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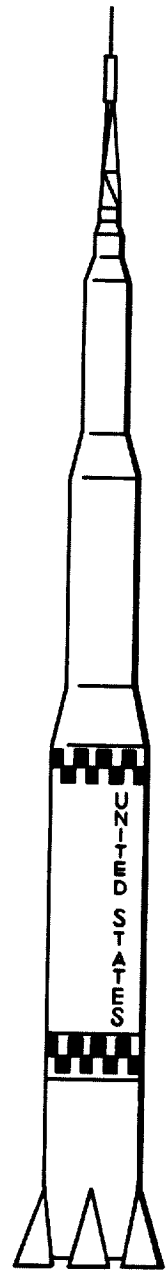
SUPPLEMENT TO MSFC-STD-200 VEHICLE-RELATED HYDROGEN HAZARDS DURING PREFLIGHT CONDITIONS



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
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SUPPLEMENT TO MSFC-STD-200

VEHICLE-RELATED HYDROGEN HAZARDS DURING PREFLIGHT CONDITIONS

Prepared

For

George C. Marshall Space Flight Center

National Aeronautics and Space Administration

Huntsville, Alabama

Final Report

Contract NASw-410

MSFC Task Order 13

June 1964

Apollo Support Department
General Electric Company
Daytona Beach, Florida

FOREWORD

This report was prepared by General Electric Company, Apollo Support Department, Daytona Beach, Florida, on NASA Contract NASw-410, George C. Marshall Space Flight Center, Task Order #13, preparation of MSFC Standard, providing requirements and criteria for the prevention of hazards, associated with the use of large quantities of hydrogen in Saturn-class launch vehicle during preflight condition. The report is intended to serve as reference and back up material for the MSFC standard depicting summaries of the studies and evaluations from which the requirement and criteria was developed.

The work was administered under the direction of propulsion and vehicle engineering laboratory, Vehicle System Division R-VE-VO. Mr. C. Jones provided the technical direction for the laboratory.

The studies and evaluation presented here were conducted in the period of April 1, through June 30, 1964 by the Apollo Support Department of the General Electric Company.

This is the final report of the task.

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SECTION I

INTRODUCTION

The realistic assessment of hazards associated with Liquid Hydrogen is assuming major importance in view of the increasing demand for this fuel in the present and future. It is the purpose of this report to identify the hazards associated with the use of liquid hydrogen as fuel applicable to Saturn-class launch vehicles and relate them to the present knowledge of prevention, detection and suppression techniques.

In order to provide an MSFC Standard for liquid hydrogen hazards related to preflight condition, it is necessary to collect the existing scientific information on the physical, combustion, flammability and detonation properties and survey conditions and practices encountered in research and engineering work involving liquid hydrogen. Therefore, this report and the MSFC Standard is based on one hand on a survey of scientific literature available and on the other hand, on information derived from the engineering experience and consultation with liquid hydrogen users.

Although large scale application of liquid hydrogen is of fairly recent date, it can be said that the use of liquid hydrogen as a propellant for launch vehicles has proceeded without serious incident. However, this fortuitous experience does not obviate the continued need for further developments in safety, and it is hoped that this report and the standard prepared will contribute towards this objective. This applies in particular to an advancement in the understanding of the hydrogen - oxygen reaction and the occurrence and effect of combustion and detonation under various conditions of confinement.

SECTION II

PROPERTIES OF HYDROGEN

2.1 PHYSICAL PROPERTIES

Hydrogen normally occurs in the diatomic molecular form. Because the hydrogen nuclei has a spin associated with it, the molecule can be differentiated by the parallel or antiparallelism of the two nuclear spins. This results in the two forms (ortho and para). At high temperatures the distribution of molecules between the two types is determined by the number of ways that each can be formed. At room temperature the ortho (high energy-parallel spin) form comprises about 75% of the molecules, while at low temperatures the para (low energy-antiparallel spin) is predominant. Because the ortho form is the higher energy form, there is a spontaneous transition to the lower energy state with a corresponding heat released which is of approximate equal value to the latent heat of vaporization. The current use of catalysts in the process of production of liquid hydrogen results in almost pure para as the normally available liquid form.

Hydrogen is a colorless, odorless gas. It is nontoxic and essentially noncorrosive at room temperature. It ignites readily in the presence of air or oxygen (if an ignition source is present), burning with a colorless flame if no impurities are present. Hydrogen is a good reducing agent at elevated temperatures.

