e.g., leakage through cracked welds, improperly mated flanges, threaded fittings, damaged seals, etc. Previous work [59] has shown that volumetric leakage rates are inversely proportional to the square root of the density, or inversely proportional to the absolute viscosity of the leaking fluid. Using the data given in table 1 we can estimate the relative volumetric leakage rates of the NBP liquid fuels and of the gases at NTP. Under these conditions the volumetric leakage flow of liquid hydrogen will be 2.4 to 8.5 (viscous flow) times as large as liquid methane leakage; volumetric leakage flow of liquid hydrogen will be 3.1 to 15 (viscous flow) times as large as liquid gasoline leakage; volumetric leakage flow of hydrogen gas will be 1.3 (viscous flow) to 2.8 times as large as gaseous methane leakage; volumetric leakage flow of hydrogen gas will be 0.6 (viscous flow) to 7.3 times as large as gasoline vapor leakage. Since care is usually taken to minimize fuel leaks the viscous leakage flows are considered to have the greatest practical significance. Thus, we conclude that liquid hydrogen is much more difficult to contain than liquid methane or liquid gasoline and that NTP gasoline vapors are more difficult to contain than either NTP hydrogen or NTP methane. In spite of these unfavorable leakage characteristics, industry has proven that both liquid and gaseous hydrogen can be safely and easily contained.

Techniques for detection of hydrogen leakage are effectively summarized by two documents [60,61] and general procedures for leak testing are detailed in the handbook by Marr [60].

The minimum spark energy required for ignition of hydrogen in air is about an order of magnitude less than that for methane or gasoline; however, the ignition energy for all three fuels is sufficiently low that ignition is relatively assured in the presence of thermal (weak) ignition sources, e.g., sparks, matches, hot surfaces or open flames. Even a weak spark due to the discharge of static electricity from a human body may be sufficient to ignite any of these fuels in air -- 10 mJ sparks may be produced in such electrostatic discharges [62].

Although hydrogen has a higher autoignition temperature than methane or gasoline, its low ignition energy characteristic makes it more readily ignitable than either of the hydrocarbon fuels. The hot air-jet ignition temperature is highest for methane and lowest for hydrogen; therefore, hydrogen is easiest to ignite by jets of hot combustion products emitted from an adjacent enclosure. The flash point is meaningless for the cryogenic fuels, hydrogen and methane, within the temperature range of interest because these fuels will flash at all temperatures above their normal boiling points. The boiling points of the cryogenic liquid fuels are so low that these fuels are considered to behave like gases. The flash point of gasoline is also well below room temperature; therefore, all three fuels must be considered volatile and will generate sufficient vapor to create a fire hazard at earth surface temperatures. Then, all three fuels are relatively easy to ignite. Hydrogen is most susceptible while methane and gasoline appear to be equally susceptible to ignition.

The burning velocity is a fundamental property of a combustible gas mixture and should not be confused with the flame speed [63]. The burning velocity influences the severity of the explosion and along with quenching gap is important in the design of flame arresters [63]. Higher burning velocities indicate a greater tendency for the combustible gas mixture to support the transition from deflagration to detonation in long tunnels or pipes. The instantaneous pressure rise due to the ignition of a fuel-air mixture contained in a spherical vessel is proportional to the cube of the burning velocity [64]. In general, faster-burning gases have smaller quenching gaps and flame arresters for faster-burning gases must have smaller apertures [63]. The quenching gap is the passage gap dimension required to prevent

propagation of an open flame through a flammable fuel-air mixture that fills the passage and it is clearly distinguishable from the MESG. The latter is the maximum permissible clearance between flanges to assure that an explosion does not propagate from within an enclosure to a flammable mixture surrounding the enclosure. Because of the high explosion pressures the MESG is always smaller than the quenching distance.

Available data [65] indicate that the pressure rise ratios for adiabatic combustion of stoichiometric mixtures of hydrogen-air and methane-air in closed vessels are nearly identical. Similar data [31] produced pressure rise ratios for hydrogen-air that were 20 to 40 percent higher than those for gasoline-air. In long tubes or tunnels, hydrogen-air mixtures will transit to detonation more rapidly than methane-air or gasoline-air mixtures; therefore, overpressure hazards in confined spaces are enhanced in hydrogen systems. Thus, the high burning velocity of hydrogen is an indication of its high explosive potential and of the difficulty of confining or arresting hydrogen flames and explosions. Industrial equipment is currently available to safely confine hydrogen explosions but pipeline flame arresters, though successful in certain hydrogen-air combustion applications, are not yet considered reliable [87].

4.0 FIRE DAMAGE

Some of the combustion characteristics discussed in the previous section are also applicable to comparisons of fire damage by the different fuels. Similarly, many of these characteristics are applicable to explosive hazard and explosive damage criteria as will be revealed in subsequent sections of this paper. In the previous section we discussed the risk or likelihood of having a fire. In this section we examine the damage potential of a fire.

The main fire damage parameters are thermal radiation, flame engulfment (fireball), smoke inhalation, fire detection and extinguishment. Explosion overpressure, impulse and shrapnel damage are related parameters that are reserved for detailed discussion under the section entitled explosive damage. Thermal radiation characteristics of the three fuels under consideration have already been discussed so we turn our attention to fireballs.

Fireball damage is the direct result of combustion of materials initiated through contact or engulfment by flames that are consuming fuels. A fireball may result from the ignition of fuel-air mixtures or from the explosion of solid or chemical explosives. The explosion fireball is short-lived but flames will persist until all of the fuel is consumed in fuel-air fires. Ignition of fuel-air mixtures above pools of spilled liquid fuels produces flames with dimensions that vary with the volume of spilled liquid, rate of spillage, nature of spillage containment surface, wind velocity, location of ignition source and time delay before ignition. A simple mathematical expression [66] seems to adequately predict the maximum equivalent spherical radii of fireballs for a wide variety of explosives including hydrogen-air and rocket bipropellants. The diameter of the fireball is given by

$$D \approx 7.93\ W_f^{1/3}\ ,$$

where D = diameter in meters and W_f = weight of fuel in kilograms. The fireball duration may be estimated from

$$t \approx 0.47\ W_f^{1/3},$$

where t is in seconds and W_f is the weight of fuel in kilograms. See reference [66] for limitations of these approximations. Various fireball and fire radiation criteria are summarized along with overpressure criteria on figures 1 and 2. The development and discussion of these figures has been treated elsewhere [66] and will not be repeated here. Although these figures were developed specifically for hydrogen they are believed to provide conservative safety criteria for methane and gasoline. It must be emphasized that these figures are based upon potential fire and explosion hazards in unbarricaded storage and experimental areas and are not indicative of industrial storage standards for fuels. Industrial hydrogen storage standards are much less stringent -- see figure 3.

Smoke inhalation is one of the major causes of injury and death in any fire. When fuel-air fires cause buildings and other combustible materials to burn, smoke inhalation is of concern for hydrogen, methane and gasoline. When fuels burn in the open air only gasoline can cause severe smoke inhalation damage as both hydrogen and methane are clean burning

fuels. Inhalation of the combustion products from hydrogen-air or methane-air fires is considered less serious because both of these fuels are buoyant and require a large influx of fresh air to sustain the fire. Also, the combustion products of hydrogen-air fires (mainly nitrogen and water vapor) and methane-air fires (mainly nitrogen, carbon dioxide and water vapor) are not foreign to the lungs as are the sooty combustion products of gasoline-air fires. Of course, the lungs can be seared by breathing hot combustion gases produced by burning any of these fuels. Breathing any of these fuels or their combustion products in sufficiently rich concentrations can also cause asphyxiation. The physiological effects of breathing aerosols, toxic gases (such as CO and CO_2), hot gases and oxygen-deficient gases are reviewed by Custer and Bright [67].

Current fire detection technology is summarized in a recent document [67] and hydrogen fire detection is reviewed in an older publication [61]. Hydrogen flames are nearly invisible in daylight but their visibility is improved by the presence of moisture and/or impurities in the air. Hydrogen fires are readily visible in the dark or in subdued light and large hydrogen fires are quite detectable in daylight because convective "heat ripples" are visible in the air at near-range distances and thermal radiation heats the skin. Small hydrogen fires are more difficult to detect and require that certain precautions be taken to avoid personnel and equipment damage. Methane flames, though clean-burning, are yellowish in color and quite visible in daylight. Gasoline flames are similar to those of methane but are mixed with large volumes of soot and smoke so that fire detection is obvious.

Two types of sensors, thermal and optical, are used to detect hydrogen fires. Thermal sensors are the conventional type and are fully discussed by Custer and Bright [67]. These conventional sensors (including smoke and ionization detectors), coupled with flame visibility, are adequate for detection of methane or gasoline fires and not quite adequate for detection of all hydrogen fires. The aerospace industry has advanced the use of optical sensors for detecting hydrogen fires in bright-field environments. The most common optical sensors detect ultraviolet or infrared radiation and several detection schemes exist [61, 67]. Closed-circuit infrared and ultraviolet television sets, equipped with appropriate filters, have been successfully used to detect hydrogen fires on rocket engine test stands [61]. Intumescent paints have also been used to detect hydrogen fires. These paints char and swell at low temperature (~200°C) and emit pungent gases. Hydrogen fires are obviously more difficult to detect than methane or gasoline fires; however, the availability of modern detection equipment makes it possible to quickly and reliably detect the flames of all three fuels.

A brief review of fire extinguishment methods and recommended fire extinguishing procedures for various combustible materials has been published by the NFPA [8]. Class B extinguishing agents [8] are generally suited for gasoline fires and water deluge, or water spray, are usually useful in fighting gasoline, methane or hydrogen fires. The water is used to cool and protect adjacent exposed combustibles and may not extinguish the fire unless it is used in a prescribed manner by skilled personnel. Water may be particularly ineffective in extinguishing liquid gasoline fires as the gasoline is less dense than water and will float on top of the water and continue to burn.

It is sometimes advisable to permit hydrogen and methane fires to burn until gas-flow is stopped or liquid-spills are consumed because of the potential explosive hazard created by extinguishing such flames. If the fuel source is neither depleted nor shut off, an explosive fuel-air mixture may be formed with far greater damage potential (if ignited) than the original fire. In those instances where extinguishment is judged imprudent, a water deluge may be used to cool surrounding combustibles and control fire damage.

Recent experiments [118] have evaluated the effectiveness of commercially available dry chemical agents and high-expansion foams in controlling and extinguishing LNG pool fires. These experimental results show that dry chemicals can be used to extinguish LNG fires and foams applied to the pool surface reduce the radiant heat flux to surroundings while reducing vapor evolution. Thus, fire control and fire extinguishment methods and equipment are commercially available to combat LNG fires.

It is anticipated that these same fire-fighting procedures would be effective in controlling liquid hydrogen fires but no such data exist. Inert gas-flooding and CO_2 extinguishers have been successfully used to extinguish gaseous hydrogen fires.

Thus, we may conclude that: 1) water deluge or water spray is useful in fighting hydrogen, methane or gasoline fires, 2) gasoline or methane (LNG) fires may be controlled or extinguished using commercial dry chemical or high-expansion foam agents and 3) the effectiveness of dry chemicals or foams in controlling or extinguishing liquid hydrogen fires has not been evaluated.

5.0 EXPLOSIVE HAZARD

The ignition of a combustible mixture of fuel-air can result in a fire or an explosion. An explosion is always accompanied by a fireball and a pressure wave (overpressure). The fireball may ignite surrounding combustibles or fuel released by the explosion so that a fire may follow an explosion. If the fuel-air mixture is partially or totally confined the explosion may propel fragments of the enclosure material at high velocities over great distances. By its nature an explosion hazard constitutes fire, overpressure, impulse and shrapnel hazards. The extent of overpressure, impulse (overpressure-force multiplied by the time interval of explosive overpressure) and shrapnel hazards is dependent upon the severity of the explosion. Detonations cause more damage than deflagrations.