Due to its low density and low molecular weight, gaseous hydrogen will rise and disperse rapidly in the atmosphere. Its density is approximately 1/14 that of air; however, gaseous hydrogen at a temperature just above its boiling point (36.5° to 41°R) is denser than dry ambient air (68°F) and will settle initially until it warms slightly.

Liquid hydrogen is a transparent, colorless liquid of low viscosity. Its density is 0.07 the density of water (0.59 pounds per gallon at the boiling point). In particular, gases like oxygen and nitrogen condense and freeze to solids in liquid hydrogen without entering into solution.

The critical point is at 33.2°K (-400°F) and 13 atmospheres (191 psia) pressure. At about 14°K (-435°F) liquid hydrogen freezes to a solid. The temperature and pressure at the triple point (at which solid, liquid and gaseous hydrogen coexist)

is 14.0°K and 0.071 atmospheres for normal hydrogen, and 13.8°K and 0.069 atmospheres for para hydrogen. Freezing of hydrogen is readily accomplished by allowing a part of the contents of liquid hydrogen in a Dewar vessel to evaporate into a vacuum. The hydrogen freezes as a white crystalline or snow-like mass.

The following table summarizes the physical properties of hydrogen.

Table 1

Physical Properties of Hydrogen

Boil Point	-423°F
Freezing Point	-435°F
Density at -423°F (Liquid)	4.42 lb/cu ft.
Density at -423°F (Vapor)	0.083 lb/cu ft.
	(1.02 times heavier than air at 32°F)
Density at 32°F (Gas and 14.7 psia)	.0059 lb/cu ft.
	(14.5 times lighter than air at 32°F)
Auto Ignition Temperature at Atmospheric Pressure	1075°F (Approx.)
Flammability Limits in Air (H_2Gas)	4.0 to 74.2 percent hydrogen (By Volume)
Viscosity at -423°F (Liquid)	140 micropoise
Critical Temperature	-400°F
Critical Pressure	188 psia
Vapor Pressure, psia	
-433°F	1.9 psia
-423°F	14.7 psia
-420°F	23.7 psia
-402°F	162.0 psia

The density of liquid hydrogen decreases from 4.42 pounds per cubic foot at its boiling point of -423°F to 3.35 pounds per cubic foot at -405°F (where the vapor pressure is 120 psia).

Solubility

Very little is known about the solubility of materials in liquid hydrogen, however, neon appears to be quite soluble and it is possible that helium is soluble to the extent of 1%.

Stability

Liquid hydrogen is exceptionally stable chemically. Because of its low boiling point and low latent heat of vaporization, long term storage is possible only in well-insulated containers. The losses from these containers vary with the nature and thickness of the insulation and can be as low as 1/10 of 1% per day.

Compatibility

Hydrogen will react spontaneously with fluorine and chlorinetrifluoride and when properly mixed will burn or detonate with oxygen.

2.2 CHEMICAL PROPERTIES

The chemical behavior of hydrogen toward oxygen is well understood through extensive research conducted in this country and abroad. A review of the intricate reaction mechanism and its correlation to the combustion and detonation properties is a necessary part of any discussion of the hazardous characteristics of hydrogen. For the purpose of this report the review has been condensed to a thumb-nail sketch as far as is consistent with the required completeness of presentation of this very complex subject. References to the highly specialized research literature are found elsewhere[1].

Molecules of hydrogen and oxygen make contact with each other in molecular collisions in the gas phase or under cryogenic conditions in the condensed phase. The possible chemical effect of such contact is determined by the energy required to dissociate H_2 and O_2 molecules into atoms. This energy is 103,000 cal/mole for H_2 and 117,000 cal/mole for O_2. Molecular collisions involving energies of

[1] B. Lewis and G. von Elbe, Combustion, Flames and Explosions of Gases, 2nd Ed., Academic Press, New York, 1961.

this order of magnitude are extremely rare even at temperatures as high as 5,000°F. Hence the probability of chemical reaction in collisions between H_2 and O_2 molecules is virtually non-existent even at high temperatures; that is, the mere contact between hydrogen and oxygen molecules in gas-phase collisions or in the condensed phase in cryogenic systems produces no chemical change.

The reaction probability is many orders of magnitude larger in the event that the species colliding with a molecule H_2 or O_2 not only possesses a chemical affinity to its collision partner but also has one or more free valence electrons capable of forming a chemical bond. Thus, a collision of an oxygen atom -O- (the hyphens denoting the two free valencies of the oxygen atom) with a molecule H_2 is likely to result in an exchange of atoms as follows:

$$-O- + H_2 \rightarrow HO- + H- \; -3{,}000 \text{ cal/mole} \qquad (a)$$

In such exchange reaction the free valencies are preserved but become attached to other chemical species, in this case a hydroyxl radical HO- and a hydrogen atom H-. Similarly,

$$HO- + H_2 \rightarrow H_2O + H- \; +15{,}500 \text{ cal/mole} \qquad (b)$$

which shifts the free valence of a hydroyxl radical to a hydrogen atom and, incidentally, produces one molecule of water. Atoms H- and molecules O_2 undergo either an exchange or association, as follows: An atom H- colliding with a molecule O_2 forms a collision complex (HOO) which is normally very short-lived and dissociates again into H- and O_2. However, when the colliding species carry kinetic and other energy in excess of a minimum--the "activation" energy--the dissociation occurs between the two oxygen atoms,

$$H- + O_2 \rightarrow HO- + -O- \; -17{,}000 \text{ cal/mole} \qquad (c)$$

shifting one free valence from H- to HO- and generating two additional free valencies attached to an atom -O-. On the other hand, when a third molecule of any kind collides simultaneously with H- and O_2 in a so-called ternary collision, the energy of the collision complex (HOO) is in part absorbed by the third molecule, so that the complex cannot dissociate and a stable free radical HOO- so formed:

$$H- + O_2 + M \rightarrow HOO- + M + 46{,}000 \text{ cal/mole} \qquad (d)$$

M denoting any third molecule. The radical HOO- is capable of an exchange reaction with H_2 according to

$$HOO- + H_2 = H_2O_2 + H- \quad -14{,}000 \text{ cal/mole} \qquad (e)$$

regenerating an atom H- and forming a molecule of hydrogen peroxide. Unlike the mildly endothermic reaction (a) and the exothermic reaction (b) which both take place readily even at room temperature, the endothermic reaction (e) occurs very infrequently in molecular collisions of HOO- and H_2 even at temperatures as high as, say, 900°F.

Atoms and free radicals are readily absorbed on solid surfaces of all kinds. In the absorbed state they ultimately combine with each other, saturating their free valencies and forming neutral molecules. Two radicals HOO-, for example, may combine to form hydrogen peroxide and oxygen:

$$HOO- + HOO- \xrightarrow{\text{surface}} H_2O_2 + O_2. \qquad (f)$$

Hydrogen peroxide formed in reactions (e) or (f) decomposes readily at high temperature, to yield H_2O and O_2.

Atoms and free radicals may also combine with each other in the gas phase. However, a binary collision of, say, two atoms H or of an atom H with a radical OH does not yield a stable bond, because the high energy residing in the collision complex drives the species apart again. Permanent association requires a ternary collision, as for example,

$$H- + H- + M \rightarrow H_2 + M + 103{,}200 \text{ cal/mole} \qquad (g)$$

and

$$HO- + H- + M \rightarrow H_2O + M + 119{,}000 \text{ cal/mole} \qquad (h)$$

the third molecule M absorbing a part of the energy of the collision complex.

Oxygen atoms formed in reaction (c) produce H and HO according to (a), and HO radicals formed in reactions (a) and (c) produce H, according to (b). Hence, whenever reaction (c) occurs the H-atom lost in the exchange is replaced by another one and two additional atoms H are generated. Each H atom either repeats the cycle of reactions (c), (a) and (b) and thus generates two more atoms or it is lost from the system by absorption on a surface or by association in the gas phase according to (g) and (h); or it associates with O_2 to form HO_2 in

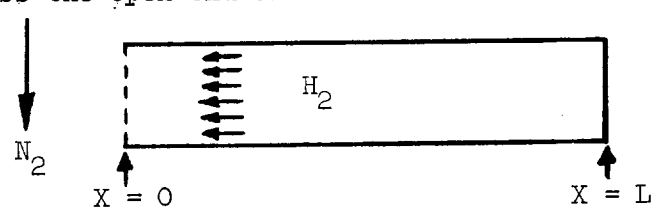
reaction (d). In the latter case it is replaced by another H if HO_2 reacts with H_2 according to (e), or it is lost from the system if HO_2 reacts according to (f).

2.3 DIFFUSION OF HYDROGEN GAS FROM REGIONS OF HIGH CONCENTRATION

The transfer of H_2 gas from regions of high concentration to ones of low concentration may occur by several means, including (1) diffusion (at constant temperature), (2) convection (either forced or natural), and (3) thermal diffusion (which occurs when there are temperature gradients as well as concentration gradients).