The same combustion parameters that influence fire hazards also influence the explosive hazards associated with each fuel; therefore the discussion on fire hazards, section 3.0, is equally applicable to this section on explosive hazards. Two of the combustion properties reviewed in section 3.0, MESC and hot air-jet ignition temperature, are vitally important to the containment of an explosion and to prevent propagation of the explosion to explosive mixtures of fuel-air surrounding the enclosure. The containment vessel must be sufficiently strong to withstand the explosion pressure without emitting jets of combustion products that are larger or hotter than those specified by the 'hot air-jet ignition temperature' and simultaneously the MESC must not be exceeded.

The limits of detonability are important in an evaluation of the explosive hazards of fuel-air mixtures. The wider these limits, the greater the probability of a high-order explosion with attendant high overpressures and severe shrapnel hazards -- detonation. The flammable limits define the fuel-air concentrations that will burn and low-order explosions may occur within these limits. Such explosions are called deflagrations and they result in lower overpressures and less shrapnel hazard than those associated with detonations. In order to have a fire or an explosion there must exist in combination an oxidant, a fuel, and an ignition source. The fuel and oxidizer are supplied and mixed by the release of fuel into the air. Hydrogen has by far the widest limits of detonability of the three fuels considered herein; therefore, it presents the greatest hazard to explosion damage. The explosive potential of all three fuels is discussed in the next section.

The ignition source may be a mechanical or electrostatic spark, flame, impact, heat by kinetic effects, friction, chemical reaction, etc. The strength of the ignition source influences whether a detonable mixture deflagrates or detonates. Weak (thermal) ignition sources initiate deflagrations in open and closed systems; however, a deflagration may develop into a detonation in a closed system due to the influence of the confining walls. Strong (shock-wave) ignition sources tend to initiate detonations in open or closed fuel-air systems. Matches, sparks, hot surfaces and open flames are considered to be thermal (weak) ignition sources while shock-wave (strong) ignition sources are blasting caps, bursting vessels, TNT, high voltage-capacity shorts (exploding wires), lightning, and other explosive charges.

The geometry of an enclosure has a strong effect on the transition from deflagration to detonation. Experimental data [111] indicate that a U-shaped enclosure plus the ground comprise sufficient confinement to support 'strong' explosions in detonable hydrogen-air mixtures that are ignited by thermal ignition sources. Geometrical changes in the confining walls that induce turbulence also enhance transition to detonation. The distance in a tunnel, pipeline, heating duct, or hallway that it takes for a reaction to progress from a deflagration to a detonation is related to the detonation induction distance. Hydrogen is a rapid burning fuel and the flame front has a tendency to accelerate in long enclosures. Consequently, detonation induction distances have been experimentally observed using hydrogen-air mixtures but no such data exist for the slower burning gasoline-air or methane-air mixtures. Transition to detonation occurs because compression of the unburned fuel-air mixture by deflagration increases the mixture temperature and pressure, both of which increase the burning velocity of the mixture. Recent experiments [87] indicate that it is difficult to design flashback arrestors that successfully disrupt deflagrative or detonative combustion in

hydrogen-rich mixtures of hydrogen, methane and air that are contained within or flowing in cylindrical pipelines. Burgess [20], Zabetakis [68], and Carhart [30] agree that methane-air and gasoline-air mixtures will transit from deflagration to detonation if the pipe is long enough and its diameter is large enough. Experimental apparatus used to determine detonation induction distance is usually small and consequently these data are yet to be determined for methane and gasoline. The largest detonation experiments conducted to date were performed by Kogarko [19] and Burgess et al. [71]. Kogarko used a 30.5 cm inside-diameter tube and Burgess et al. used a 61 cm diameter pipe and earthen tunnels with cross sectional areas ranging from 0.025 to 1.39 m^2. We have no assurance that gasoline-air or methane-air mixtures will not detonate from spark ignition in long tunnels or corridors; however, we can be quite sure that hydrogen-air mixtures will detonate under the proper circumstances ($L/D \gtrsim 100$).

We are belaboring the fuel detonation characteristics as they are believed to be of vital importance in future fuel applications. The tendency of hydrogen to detonate from spark ignition is perhaps the most significant deterrent to its widespread use. The pressure rise ratio of a detonation may easily be an order of magnitude higher than that of a deflagration -- see detailed discussion in reference [66]. The static pressure rise ratio will not exceed 8:1 in a confined deflagration [65] of hydrogen-air or methane-air. These explosion pressures are about 20 to 40 percent higher than those measured [31] for confined deflagrations of gasoline-air. Overpressures due to deflagrations in open air are usually considered negligible; however, open-air deflagrations can cause structural damage if they are close to the structure and are of sufficiently large volume, e.g. see reference [69].

Shrapnel hazards relate directly to explosion overpressures so that all of the foregoing arguments concerning overpressure apply to the evaluation of shrapnel hazards for the different fuels. Thus, we see that overpressure and shrapnel hazards associated with ordinary enclosures ($L/D \lesssim 30$) are about the same for hydrogen-air and methane-air and somewhat less stringent for gasoline-air. In long tunnels, etc. hydrogen is a greater explosion threat than either of the other two fuels because it has a greater tendency to transit to detonation. The wider flammable limits and detonable limits of hydrogen also tend to make hydrogen a greater explosive threat than methane or gasoline.

A number of preventive measures can be enacted to minimize the explosive threat of all three fuels and are particularly helpful for the rapid-dispersion fuels, hydrogen and methane. Roof vents and forced ventilation, where practical, are accepted methods of minimizing accumulations of gaseous fuel within enclosures. In some applications the quantity of fuel permitted within an enclosure can be restricted. Ignition sources can be minimized but seldom are they eliminated. Frangible (weak) walls can be used to relieve deflagration overpressures within enclosures -- rupture discs can be used to provide the same protection for pressure vessels. Frangible walls and discs are of little value in relieving detonation overpressures, although in some instances they may prevent or lessen the effects of detonation [66]. It appears that weak but pressure-wave reflecting walls will support transition from deflagration to detonation -- the use of elastic membranes (plastic curtains) may inhibit or prevent transition to detonation. Fuel storage tanks can be buried or storage areas can be diked (for fuel containment), barricaded and confining structures minimized. Major spillage can be avoided by using storage vessels constructed of ductile materials and by adherence to established safety procedures.

6.0 EXPLOSIVE DAMAGE

The elements of explosive damage, fireball, ensuing fires, overpressure and shrapnel, have already been discussed and only overpressure and shrapnel warrant additional attention.

Explosions that create overpressures and shrapnel may be rated in terms of the amount of energy that is released. This energy release may be evaluated directly in energy units such as kJ although it is commonly expressed as an equivalent quantity of TNT (symmetrical trinitrotoluene). The explosive strength of TNT is well-known and reproducible and it is a good standard for rating the explosive potential of various substances. Expressing explosive potential in terms of an equivalent mass of TNT is a good technique for evaluating damage potential at distances well-removed from the explosion; however, at distances inside or near the reaction zone, this procedure is less accurate because of the differences in shape and peak magnitude of the impulse diagrams for TNT and fuel-air mixtures. A fuel-air explosion may deliver a considerably lower overpressure, relative to TNT, over a longer time interval and thus have

less crushing effect on some structures, but a greater overturning moment. Although there is general dissatisfaction [85] with the TNT concept, it will continue to be used until non-ideal explosions can be characterized more definitively. To provide conservative results the TNT equivalent concept can be used [66] to evaluate impulse and overpressure effects at distances far from the explosion source, and to evaluate impulse effects in the near-combustion zone.

The theoretical TNT equivalent, of various fuels, can be determined [70] by using the decrease in Helmholtz free energy to compute the maximum energy available for explosive yield. Following this procedure we obtain the theoretical limiting values of explosive potential for hydrogen, methane and gasoline as recorded in table 1. Note that hydrogen is the most potent on a mass basis and the least potent on a volumetric basis. The explosive potential per kJ of stored heating value (based on the high heat of combustion) is 0.17 (g TNT)/kJ for hydrogen, 0.19 (g TNT)/kJ for methane and 0.21 (g TNT)/kJ for gasoline. Thus, for equivalent energy storage, hydrogen has the least theoretical explosive potential of the three fuels.

It must be emphasized that only a fraction of this theoretical explosive yield can be realized in an actual open-air mishap because it is virtually impossible to spill or release a large quantity of fuel and have all of it mixed in proper proportions with air prior to ignition. Experimental data and computations indicate that the fraction [66, 85, 96] of fuel within the combustible range at any time following a massive or continuous fuel spillage will be less than ten percent of the quantity spilled. Such explosive yield data are meager for all three fuels; however, the vapor or gas phase mixing limitations are equally applicable to all fuels. Hydrogen disperses much more rapidly than methane or gasoline, but it also has much wider flammable and detonable limits, etc. Thus, in the absence of more definitive experimental data it is impossible to accurately assess the probable explosive yield attributable to accidental release and ignition of hydrogen, methane or gasoline in air. The 'energy of explosion' values listed in table 1 should be considered theoretical maximums and yield factors of ten percent are considered reasonable for fuel-air explosions. Higher yield factors are possible in liquid bipropellant explosions [74].

A recent document [119] provides a new approach to the prediction of hazards and damage from explosions of lightweight bipropellant tanks and from bursting lightweight gas storage vessels. This approach evaluates explosive yield, overpressure, impulse and fragment characteristics directly and avoids the use of conventional TNT equivalency. This study also assesses the damage effects of blast and fragments on structures, facilities and humans, and appears to be the first attempt to provide more realistic explosion-damage predictions than can be obtained using TNT equivalents.

Overpressure damage is highly dependent upon the nature of the explosion. A confined and unvented deflagration [65] of hydrogen-air or methane-air will produce a static pressure rise ratio of less than 8:1. Explosion pressures [31] for confined deflagrations of gasoline-air are about 70 to 80 percent of those for hydrogen-air. Unconfined deflagration overpressures are usually less than 7 kPa; however, 3 to 4 kPa is sufficient side-on pressure to cause structural damage [69] to buildings and unconfined large volume gas-phase explosions can be destructive. Ordinary glass window panes fracture under pressures of 3 to 7 kPa, non-reinforced masonry walls fail at pressures below 55 kPa, and human eardrums rupture at pressures of approximately 35 kPa. Thus, it is apparent that confined deflagrations (even if relieved) can be very devastating -- up to 8 atmospheres (811 kPa) of explosion pressure -- and unconfined deflagrations can cause slight to moderate structural damage and injure people via fire, window-glass shrapnel, etc.

Detonations, whether confined or unconfined, can be expected to severely damage or totally destroy ordinary buildings in the near vicinity of the explosion. TNT pressure-distance data [74] can be used [71, 74] to estimate overpressures resulting from fuel-air detonations. The applicability of TNT equivalence to vapor or gas-cloud explosions is fully reviewed in references [74, 85]. Determination of blast yield for liquid-phase explosions was recently reviewed by Baker et al. [86,119]. The pressure accompanying detonation of any fuel is approximately double [72] that obtained by adiabatic combustion of a stoichiometric mixture of the fuel in air at constant volume. Consequently, we could expect static pressure rise ratios of ~15:1 for hydrogen-air or methane-air detonations and a ratio of ~12:1 for a gasoline-air detonation. Much higher reflected pressure rises can be attained if the explosion transits from deflagration to detonation because the deflagration compresses the unburned fuel-air mixture prior to transition to detonation, e.g., a reflected pressure rise ratio of 120:1 (8:1 X 15:1) could be achieved where a hydrogen or methane deflagration transits to detonation. Such transitions are more easily accomplished with hydrogen than with methane or gasoline.

The impulse created by explosion overpressures is of concern in evaluating explosion damage and in the design of barricades or structures to withstand explosions. Although the overpressure created by a gas-phase explosion is of lower peak magnitude and longer duration [73] than the overpressure due to an equivalent quantity of TNT, the extensive TNT data may be used [71, 73, 74] for design purposes. The fundamentals of dynamic blast loads and structural response to shock waves is treated elsewhere [28, 70, 71] as is the applicability [70, 71, 73, 74, 85, 86] of TNT explosive data to the design of structures to withstand gas-phase explosions.

Unbarricaded distances required for the protection of personnel in inhabited buildings that are exposed to shrapnel from TNT explosions are indicated by curve 6 on figure 1. These data also predict the maximum observed fragment distances for space vehicle explosions [74] and are more restrictive than the unbarricaded distances required for shrapnel protection of personnel on roadways -- see curve 2 on figure 1. Fletcher [75] has suggested that TNT shrapnel hazard data may be used to estimate propellant-explosion shrapnel hazards if the appropriate TNT equivalent is used. There is evidence [75] that large low-velocity fragments emitted from such 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 [75] for an equivalent quantity of TNT. An an interim measure the Department of Defense and NASA have adopted [74] the TNT shrapnel hazard data for propellant explosives at range launch pads and rocket engine test stands. These TNT data adequately predict [74] maximum fragment distances for known incidents involving propellant explosions. A thorough compilation, analysis and correlation of available fragmentation data for liquid propellant tank explosions was recently published by Baker et al. [86,119].

Design for shrapnel protection is difficult because it is necessary to estimate the size, mass, and velocity of fragments emitted from explosions of varied type, strength, and location. Some guidance on this subject may be found in references [75-86,119]. In brief, shrapnel shields made of materials with large modulus of elasticity (Young's) are the most effective; for example, steel is more shrapnel resistant than copper and copper is more resistant than aluminum, etc. The opposite is true for shrapnel projectiles themselves. A projectile having a given size and momentum will penetrate deeper if it has a lower density -- aluminum will penetrate deeper than copper and copper deeper than steel, etc. Recall that momentum is mass X velocity and a constant momentum and size require a higher velocity for the lower density projectiles -- see reference [82].

Figures 1 and 2 summarize much of the fire and explosive hazard data presented herein. These figures illustrate the variation in conservatism of various authorities that generate safety criteria. Obviously, when in doubt, the more conservative criteria should be used. The overpressure band on figure 1 corresponds to breakage of ordinary window glass (3.5 to 7 kPa) and the overpressure band on figure 2 relates to the estimated external pressure capability of liquid hydrogen storage dewars. The derivation and use of data shown on these figures (safe unbarricaded distances) are fully discussed in a summary document [66] treating the explosive hazards of hydrogen. Safe barricaded distances for TNT and fuel-air explosions may also be estimated from data made available in references [66, 74, 84]. A single series of documents [74] offer comprehensive treatment of overpressure, impulse, fireballs, shrapnel, barricades, structural response and physiological effects, as they relate to propellant explosions. The author feels that these documents are applicable to fuel-air explosions where the TNT equivalent is properly estimated. Care should be exercised when attempting to assess the damage potential of large-volume gas-phase explosions because line-of-sight from such explosions to vulnerable targets may pass over or around barricades that were erected to provide protection from concentrated explosives.

Figure 3 provides a ready comparison of industrially accepted fuel storage standards for hydrogen, LNG and gasoline. By comparing curves 1 and 4 on figure 3 with the data given on figures 1 and 2, we find that the industrial quantity-distance standards (figure 3) for hydrogen are less demanding than those suggested for experimental areas (figures 1 and 2). Also, by comparing curves 1, 2, 3 and curves 4, 5, 6 on figure 3 we observe that industrial storage standards are more restrictive for hydrogen, methane and gasoline, respectively.

Curve 3 on figure 3 represents the minimal distance for separation of two adjacent above-ground gasoline storage tanks. The distance [117] between such tanks shall not be less than three feet and not less than one-sixth the sum of the diameters of two adjacent tanks. When the diameter of one tank is less than one-half the diameter of the adjacent tank, the distance [117] between the two tanks shall not be less than one-half the diameter of the smaller tank.

Curves 6A and 6B on figure 3 represent the variation in quantity-distance standards for the protection of personnel in buildings adjacent to gasoline storage tanks. These curves bound standards [117] that vary with type of tank construction, fire control measures and protection for exposures, tank operating pressure and emergency venting equipment.

The distance [117] from any part of an underground tank (storing gasoline) to the nearest wall of any basement or pit shall be not less than one foot, and not less than three feet from inhabited buildings.

It is apparent that industrial storage standards are least restrictive for gasoline; however, the industrial storage standards for LNG and hydrogen fuels are not prohibitive and should not limit their use.

7.0 COMPARISON OF FUEL STORAGE METHODS

Hydrogen may be stored in the compressed gas, liquid or hydride forms. The relative costs [88] of storage in these various forms are dependent upon the quantity of hydrogen stored and upon desired storage pressure and storage duration.

Currently, the most promising alloys for metallic hydride storage contain titanium and magnesium. Storage data [89] for magnesium-nickel (Mg-Ni) and iron-titanium (Fe-Ti) hydrides are available and hydride storage system evaluations are in progress [90]. Safety standards for the production, processing, handling and storage of titanium and magnesium are well documented [91]; however, the safety hazards are much less certain for the candidate Fe-Ti and Mg-Ni ores in combination with stored hydrogen. A recent experimental evaluation [92] indicates that Fe-Ti hydride can be considered a safe method of storing hydrogen. Hydride storage appears attractive [90] for certain short-term storage applications but excessive weight, volume or cost restraints could limit the use of hydrides in transportation applications.

Hydrogen is routinely stored as a compressed gas in industry and this practice must be considered safe. It is usually stored in metal containers at pressures ranging from near-ambient to more than 20 MPa. It may also be possible to store compressed hydrogen in abandoned natural gas fields, caverns, aquifers, etc. Metal storage containers are normally constructed of a hydrogen-compatible ductile steel and are not generally susceptible to catastrophic failures. Such containers are normally equipped with pressure and thermally-induced pressure relief devices. Vessel fracture would most likely be accompanied by autoignition of the released hydrogen and air mixture with an ensuing conflagration lasting until the contents of the ruptured vessel are consumed. Considerable experimental data substantiate this statement -- see references [66, 93]. Adjacent metal storage vessels are relatively shrapnel and fire resistant and may be water-cooled or buried in sand for additional fire and blast resistance.

Hydrogen is also routinely stored as a liquid in industry and in university and government laboratories supporting the U.S. space exploration program. Again, catastrophic failures are not technically plausible as dewars are constructed of ductile metals and are diked to confine the liquid contents of the dewar in the event of spillage. The purpose of the dike is to reduce the liquid evaporation rate and to confine the potential conflagration to the vicinity of the defective dewar. The double wall construction of liquid storage dewars provides good protection against fire and shrapnel and additional fire resistance for adjacent storage dewars can be provided with a water deluge system. Liquid hydrogen storage dewars are usually built with carbon steel vacuum jackets and aluminum or stainless steel inner vessels. Liquid hydrogen has been safely stored in large metal dewars for nearly 20 years.

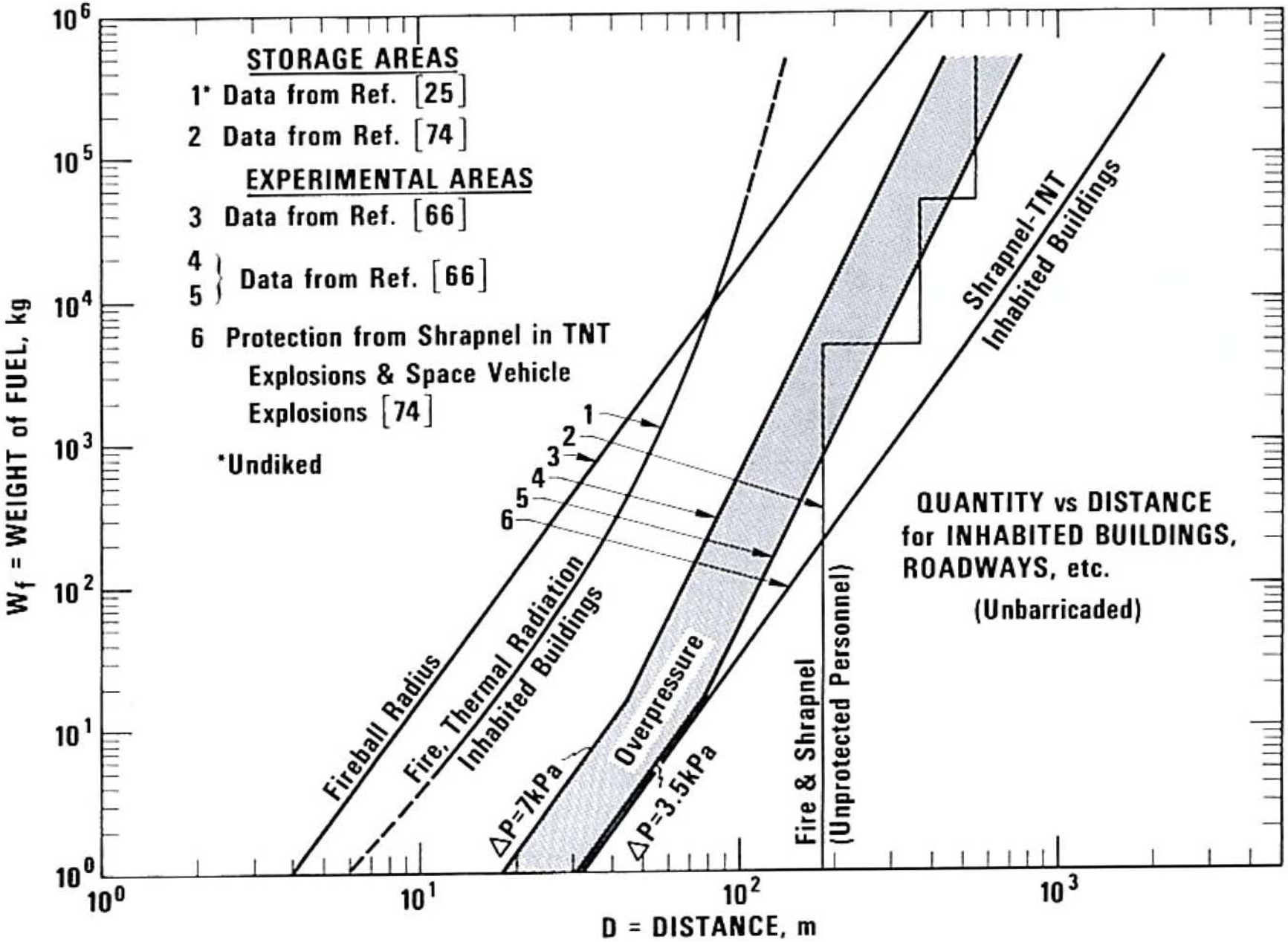

Figure 1. Quantity-distance relationships for the protection of personnel near liquid hydrogen storage and experimental areas (unbarricaded).

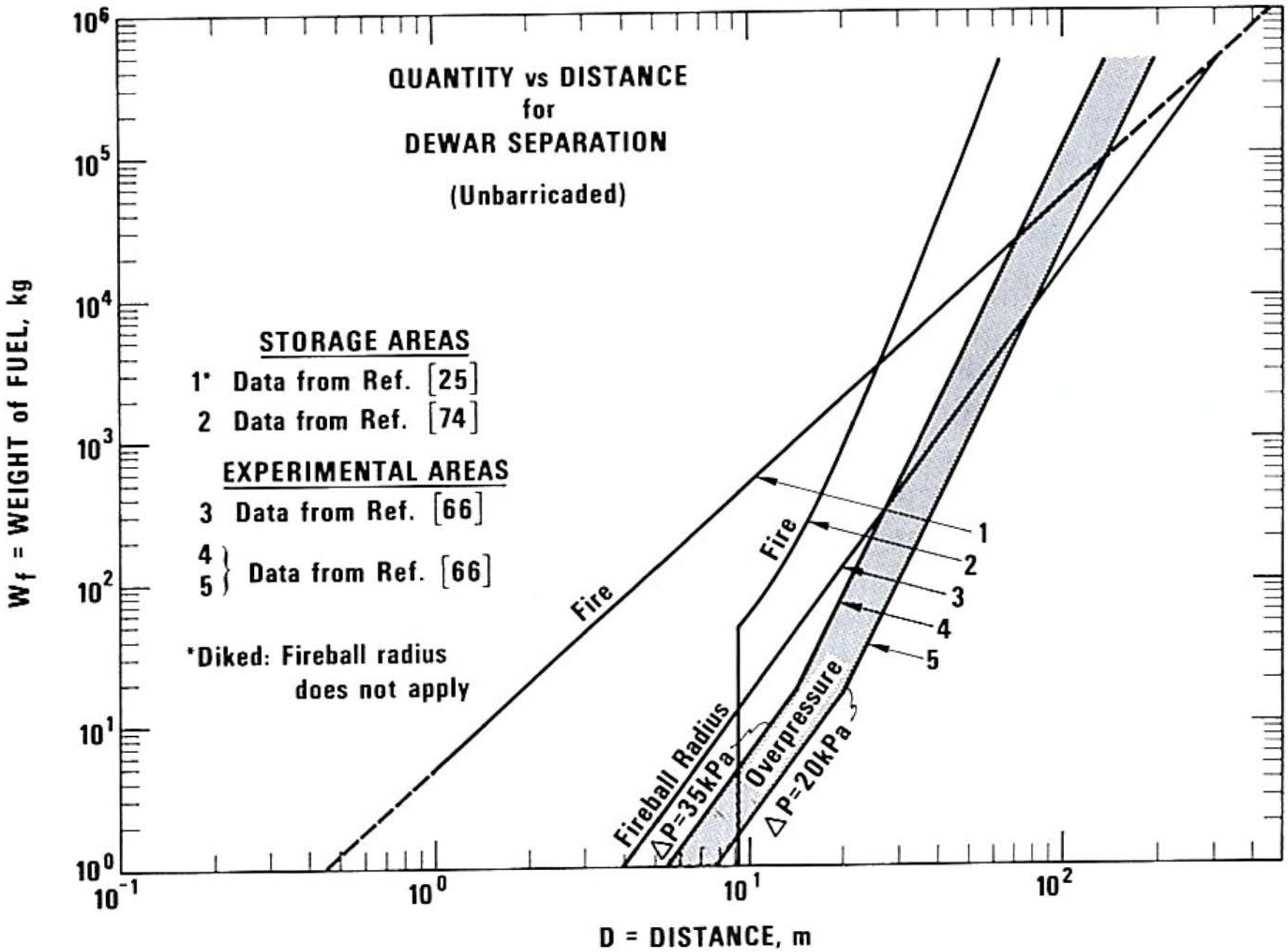

Figure 2. Quantity-distance relationships for liquid hydrogen dewar separation in storage and experimental areas (unbarricaded).

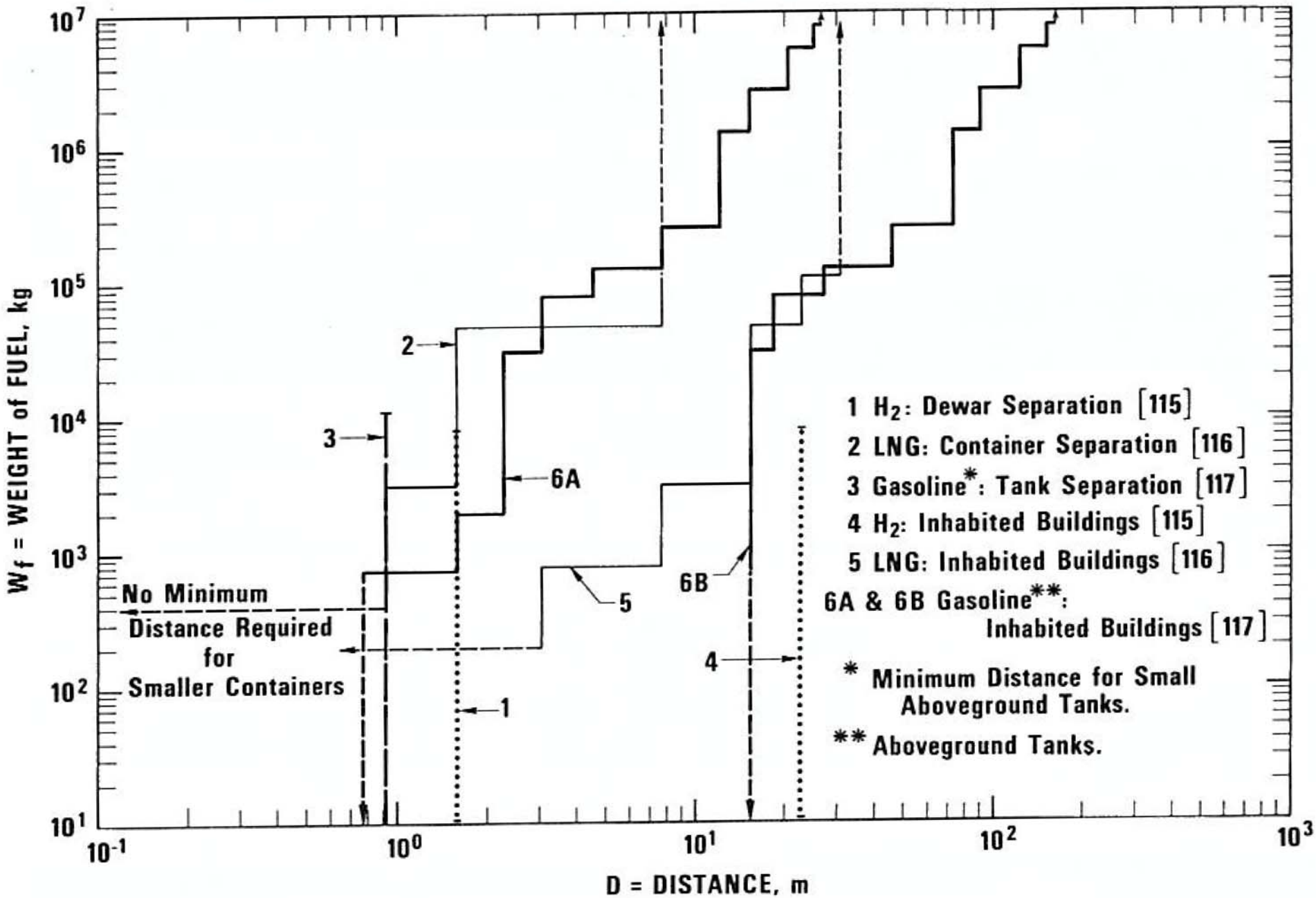

Figure 3. Industrial storage standards (quantity-distance) for hydrogen, liquefied natural gas (LNG) and gasoline.

Hydrogen has not been used extensively in commercial applications although it has been successfully piped cross-country as a compressed gas in a few locales. A demonstration project [90] is currently in progress to evaluate the feasibility of using hydrogen in electrical utility load-leveling operations. The electrical utility industry has also successfully used hydrogen gas to cool the rotor and stator coils in large turbine-generators for more than forty years. No significant hydrogen safety problems are foreseen in the commercial sector.

Hydrogen is a potential replacement fuel in the voracious transportation market. Conceptually, and technically, hydrogen can be used to fuel aircraft [98], ships [99, 100], trains [101], trucks and buses [102, 103] and automobiles [104, 105]; however, the economics, logistics and safety of supplying and distributing hydrogen to fuel these vehicles are as yet undetermined. Excluding a few demonstration projects with automobiles, trucks, buses and airplanes, we find that hydrogen is a relatively untried fuel in the transportation market. Hydrogen was tried briefly as an auto fuel in the mid-thirties [106, 107] and as an inflatant for balloons and dirigibles prior to the ill-fated Hindenberg fire of 1937. Considerable safety analysis is in order prior to the widespread use of hydrogen fuel in transportation -- particularly in highway vehicles where personnel exposure is maximum and fuel handling procedures are most difficult or impossible to enforce. Hydrogen is already the accepted fuel of the aerospace industry and is safely handled in large quantities. Preliminary safety analyses of hydrogen-fueled aircraft for military [108] and civilian [109] applications are currently in progress. Bowen [112] recently completed a review of some of the hazards associated with the use of hydrogen as a military fuel.

Hydrogen can also be used to supply residential fuel needs because appliances, furnaces, etc. can be made to operate on hydrogen gas. From a technical viewpoint this application can be readily satisfied, but from a safety viewpoint there are a number of significant concerns. The major concerns relate to the problems of gas leakage, detection and the potential severity of explosions of hydrogen-air mixtures in confined or partially-confined spaces. More experimental data and safety analyses are needed to fully resolve these questions and to determine the comparative risks of hydrogen and natural gas as residential fuels; however, hydrogen-enriched gases (coal gas, town gas, producer gas, etc.) have been successfully used [106, 110] in European countries to satisfy residential fuel needs during the last century. Thus, there also appears to be ample precedent for acceptably safe use of hydrogen in the residential sector.

9.0 SUMMARY

The safety aspects of any fuel are intimately related to the fuel application and to the postulated accident criteria. Thus, specific conclusions await hard comparisons of competing fuels in applications where credible accidents can be specified; however, generalized conclusions and judgments may be drawn from the comparative technical data and discussions presented herein.

A comprehensive list of thermophysical and combustion properties of hydrogen, methane and gasoline was compiled and presented in this paper. These data provide the bases for future safety analysis and for direct safety comparisons of hydrogen, methane and gasoline.

Liquid hydrogen is more difficult to contain than either liquid methane or liquid gasoline and NTP gasoline vapors are more difficult to contain than either NTP hydrogen or NTP methane. Industry has proven that all three fuels can be safely and easily contained in both gaseous and liquid phases.

In the event of a fuel spill, we can expect a fire hazard to develop most rapidly with hydrogen, methane and gasoline respectively, and the fire hazard should persist in the inverse order. For a specified liquid spillage volume and ensuing fire we can expect gasoline fires to last the longest and hydrogen fires to be the shortest lived, while all three fuels burn at nearly the same flame temperature. The scene of a hydrogen fire may be hotter (1.3 X to 1.8 X) than that of a hydrocarbon fire, but the hydrocarbon fires will endure five to ten times longer than hydrogen fires (for spillage of identical liquid fuel volumes).

All three fuels are easily ignited by weak ignition sources such as matches. Even a weak spark generated by the discharge of static electricity from a human body may be sufficient to ignite any of these fuels in air. Hydrogen is more readily ignitable than either of the hydrocarbon fuels which appear to be equally susceptible to ignition.

Hydrogen fires are more difficult to detect than methane or gasoline fires but modern detection equipment makes it possible to quickly and reliably detect the flames of all three fuels. In some applications hydrogen and methane fires should be allowed to burn until gas flow is stopped or until liquid spills are consumed because of the potential explosive hazard created by extinguishing such flames; however, the fire should be controlled in all situations and in many cases it is advisable to extinguish the fire. Water may be used to fight fires of all three fuels and commercial dry chemicals and high-expansion foams can be used to extinguish LNG and gasoline fires.

The potential for smoke inhalation damage is judged to be most severe in gasoline, methane and hydrogen fires respectively.

The wider flammable limits and detonable limits of hydrogen coupled with its rapid burning velocity tend to make hydrogen a greater explosive threat than methane or gasoline. Unconfined fuel-air explosions are not normally very destructive; however, confined fuel-air explosions can be devastating and hydrogen presents the greatest confined-explosion threat of the three fuels considered.

For equivalent energy storage or for equivalent volume storage, hydrogen has the least theoretical explosive potential of the three fuels considered -- even though it has the highest heat of combustion (and explosive potential) on a mass basis.

Hydrogen is currently being safely stored and used in industry in both the compressed gas and liquid forms and it is anticipated that metal hydride storage will be equally safe. Of the three fuels examined, gasoline is the easiest and perhaps the safest fuel to store because of its lower volatility and narrower flammable and detonable limits.

Personnel and equipment safety criteria (fuel quantity-distance) are concisely charted on figures presented herein. It is believed that these figures provide safe exposure distances for all three fuels.

Consideration of future hydrogen applications reveals no safety problems in the industrial and commercial markets. Hydrogen safety problems may exist in the transportation and residential fuel markets and additional safety analyses are needed in these areas. Lower risk (or lower cost) fuels will most likely be used to satisfy many of these markets over the next few decades; however, hydrogen cannot currently be considered unsafe and cannot be excluded from consideration in any of these applications on the grounds of safety. It is the author's belief that fuel availability and cost will outweigh fuel safety in the selection of fuels in the future and hydrogen must be considered a contender in the chemical fuel market.

Finally, hydrogen safety guidelines and applicable regulatory codes are summarized and tabulated in the Appendix of this paper.

10.0 REFERENCES

[1] Schmidt, A. F., Recommended materials and practices for use with cryogenic propellants, Aerospace Information Report, AIR 839B, Soc. of Auto. Engrs., 68 pages (Apr. 1969).

[2] Mechanical Engineers' Handbook, 5th edition, Book, Ed. by L. S. Marks, p. 342 (McGraw-Hill Book Company, Inc., New York, 1951).

[3] McCarty, R. D., and Weber, L. A., Thermophysical properties of parahydrogen from the freezing liquid line to 5000 R for pressures to 10,000 psia, Nat. Bur. Stand. (U.S.) Tech. Note TN-617 (Apr. 1972).

[4] Lewis, B., and von Elbe, G., Combustion, Flames and Explosions of Gases, 2nd edition, Book, p. 685 (Academic Press, Inc., New York, 1961).

[5] Goodwin, R. D., The thermophysical properties of methane, from 90 to 500 K at pressures to 700 bar, Nat. Bur. Stand. (U.S.) Tech. Note TN-653 (Apr. 1974).

[6] McCarty, R. D., Cryogenics Division, Nat. Bur. Stand., Boulder, Colorado, private communication to the author (1975).

[7] Standard Table of Physical Constants of Paraffin Hydrocarbons and Other Components of Natural Gas, GPA Publication 2145-75 (1975); (available from Gas Processors Assoc., 1812 First Place, Tulsa, OK 74103).

[8] Fire Hazard Properties of Flammable Liquids, Gases, Volatile Solids 1969, NFPA Pamphlet No. 325M (1969); (available from National Fire Protection Assoc., 470 Atlantic Ave., Boston, MA 02210).

[9] Engineering Data Book, 9th edition, Section 16, Physical Properties, Book, Compiled and Ed. by Gas Processors Assoc. (1972); (available from Gas Processors Suppliers Assoc., 1812 First Place, Tulsa, OK 74103).

[10] Handbook of Chemistry and Physics, 39th edition, Book, Ed. by C. D. Hodgman, R. C. Weast and S. M. Selby, p. 2343 (The Chemical Rubber Co., Cleveland, Ohio, 1957-58).

[11] Ibid., p. 2011.

[12] Handbook of Tables for Applied Engineering Science, Book, Ed. by R. E. Bolz and G. L. Tuve, p. 68 (The Chemical Rubber Co., Cleveland, Ohio, 1970).

[13] Lewis and von Elbe, op. cit., pp. 692-693.

[14] Coward, H. F., and Jones, G. W., Limits of flammability of gases and vapors, Bureau of Mines Bulletin 503 (1952); (available from Superintendent of Documents, U.S. Gov't. Printing Office, Washington, DC 20402).

[15] Lewis and von Elbe, op. cit., p. 535.

[16] Lewis and von Elbe, op. cit., pp. 329-335.

[17] Handbook of Chemistry and Physics, op. cit., p. 1790.

[18] Zabetakis, M. G., Flammability characteristics of combustible gases and vapors, Bureau of Mines Bulletin 627 (1965); (available from Superintendent of Documents, U.S. Gov't. Printing Office, Washington, DC 20402).

[19] Kogarko, S. M., Detonation of methane-air mixtures and the detonation limits of hydrocarbon-air mixtures in a large-diameter pipe, Sov. Phys. Tech. Phys. 28, No. 3 (1959).

[20] Burgess, D. S., Bureau of Mines, Pittsburgh, Pennsylvania, private communication to the author (1975).

[21] Magison, E. C., Electrical Instruments in Hazardous Locations, 2nd edition, Book, p. 74 (Instrument Society of America, Pittsburgh, Pennsylvania, 1972).

[22] Ibid., p. 304.

[23] Lewis and von Elbe, op. cit., p. 706.

[24] Handbook of Tables for Applied Engineering Science, op. cit., p. 303.

[25] Zabetakis, M. G., and Burgess, D. S., Research on the hazards associated with the production and handling of liquid hydrogen, Bureau of Mines Report of Investigations 5707 (1961).

[26] Burgess, D. S., and Zabetakis, M. G., Fire and explosion hazards associated with liquefied natural gas, Bureau of Mines Report of Investigations 6099 (1962); (available from NASA Scientific and Technical Information Facility, N63-18682).

[27] Lewis and von Elbe, op. cit., pp. 381-382.

[28] Zabetakis, M. G., Safety with Cryogenic Fluids, Book, p. 57 (Plenum Press, New York, 1967).

[29] Lewis and von Elbe, op. cit., p. 530.

[30] Carhart, H., Naval Research Laboratory, Washington, D.C., private communication to the author (1975).

[31] An Investigation of Fifteen Flammable Gases or Vapors with Respect to Explosion-proof Electrical Equipment, Underwriters' Laboratories Bulletin of Research No. 58 (Apr. 1970); (available from Underwriters' Laboratories, Publication Stock, 333 Pfingsten Road, Northbrook, IL 60062).

[32] Magison, op. cit., p. 116.

[33] Ibid., pp. 26-27.

[34] Lewis and von Elbe, op. cit., p. 698.

[35] Bollinger, L. E., Experimental detonation velocities and induction distances in hydrogen-air mixtures, AIAA J. 2, No. 1, pp. 131-133 (Jan. 1964).

[36] Cousins, E. W., and Cotton, P. E., Design closed vessels to withstand internal explosions, Chem. Engr. pp. 133-137 (Aug. 1951).

[37] Sax, N. I., Dangerous Properties of Industrial Materials, 4th edition, Book, p. 817 (Van Nostrand Reinhold Co., New York, 1975).

[38] Ibid., p. 903.

[39] Ibid., p. 785.

[40] Lewis and von Elbe, op. cit., p. 312.

[41] Ibid., pp. 511-554.

[42] Magison, op. cit., pp. 30-36.

[43] Lewis and von Elbe, op. cit., pp. 323-346.

[44] Ibid., pp. 346-366.

[45] Vanpee, M., and Wolfhard, H. G., Ignition by hot gases, Bureau of Mines Report of Investigations 5627 (1960).

[46] Kuchta, J. M., Cato, R. J., Martindill, G. H., and Gilbert, W. H., Ignition characteristics of fuels and lubricants, Bureau of Mines Technical Report AFAPL-TR-66-21 (March 1966); (available from Clearinghouse for Federal Scientific and Technical Information, AD632730).

[47] Lewis and von Elbe, op. cit., pp. 615-638.

[48] Rohsenow, W. M., and Choi, H., Heat, Mass and Momentum Transfer, Book, pp. 379-386 (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1961).

[49] Ibid., pp. 397-401.

[50] Bird, R. B., Stewart, W. E., and Lightfoot, E. N., Transport Phenomena, Book, p. 60 and p. 182 (John Wiley and Sons, Inc., New York, 1960).

[51] Mechanical Engineers' Handbook, 5th edition, op. cit., p. 1483.

[52] Magison, op. cit., pp. 107-140.

[53] Ibid., pp. 37-92.

[54] Bollinger, L. E., Fong, M. C., Laughrey, J. A., and Edse, R., Experimental and theoretical studies on the formation of detonation waves in variable geometry tubes, NASA Technical Note D-1983 (June 1963).

[55] Standard Method of Test for Flash and Fire Points by Cleveland Open Cup, ASTM Designation D92-66; Standards Method of Test for Flash Point by Pensky-Martens Closed Tester, ASTM Designation D93-71; Standard Method of Test for Flash Point of Volatile Flammable Materials by Tag Open-Cup Apparatus, ASTM Designation D1310-67; (ASTM Standards available from American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103).

[56] Sax, op. cit., p. 5.

[57] Ibid., pp. 12-13.

[58] Arvidson, J. M., Hord, J., and Mann, D. B., Efflux of gaseous hydrogen or methane fuels from the interior of an automobile, Nat. Bur. Stand. (U.S.) Tech. Note TN-666 (Mar. 1975).

[59] Hord, J., Correlations for predicting leakage through closed valves, Nat. Bur. Stand. (U.S.) Tech. Note TN-355 (Aug. 1967).

[60] Marr, J. W., Leakage Testing Handbook, prepared for Jet Propulsion Laboratory, NASA, Pasadena, California, under contract NAS 7-396, S-67-1014 (June 1967); (also available as NASA CR-952, Apr. 1968).

[61] Rosen, B., Dayan, V. H., and Proffit, R. L., Hydrogen leak and fire detection, a survey, NASA SP-5092 (1970).

[62] Static Electricity 1972, NFPA Pamphlet No. 77 (1972); (available from National Fire Protection Assoc., 470 Atlantic Ave., Boston, MA 02210).

[63] Guide to the Use of Flame Arresters and Explosion Reliefs, New Series No. 34, Ministry of Labour, Her Majesty's Stationery Office, England.

[64] Zabetakis, Safety with Cryogenic Fluids, op. cit., p. 38.

[65] Ibid., p. 49.

[66] Hord, J., Explosion criteria for liquid hydrogen test facilities, Nat. Bur. Stand. (U.S.), Unpublished report (Feb. 1972).

[67] Custer, R. L. P., and Bright, R. G., Fire detection: the state-of-the-art, NASA CR-134642, NBS TN-839 (June 1974); (available from National Technical Information Service, Springfield, VA 22151).

[68] Zabetakis, M. G., U.S. Bureau of Mines, private communication to the author (1975).

[69] Reider, R., Otway, H. J., and Knight, H. T., An unconfined large-volume hydrogen/air explosion, Pyrodynamics 2, pp. 249-261 (1965).

[70] Kinney, G. F., Explosive Shocks in Air, Book, (The Macmillan Company, New York, 1962).

[71] Burgess, D. S., Murphy, J. N., Hanna, N. E., and Van Dolah, R. W., Large-scale studies of gas detonations, Bureau of Mines Report of Investigations 7196 (1968).

[72] Zeldovich, Y., and Kompaneets, A. S., Theory of Detonation, Book, p. 84 (Academic Press, New York, 1960).

[73] Fletcher, R. F., Characteristics of liquid propellant explosions, Annals of the New York Acad. of Sci. 152, pp. 432-440 (Oct. 1968).

[74] General Safety Engineering Design Criteria, Vol. 1, CPIA public. 194, (Oct. 1971); also, Liquid Propellant Handling, Storage and Transportation, Vol. 3, CPIA public. 194 (May 1972) -- documents prepared by the JANNAF propulsion committee of the JANNAF Hazards Working Group and are available from the Chemical Propulsion Information Agency (CPIA) of the Johns Hopkins University Applied Physics Laboratory, 8621 Georgia Ave., Silver Spring, MD 20910; (also available to the public through National Technical Information Service, Springfield, VA 22150: Vol. 1 Accession No. AD 889 763, Vol. 3 Accession No. AD 870 259).

[75] Fletcher, R. F., Liquid-propellant explosions, J. of Spacecraft and Rockets 5, No. 10, pp. 1227-1229 (Oct. 1968).

[76] Hydrogen Safety Manual, NASA Lewis Research Center, NASA Tech. Memo TM-X-52454 (1968).

[77] Willoughby, A. B., Wilton, C., and Mansfield, J., Liquid propellant explosive hazards - Vols. 1, 2 and 3, prepared by URS Research Co. for USAF, Report No. AFRPL-TR-68-92, USAF Contract AF04(611)10739, Vol. 1 DDC Access. No. AD 855 086, Vol. 2 Access. No. AD 857 342, Vol. 3 Access. No. AD 855 087, (Dec. 1968); also, Mansfield, J. A., Heat transfer hazards of liquid rocket propellant explosions - final report, Report No. AFRPL-TR-69-89, USAF Contract AF04(611)-69-C-0004, DDC Access. No. AD 857 343, (Feb. 1969) --- these four volumes constitute Project Pyro Reports.

[78] Zabetakis, M. G., Furno, A. L., and Perlee, H. L., Hazards in using liquid hydrogen in bubble chambers, Bureau of Mines Report No. 6309 (1963).

[79] Gayle, J. B., Investigation of S-IV all systems vehicle explosion, NASA Tech. Note TN D-563 (Sept. 1964).

[80] Structures to resist the effects of accidental explosions, Dept. of the U.S. Army TM 5-1300 (June 1969).

[81] Randall, P. N., Bland, J., Dudley, W. M., and Jacobs, R. B., Effects of gaseous detonations, Chem. Engr. Prog. 53, No. 12, pp. 574-580 (Dec. 1957).

[82] Collins, R. D., Jr., and Kinard, W. H., The dependency of penetration on the momentum per unit area of the impacting projectile and the resistance of materials to penetration, NASA Tech. Note D-238 (May 1960).

[83] Siewert, R. D., Evacuation areas for transportation accidents involving propellant tank pressure bursts, NASA Tech. Memorandum NASA TM X-68277 (1972).

[84] Safety Manual, U.S. Army Materiel Command, AMCR 385-100 (Apr. 1970).

[85] Strehlow, R. A., and Baker, W. E., The characterization and evaluation of accidental explosions, NASA CR-134779 (June 1975); (available from National Technical Information Service, Springfield, VA 22151).

[86] Baker, W. E., Parr, V. B., Bessey, R. L., and Cox, P. A., Assembly and analysis of fragmentation data for liquid propellant vessels, NASA CR-134538 (Jan. 1974); (available from National Technical Information Service, Springfield, VA 22151).

[87] Howard, W. B., Rodehorst, C. W., and Small, G. E., Flame arresters for high-hydrogen fuel-air mixtures, Loss Prevention 9 (American Institute of Chemical Engineers, 345 East 47th Street, New York, NY 10017, 1975).

[88] Hord, J., and Parrish, W. R., Economics of hydrogen (to be published as Chapter 1 of Volume 5, Implications of Hydrogen, in the book: Hydrogen, Its Technology and Implications, CRC Press).

[89] Wiswall, R. H., Jr., and Reilly, J. J., Metal hydrides for energy storage, Proc. of 7th Intersociety Energy Conversion Engr. Conf., ACS, Washington, D.C., pp. 1342-1348 (1972).

[90] Salzano, F. J., Braun, C., Beaufrere, A., Srinivasan, S., Strickland, G., and Reilly, J. J., Hydrogen for energy storage: a progress report of technical developments and possible applications, presented at the Energy Storage Conf., Asilomar Conf. Grounds, Pacific Grove, California, Feb. 8-13, 1976 (Jan. 1976).

[91] NFPA National Fire Codes, Volume 3 (1975); (available from National Fire Protection Assoc., 470 Atlantic Ave., Boston, MA 02210).

[92] Lundin, C. E., and Lynch, F. E., The safety characteristics of FeTi hydride, Proc. of 10th Intersociety Energy Conversion Engr. Conf., p. 1386 (Aug. 1975).

[93] Ordin, P. M., Review of hydrogen accidents and incidents in NASA operations, Proc. of 9th Intersociety Energy Conversion Engr. Conf., San Francisco, California, p. 442 (Aug. 1974).

[94] LNG Information Book . . .1973, American Gas Assoc., 1515 Wilson Blvd., Arlington, VA 22209 (1973).

[95] Parrish, W. R., Voth, R. O., Hust, J. G., Flynn, T. M., Sindt, C. F., and Olien, N. A., Selected topics on hydrogen fuel, Ed. by J. Hord, Nat. Bur. Stand. (U.S.) SP 419 (May 1975).

[96] Burgess, D. S., Murphy, J. N., Zabetakis, M. G., and Perlee, H. E., Volume of flammable mixtures resulting from the atmospheric dispersion of a leak or spill, 15th Int'l. Symp. on Combustion, The Combustion Institute, Pittsburgh, PA, Paper No. 29 (in press).

[97] Commodity Data Summaries, 1976, Bureau of Mines (Jan. 1976); see also, Adkins, D. C., and Jaske, R. J., Hydrogen, a chapter from Mineral Facts and Problems, Bureau of Mines Bulletin 667 (1975).

[98] Brewer, G. D., Aviation usage of liquid hydrogen fuel, Symposium Proc. of Hydrogen Energy Fundamentals, Miami Beach, Florida, Paper S4-3 (March 1975).

[99] Berkowitz, B., DeVore, J., Harris, S., Haun, L., McNamara, W., and Slager, W., Alternative, synthetically fueled, Navy systems: force element missions and technology, General Electric Company-Tempo report GE74TMP-46 (Nov. 1974); (available from Advanced Research Projects Agency, 1400 Wilson Blvd., Arlington, VA 22209).

[100] Carhart, H. W., Affens, W. A., Boss, B. D., Hazlett, R. N., and Schuldiner, S., Hydrogen as a Navy fuel, Naval Research Laboratory Report 7754 (June 1974); (available from National Technical Information Service, Springfield, VA 22151, AD-781 262).

[101] Gier, H. L., Hydrogen fuel for the railroads: a proposal, Proc. of the 1st World Hydrogen Energy Conf., Miami Beach, Florida, Vol. III, Ed. by T. N. Veziroglu, Paper 7C-43 (March 1976).

[102] Billings, R. E., A hydrogen-powered mass transit system, Proc. of the 1st World Hydrogen Energy Conf., Miami Beach, Florida, Vol. III, Ed. by T. N. Veziroglu, Paper 7C-27 (March 1976).

[103] Wall, T., Feeney, R., Hollenberg, J., McAlevy, R. F. III, Engineering study of hydrogen-fueled bus operation, Proc. of the 1st World Hydrogen Energy Conf., Miami Beach, Florida, Vol. III, Ed. by T. N. Veziroglu, Paper 7C-25 (March 1976).

[104] VanVorst, W. D., and Finegold, J. G., Automotive hydrogen engines and onboard storage methods, Symposium Proc. of Hydrogen Energy Fundamentals, Miami Beach, Florida, Paper S4-65 (March 1975).

[105] Ecklund, E. E., Kester, F. L., Hydrogen storage on highway vehicles: update '76, Proc. of the 1st World Hydrogen Energy Conf., Miami Beach, Florida, Vol. II, Ed. by T. N. Veziroglu, Paper 3B-3 (March 1976).

[106] Weil, K. H., The hydrogen I.C. engine - its origins and future in the emerging energy-transportation-environment system, Proc. of 7th Intersociety Energy Conversion Engr. Conf., ACS, Washington, D.C., pp. 1355-1363 (1972).

[107] Billings, R. E., and Lynch, F. E., History of hydrogen-fueled internal combustion engines, Energy Research Publication 73001; (available from Billings Energy Research Corporation, P.O. Box 555, Provo, UT 84601).

[108] Mikolowsky, W. T., and Noggle, L. W., The potential of liquid hydrogen as a military aircraft fuel, Proc. of the 1st World Hydrogen Energy Conf., Miami Beach, Florida, Vol. III, Ed. by T. N. Veziroglu, Paper 5C-31 (March 1976).

[109] Witcofski, R. D., Langley Research Center, NASA, Hampton, VA, private communication to the author (June 1976).

[110] Marchetti, C., Hydrogen and energy, CEER 5, No. 1, pp. 7-25 (Jan. 1973).

[111] On an investigation of hazards associated with the storage and handling of liquid hydrogen, Final Report C-61092, Contract No. AF 18(600)-1687, prepared by Arthur D. Little, Inc., DDC Access. No. AD 324194, 137 pages (Mar. 1960).

[112] Bowen, T. L., Investigation of hazards associated with using hydrogen as a military fuel, Report 4541, Naval Ship Research and Development Center, Bethesda, MD 20084 (Aug. 1975).

[113] Ludtke, P. R., Register of specialized sources for information on selected fuels and oxidizers, NASA CR-134807 (Mar. 1975).

[114] Ludtke, P. R., Register of hydrogen technology experts, NASA CR-2624 (Oct. 1975).

[115] Standard for Liquefied Hydrogen Systems at Consumer Sites, NFPA Pamphlet No. 50B (ANSI Z292.3).

[116] Standard for the Production, Storage and Handling of Liquefied Natural Gas (LNG), NFPA Pamphlet No. 59A (ANSI Z225.1).

[117] Flammable and Combustible Liquids Code, NFPA Pamphlet No. 30 (ANSI Z288.1).

[118] LNG Safety Program, Phase II, Consequences of LNG Spills on Land, American Gas Association Project IS-3-1 (Nov. 1973); see also, Wesson, H. R., Brown, L. E., and Welker, J. R., Vapor dispersion, fire control, and fire extinguishment of high evaporation rate LNG spills, paper 74-D-36 in 1974 Operating Section Proceedings of the American Gas Association, 1515 Wilson Boulevard, Arlington, VA 22209 (1974).

[119] Baker, W. E., Kulesz, J. J., Ricker, R. E., Bessey, R. L., Westine, P. S., Parr, V. B., and Oldham, G. A., Workbook for predicting pressure wave and fragment effects of exploding propellant tanks and gas storage vessels, NASA CR-134906 (Nov. 1975).

Appendix: Hydrogen Safety Guidelines and Applicable Regulatory Codes

Various industrial, university and government organizations have published guidelines for safe production and handling of hydrogen. Some of the more substantial documents are listed in table A1.

Table A1: Hydrogen Safety and Equipment Guidelines (nonmandatory)

SAFETY ITEM	REFERENCES
Handling procedures (includes safety in production, transportation and distribution, personnel training, etc.)	A1-A25
Storage	A1, A16, A17, A21, A22, A23, B1
Explosive Criteria	Summarized in A1 and C1 See also C2 and C3
Leak Detection & Fire Detection, Prevention, Control	D1-D6, A1, G4 & G5
Facilities	A1 and C1
Mechanical Equipment	F1-F18
Electrical Equipment	G1-G10

Some of these documents are accepted as national standards and become mandatory and enforceable when specified by regulatory bodies such as the DoT, state and local authorites, etc. Insurance companies usually adopt or specify existing standards, practices and procedures as a condition of insurability for industrial organizations. Examples of nonmandatory standards that may be adopted by regulatory bodies are those issued by the ASME, ANSI, ISA, NFPA, UL, ASTM, etc. Current regulations that pertain to hydrogen are listed in table A2.

Equipment specifications and shipping and carrier regulations for gaseous and liquid hydrogen are given in CFR, Title 49, Parts 170-179. Pipeline transmission of flammable compressed gases (presumably including hydrogen) is regulated by CFR, Title 49, Parts 190-192. The DoT classifies and treats liquid hydrogen as a flammable compressed gas (Part 172.5 of CFR, Title 49). Air transportation of compressed hydrogen gas is regulated by CFR, Title 14, Part 103 and the commercial carrier IATA tariffs [H6]. Liquid hydrogen is not currently accepted for air shipments. Transportation of compressed hydrogen gas by water is regulated by CFR, Title 46, Part 146 and liquid hydrogen cannot currently be shipped by water; however, the NASA has barged liquid hydrogen over distances of 84 km offshore Louisiana-Mississippi under special permit of the U.S. Coast Guard.

Federal regulations apply to the interstate transportation of hydrogen and are administered by the various branches of the Department of Transportation: the Federal Highway Administration for transport by highway; the Federal Railroad Administration for transport by railway; the Federal Aviation Administration for air transport; and the U.S. Coast Guard for water transport. In addition to the regulations and standards set forth in table A2, municipal and state regulations may be imposed for the storage and intrastate transportation of hydrogen.

Table A2. Regulations (mandatory) for Distribution of Hydrogen

Distribution of Hydrogen by	Equipment Specifications	Transportation Regulations
Cylinders filled with liquid (< 1000 pounds water capacity)--by highway only	CFR, Title 49, Part 178.57 Ref. [H2]	CFR, Title 49, Parts 173.316, 177.823, 177.840 Ref. [H2]
Railway tank cars filled with liquid	CFR, Title 49, Parts 179.400, 179.401, Ref. [H2]	CFR, Title 49, Part 173.316, Ref. [H2]
Highway truck trailers filled with liquid	CGA*-341 and DoT Approval prior to fabrication Ref. [F17]	Special permit from Hazardous Materials Regulation Board of DoT (see CFR, Title 49, Parts 173.33, 177.823) Ref. [H2]
Container filled with liquid--by air or waterway	----	Not allowed under current regulations (see CFR, Title 14, Parts 103.7, 103.9 and CFR, Title 46, Part 146.24), Ref's. [H3,H4]. Shipment by tank barge has been allowed under special permit of the U.S. Coast Guard Commandant.
Liquid pipeline	ANSI B31.8, B31.3*, B31.10*, Ref's. [H1,F5,F6]	CFR, Title 49, Parts 190-192, Ref. [H2]
Cylinders filled with compressed gas--by highway or rail	CFR, Title 49, Parts 173.34, 178.36, 178.37 Ref. [H2]	CFR, Title 49, Parts 173.301, 173.302, 176.703, 177.823, Ref. [H2]
Railway tank cars filled with compressed gas	CFR, Title 49, Parts 173.31, 179.500 Ref. [H2]	CFR, Title 49, Part 173.314, Ref. [H2]
Highway truck trailers filled with compressed gas	CFR, Title 49, Parts 173.34, 178.36, 178.37, Ref. [H2]	CFR, Title 49, Parts 173.301, 173.302, 177.823, Ref. [H2]
Container filled with compressed gas--by air	CFR, Title 49, Parts 173.34, 178.36, 178.37 Ref. [H2]	CFR, Title 14, Part 103.9, Ref. [H4]. DoT approved cylinders on cargo aircraft only, with a maximum charge of 300 pounds (136 kg) of H_2 per cylinder. See also CAB No. 82 Ref's. [H2,H6]
Container filled with compressed gas--by waterway	CFR, Title 49, Parts 173.31, 173.34, 178.36, 178.37, 179.500 and CFR, Title 46, Part 146.24, Ref's. [H2,H3]	CFR, Title 46, Part 146.24. DoT approved cylinders on cargo vessels only and DoT approved railway tank cars on trainships only, Ref. [H3]
Gas pipeline	ANSI B31.8, B31.3*, Ref's. [H1,F5]	CFR, Title 49, Parts 190-192 Ref. [H2]

Storage of Hydrogen @ Consumer Sites as	Equipment Specifications	Industrial Standards
Compressed gas	ASME*, Section VIII, Divisions 1 & 2, Ref's. [F1,F2]	NFPA* 50A, Ref. [A21]
Liquid	ASME*, Section VIII, Divisions 1 & 2, Ref's. [F1,F2]	NFPA* 50B, Ref. [A22]

General industrial safety matters, including the production and handling of flammable compressed and liquefied gases, are regulated by OSHA PL 91-596, Ref. [H5].

* Not mandatory but industrially accepted standards.

Appendix References

Note: In the references that follow,

CGA = Compressed Gas Association, Inc., 500 Fifth Ave., New York, NY 10036.
ANSI = American National Standards Institute, 1430 Broadway, New York, NY 10018.
NFPA = National Fire Protection Association, Publication Sales Department, 470 Atlantic Ave., Boston, MA 02210.
ASME = American Society of Mechanical Engineers, United Engineering Center, 345 East 47th Street, New York, NY 10017.
UL = Underwriters' Laboratories, Publication Stock, 333 Pfingsten Road, Northbrook, IL 60062.
ISA = Instrument Society of America, 400 Stanwix Street, Pittsburgh, PA 15222.

[A1] General Safety Engineering Design Criteria, Vol. 1, CPIA public. 194, (Oct. 1971); also, Liquid Propellant Handling, Storage and Transportation, Vol. 3, CPIA public. 194, (May 1972) -- documents prepared by the JANNAF propulsion committee of the JANNAF Hazards Working Group and are available from the Chemical Propulsion Information Agency (CPIA) of the Johns Hopkins University Applied Physics Laboratory, 8621 Georgia Ave., Silver Spring, MD 20910; (also available to the public through National Technical Information Service, Springfield, VA 22150: Vol. 1 Accession No. AD 889 763, Vol. 3 Accession No. AD 870 259).

[A2] Hydrogen safety manual, NASA Lewis Research Center, NASA Tech. Memo TM-X-52454 (1968).

[A3] On an investigation of hazards associated with the storage and handling of liquid hydrogen, Final Report C-61092, Contract No. AF 18(600)-1687, prepared by Arthur D. Little, Inc., DDC Access. No. AD 324194, 137 pp. (Mar. 1960).

[A4] Liquid hydrogen, a guide for the safe handling and storage of liquid hydrogen at LASL Facilities, Los Alamos Scientific Laboratory, P.O. Box 1663, Los Alamos, NM 87544.

[A5] Weintraub, A. A., Control of liquid hydrogen hazards at experimental facilities: a review, health and safety laboratory, U.S. Atomic Energy Comm., New York, NY (May 1965); also, Grumer, J., Strasser A., and Van Meter, R. A., Principles for safe handling of liquid hydrogen, Bur. of Mines Tech. Rept. (June 1967).

[A6] Chelton, D. B., Safety in the use of liquid hydrogen, Book, Technology and Uses of Liquid Hydrogen, Ed. by R. B. Scott, W. H. Denton, and C. M. Nicholls, pp. 359-378 (The Macmillan Co., New York, 1964).

[A7] Connolly, W. W., A practical safety standard for commercial handling of liquefied hydrogen, Book, Advances in Cryogenic Engineering 12, Ed. by K. D. Timmerhaus, pp. 192- 197, (Plenum Press, New York, 1967).

[A8] Recommended materials and practices for use with cryogenic propellants, Aerospace Information Report, AIR 839B, 68 pp. (Soc. of Auto. Engrs., Apr. 1969).

[A9] Cryogenics safety manual, a guide to good practice, (British Cryogenics Council, 16 Belgrave Square, London, SW1X8PT, 1970).

[A10] Hernandez, H. P., Safety guidelines for accelerator installations, Lawrence Radiation Laboratory Rept. No. UCRL-18555 (Feb. 1969).

[A11] Handbook of Compressed Gases, Compressed Gas Assoc., Inc., (Reinhold Publishing Corp., New York, 1966).

[A12] Safe Handling of Compressed Gases in Containers, CGA Pamphlet P-1.

[A13] Method of Marking Portable Compressed Gas Containers to Identify the Material Contained, CGA Pamphlet C-4; [also ANSI Z48.1-1954 (R 1971)].

[A14] Guide to the Preparation of Precautionary Labeling and Marking of Compressed Gas Containers, CGA Pamphlet C-7.

[A15] Hydrogen, CGA Pamphlet G-5.

[A16] Standard for Gaseous Hydrogen at Consumer Sites, CGA Pamphlet G-5.1.

[A17] Standard for Liquefied Hydrogen Systems at Consumer Sites, CGA Pamphlet G-5.2.

[A18] Commodity Specification for Hydrogen, CGA Pamphlet G-5.3; see also, Hydrogen Commodity Specification, MIL-P-27201B (June 1971); (available from USN Supply Depot, 5801 Tabor Ave., Philadelphia, PA 19120).

[A19] Lightning Protection Code, NFPA Pamphlet No. 78 (ANSI C5.1).

[A20] Static Electricity, NFPA Pamphlet No. 77.

[A21] Standard for Gaseous Hydrogen Systems at Consumer Sites, NFPA Pamphlet No. 50A (ANSI Z292.2).

[A22] Standard for Liquefied Hydrogen Systems at Consumer Sites, NFPA Pamphlet No. 50B (ANSI Z292.3).

[A23] Standard for the Installation and Operation of Oxygen-Fuel Gas Systems for Welding and Cutting, NFPA Pamphlet No. 51; see also, Standard on Safety in Welding and Cutting, ANSI Z49.1.

[A24] Siewert, R. D., Evacuation areas for transportation accidents involving propellant tank pressure bursts, NASA TMX-68277 (Nov. 1972).

[A25] Emergency services guide for selected hazardous materials (spills, fire, evacuation area), Dept. of Transportation, Office of the Secretary, Office of Hazardous Materials, Washington, D.C. 20590 (Apr. 1974).

[B1] Zabetakis, M. G., and Burgess, D. S., Research on the hazards associated with the production and handling of liquid hydrogen, Bureau of Mines Report, RI-5707 (1961).

[C1] Hord, J., Explosion criteria for liquid hydrogen test facilities, Nat. Bur. Stand. (U.S.), NBS Report (Feb. 1972).

[C2] Explosion Venting, NFPA Pamphlet No. 68.

[C3] Explosion Prevention Systems, NFPA Pamphlet No. 69.

[D1] Rosen, B., Dayan, V. H., and Proffit, R. L., Hydrogen leak and fire detection, NASA SP-5092 (1970).

[D2] Automatic Fire Detectors, NFPA Pamphlet No. 72E.

[D3] Fire Hazard Properties of Flammable Liquids, Gases, Volatile Solids, NFPA Pamphlet No. 325M.

[D4] National Fire Codes, NFPA Volumes 1 and 2 (general fire-fighting and fire control).

[D5] Donnini, J. M., Hydrogen fire blink detector, U.S. Patent Application S/N 51477 (July 1970).

[D6] Custer, R. L. P., and Bright, R. G., Fire detection: the state of the art, Nat. Bur. Stand. (U.S.) Tech. Note TN-839 (June 1974).

[F1] ASME Boiler and Pressure Vessel Code, Section VIII, Division 1, Pressure Vessels: this reference applies to gaseous and liquid containers for portable and stationary applications.

[F2] ASME Boiler and Pressure Vessel Code, Section VIII, Division 2, Pressure Vessels: Alternative Rules: this reference applies to gaseous and liquid containers for stationary applications only.

[F3] ASME Boiler and Pressure Vessel Code, Section IX, Welding and Brazing Qualifications.

[F4] ASME Boiler and Pressure Vessel Code, Section III, Nuclear Power Plant Components: a series of standards applicable to nuclear plants and installations.

[F5] American National Standard Code for Pressure Piping, Petroleum Refinery Piping, ANSI B31.3, (ASME, New York): this reference applies to gaseous and liquid piping.

[F6] American National Standard Code for Pressure Piping, Cryogenic Piping Systems, ANSI B31.10 (in preparation).

[F7] Vacuum insulated cryogenic pipes, some recommendations concerned with pipe and coupling design, (British Cryogenics Council, 16 Belgrave Square, London SWIX8PT, 1972).

[F8] Safety Relief Device Standards, Part 1 - Cylinders for Compressed Gases, CGA Pamphlet S-1.1; Part 2 - Cargo and Portable Tanks for Compressed Gases, CGA Pamphlet S-1.2; Part 3 - Compressed Gas Storage Containers, CGA Pamphlet S-1.3.

[F9] Recommended Practice for the Manufacture of Fusible Plugs, CGA Pamphlet S-4.

[F10] Frangible Disc Safety Device Assembly, CGA Pamphlet S-3.

[F11] Compressed Gas Cylinder Valve Outlet and Inlet Connections, CGA Pamphlet V-1 (also Canadian Standards Association CSA B96-1965 and American Standards Association ASA B57.1-1965).

[F12] Methods for Hydrostatic Testing of Compressed Gas Cylinders, CGA Pamphlet C-1.

[F13] Standards for Welding and Brazing on Thin Walled Containers, CGA Pamphlet C-3.

[F14] Cylinder Service Life, Seamless, High-Pressure Cylinder Specifications ICC-3, ICC-3A, ICC-3AA, CGA Pamphlet C-5.

[F15] Standards for Visual Inspection of Compressed Gas Cylinders, CGA Pamphlet C-6.

[F16] Standard for Requalification of DoT-3HT Cylinders, CGA Pamphlet C-8.

[F17] Tentative Standard for Insulated Tank Truck Specification for Cold Liquefied Gases, CGA Pamphlet CGA-341.

[F18] Voth, R. O., Safety of hydrogen pressure gauges, Book, Advances in Cryogenic Engineering, 17, Ed. by K. D. Timmerhaus, pp. 182-187 (Plenum Press, New York, 1972).

[G1] Standard for Intrinsically Safe Process Control Equipment for Use in Class I Hazardous Locations, NFPA Pamphlet No. 493.

[G2] Standard for Purged and Pressurized Enclosures for Electrical Equipment in Hazardous Locations, NFPA Pamphlet No. 496.

[G3] National Electrical Code, Chap. 5, Articles 500-501, NFPA Pamphlet No. 70.

[G4] Fire Protection Equipment List, (Jan. 1975), available from UL.

[G5] Hazardous Location Equipment List, (June 1974), available from UL.

[G6] Electrical Instruments in Hazardous Atmospheres, ISA-RP 12.1 (1960).

[G7] Intrinsically Safe and Non-Incendive Electrical Instruments, ISA-RP 12.2 (1965).

[G8] Instrument Purging for Reduction of Hazardous Area Classification, ISA-S12.4 (1970).

[G9] Electrical Safety Practices, ISA Monograph 113 (1972).

[G10] Magison, E. C., Electrical Instruments in Hazardous Locations, 2nd edition, Book, 321 pp. (Instrument Society of America, Pittsburgh, Pennsylvania, 1972).

[H1] American National Standard Code for Pressure Piping, Gas Transmission and Distribution Piping Systems, ANSI B31.8.

[H2] Code of Federal Regulations, Title 49, Transportation, Parts 100 to 199, U.S. Government Printing Office, Washington, D.C. 20402.

[H3] Code of Federal Regulations, Title 46, Shipping, Parts 140 to 149, U.S. Government Printing Office, Washington, D.C. 20402.

[H4] Code of Federal Regulations, Title 14, Aeronautics and Space, Parts 60 to 199, U.S. Government Printing Office, Washington, D.C. 20402.

[H5] Occupational Safety and Health Act of 1970, PL 91-596 (Dec. 29, 1970) in United States Statutes at Large, 91st Congress, Second Session, 84, Part 2, pp. 1590-1620, (U.S. Government Printing Office, Washington, D.C. 20402, 1971).

[H6] Official Air Transport Restricted Articles Tariff No. 6-D, Civil Aeronautics Board (CAB) No. 82, Section I (pp. 14-15), Section II (p. 53) and Section III - Part A (p. 94), issued by the Airline Tariff Publishing Company, Dulles International Airport, P.O. Box 17415, Washington, D.C. 20041.

NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBS-TN-690	2. Gov't Accession No.	3. Recipient's Accession No.
4. TITLE AND SUBTITLE Is Hydrogen Safe?			5. Publication Date October 1976
			6. Performing Organization Code 275.05
7. AUTHOR(S) J. Hord			8. Performing Organ. Report No.
9. PERFORMING ORGANIZATION NAME AND ADDRESS NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234			10. Project/Task/Work Unit No. 2750900
			11. Contract/Grant No.
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) Same as item 9.			13. Type of Report & Period Covered
			14. Sponsoring Agency Code
15. SUPPLEMENTARY NOTES			

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

The safety aspects of hydrogen are systematically examined and compared with those of methane and gasoline. Physical and chemical property data for all three fuels are compiled and used to provide a basis for comparing the various safety features of the three fuels. Each fuel is examined to evaluate its fire hazard, fire damage, explosive hazard and explosive damage characteristics. The fire characteristics of hydrogen, methane and gasoline, while different, do not largely favor the preferred use of any one of the three fuels; however, the threat of fuel-air explosions in confined spaces is greatest for hydrogen. Gasoline is believed to be the easiest and perhaps the safest fuel to store because of its lower volatility and narrower flammable and detonable limits. It is concluded that all three fuels can be safely stored and used; however, the level of safety risk for each fuel will vary from one application to another. Generalized safety comparisons are made herein but detailed safety analyses will be required to establish the relative safety of different fuels for each specific fuel application and stipulated accident. The technical data supplied in this paper will provide much of the framework for such analyses. Hydrogen safety guidelines, regulatory codes applicable to the distribution of hydrogen, and safety criteria for liquid hydrogen storage are compiled and presented.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Explosion; fire; fuel; gasoline; hydrogen; methane; safety.

18. AVAILABILITY	19. SECURITY CLASS (THIS REPORT)	21. NO. OF PAGES
[X] Unlimited	UNCLASSIFIED	38
[ ] For Official Distribution. Do Not Release to NTIS		
[X] Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13.46:690	20. SECURITY CLASS (THIS PAGE)	22. Price
[ ] Order From National Technical Information Service (NTIS) Springfield, Virginia 22151	UNCLASSIFIED	$0.85

NBS TECHNICAL PUBLICATIONS

PERIODICALS

JOURNAL OF RESEARCH reports National Bureau of Standards research and development in physics, mathematics, and chemistry. It is published in two sections, available separately:

- **Physics and Chemistry (Section A)**

Papers of interest primarily to scientists working in these fields. This section covers a broad range of physical and chemical research, with major emphasis on standards of physical measurement, fundamental constants, and properties of matter. Issued six times a year. Annual subscription: Domestic, $17.00; Foreign, $21.25.

- **Mathematical Sciences (Section B)**

Studies and compilations designed mainly for the mathematician and theoretical physicist. Topics in mathematical statistics, theory of experiment design, numerical analysis, theoretical physics and chemistry, logical design and programming of computers and computer systems. Short numerical tables. Issued quarterly. Annual subscription: Domestic, $9.00; Foreign, $11.25.

DIMENSIONS/NBS (formerly Technical News Bulletin)—This monthly magazine is published to inform scientists, engineers, businessmen, industry, teachers, students, and consumers of the latest advances in science and technology, with primary emphasis on the work at NBS. The magazine highlights and reviews such issues as energy research, fire protection, building technology, metric conversion, pollution abatement, health and safety, and consumer product performance. In addition, it reports the results of Bureau programs in measurement standards and techniques, properties of matter and materials, engineering standards and services, instrumentation, and automatic data processing.

Annual subscription: Domestic, $9.45; Foreign, $11.85.

NONPERIODICALS

Monographs—Major contributions to the technical literature on various subjects related to the Bureau's scientific and technical activities.

Handbooks—Recommended codes of engineering and industrial practice (including safety codes) developed in cooperation with interested industries, professional organizations, and regulatory bodies.

Special Publications—Include proceedings of conferences sponsored by NBS, NBS annual reports, and other special publications appropriate to this grouping such as wall charts, pocket cards, and bibliographies.

Applied Mathematics Series—Mathematical tables, manuals, and studies of special interest to physicists, engineers, chemists, biologists, mathematicians, computer programmers, and others engaged in scientific and technical work.

National Standard Reference Data Series—Provides quantitative data on the physical and chemical properties of materials, compiled from the world's literature and critically evaluated. Developed under a world-wide program coordinated by NBS. Program under authority of National Standard Data Act (Public Law 90-396).

NOTE: At present the principal publication outlet for these data is the Journal of Physical and Chemical Reference Data (JPCRD) published quarterly for NBS by the American Chemical Society (ACS) and the American Institute of Physics (AIP). Subscriptions, reprints, and supplements available from ACS, 1155 Sixteenth St. N.W., Wash. D. C. 20056.

Building Science Series—Disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

Technical Notes—Studies or reports which are complete in themselves but restrictive in their treatment of a subject. Analogous to monographs but not so comprehensive in scope or definitive in treatment of the subject area. Often serve as a vehicle for final reports of work performed at NBS under the sponsorship of other government agencies.

Voluntary Product Standards—Developed under procedures published by the Department of Commerce in Part 10, Title 15, of the Code of Federal Regulations. The purpose of the standards is to establish nationally recognized requirements for products, and to provide all concerned interests with a basis for common understanding of the characteristics of the products. NBS administers this program as a supplement to the activities of the private sector standardizing organizations.

Consumer Information Series—Practical information, based on NBS research and experience, covering areas of interest to the consumer. Easily understandable language and illustrations provide useful background knowledge for shopping in today's technological marketplace.

Order **above** *NBS publications from: Superintendent of Documents, Government Printing Office, Washington, D.C. 20402.*

Order **following** *NBS publications—NBSIR's and FIPS from the National Technical Information Services, Springfield, Va. 22161.*

Federal Information Processing Standards Publications (FIPS PUBS)—Publications in this series collectively constitute the Federal Information Processing Standards Register. Register serves as the official source of information in the Federal Government regarding standards issued by NBS pursuant to the Federal Property and Administrative Services Act of 1949 as amended, Public Law 89-306 (79 Stat. 1127), and as implemented by Executive Order 11717 (38 FR 12315, dated May 11, 1973) and Part 6 of Title 15 CFR (Code of Federal Regulations).

NBS Interagency Reports (NBSIR)—A special series of interim or final reports on work performed by NBS for outside sponsors (both government and non-government). In general, initial distribution is handled by the sponsor; public distribution is by the National Technical Information Services (Springfield, Va. 22161) in paper copy or microfiche form.

BIBLIOGRAPHIC SUBSCRIPTION SERVICES

The following current-awareness and literature-survey bibliographies are issued periodically by the Bureau:

Cryogenic Data Center Current Awareness Service. A literature survey issued biweekly. Annual subscription: Domestic, $20.00; Foreign, $25.00.

Liquified Natural Gas. A literature survey issued quarterly. Annual subscription: $20.00.

Superconducting Devices and Materials. A literature survey issued quarterly. Annual subscription: $20.00. Send subscription orders and remittances for the preceding bibliographic services to National Bureau of Standards, Cryogenic Data Center (275.02) Boulder, Colorado 80302.

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

OFFICIAL BUSINESS

Penalty for Private Use, $300

POSTAGE AND FEES PAID
U.S. DEPARTMENT OF COMMERCE
COM-215

U.S.MAIL

Fourth Class Mail

AMERICAN REVOLUTION BICENTENNIAL 1776-1976

75 YEARS NBS 1901-1976