In order to arrive at some numerical values for the rate at which H_2 will transfer from regions of high concentrations, we shall consider the simplest mode of transfer: diffusion at constant temperature. In addition to being the simplest mode, diffusion will give the most conservative answers (the lowest mass transfer rates). If convection were superimposed on the diffusion rates, considerably higher transfer rates would result.

A one dimensional problem can be set up as follows. Consider the open ended tube in the figure below. The tube is initially filled with pure H_2 gas. Another gas, say N_2, moves slowly across the open end of the tube.



Because of the strong concentration gradient that exists initially at x = 0, the H_2 will begin to diffuse out of the container and be swept away by the N_2 stream. Thus, the H_2 concentration to the left of x = 0 is always zero. The H_2 will gradually leave the enclosed volume, and will be replaced by N_2, which diffuses in an opposite direction to the H_2 stream at an equimodal rate.

We shall assume no convection currents anywhere within the tube. The problem is one-dimensional, as diffusion will take place only along the axis of the tube.

The equation describing the one-dimensional transient diffusion phenomenon is (Reference 1):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{1}$$

where D is the "diffusion coefficient" (in cm^2/sec), x is distance along the tube axis (in cm), t is time (in sec), and c is the concentration of H_2. The concentration may be expressed in any consistent unit such as g/cc, moles/cc, or in terms of partial pressure, p_{H_2}. We could also substitute for c, the partial pressure ratio P (which is equal to the mole fraction)

$$P = \frac{p_{H_2}}{P_{total}}$$

Thus equation (1) becomes:

$$\frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} \tag{2}$$

This equation is identical to the one-dimensional transient heat transfer equation, with partial pressure ratio taking the place of temperature, and the diffusion coefficient taking the place of thermal diffusivity. There are many solutions available in heat transfer literature for various boundary and initial conditions. The answer we desire is the partial pressure ratio within the tube as a function of time and distance along the tube.

The initial conditions will be that the tube is filled completely with H_2 at t = 0. At times greater than zero, the H_2 concentration is zero at x = 0.

For the first case, assume an infinitely long tube. This corresponds to the heat transfer problem of a semi-infinite solid, originally at one temperature, suddenly subjected to a different temperature at the face. The solution is (Reference 2):

$$P = \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{3}$$

where the error function is defined: $\mathrm{erf}\,(w) = \frac{2}{\sqrt{\pi}} \int_0^w e^{-\beta^2} d\beta$

and β is a dummy variable.

The value used for the diffusion coefficient, D, was 0.634 cm^2/sec (Reference 4). This is the value of the diffusion coefficient for H_2 into air at 0 deg C.

Values of the error function were obtained from published tables (Reference 3). The solution is plotted on Figure 1, for various values of time. It is apparent from Figure 1 that an explosive mixture builds up within the tube as the concentration of H_2 falls, and very long times are required for a "safe" mixture (less than 4% H_2) to penetrate along the tube. For example, after 5 minutes, the "safe" mixture has penetrated only about 1 cm.

The slowness with which the H_2 clears the tube in the above case is partly due to the assumption of infinite tube length; the H_2 deep within the tube must diffuse a long distance along a low concentration gradient. If shorter tube lengths were assumed, the concentration of H_2 would drop more quickly. As an example, assume the same initial conditions as above, but a tube of finite length, say 8 cm. This new boundary condition results in a more complex solution, which can be given as the sum of an infinite series. Plots of the solutions are available in the literature for these boundary conditions (References 5,6,7). The plot of (Reference 7) was used to generate the curves of Figure 2, which is the solution for a tube of 8cm length.

Figure 2 shows a drop in H_2 concentration about the same as the longer tube for the first 5 sec., but at 20 sec. and longer the drop in concentration is more rapid due to depletion of H_2 within the tube. In less than 5 minutes, the tube has almost completely been cleared of H_2. Still, the penetration of a "safe" mixture is quite slow for this tube of 8 cm. length.

The above results indicate the inadequacy of diffusion alone to clear away rapidly H_2 which has been trapped in pockets and voids. It is apparent that convection currents of inert gas must be relied upon to sweep away concentrations of hydrogen if a safe mixture is to be produced within a deep void space in a fraction of a second.

Further work which might be done in the area of diffusion and convection is listed below:

1. Determine the relationship between penetration depth of a "safe" mixture and time, for tubes of various lengths.
2. Determine the time required to reduce H_2 concentrations to safe levels by a stream of inert gas, for various configurations.
3. Determine the order of magnitude of <u>thermal</u> diffusion, where large temperature gradients exist.

PARTIAL PRESSURE RATIO OF H_2 vs. DISTANCE

INFINITE LENGTH TUBE - D = 0.634 $CM^2/SEC.$

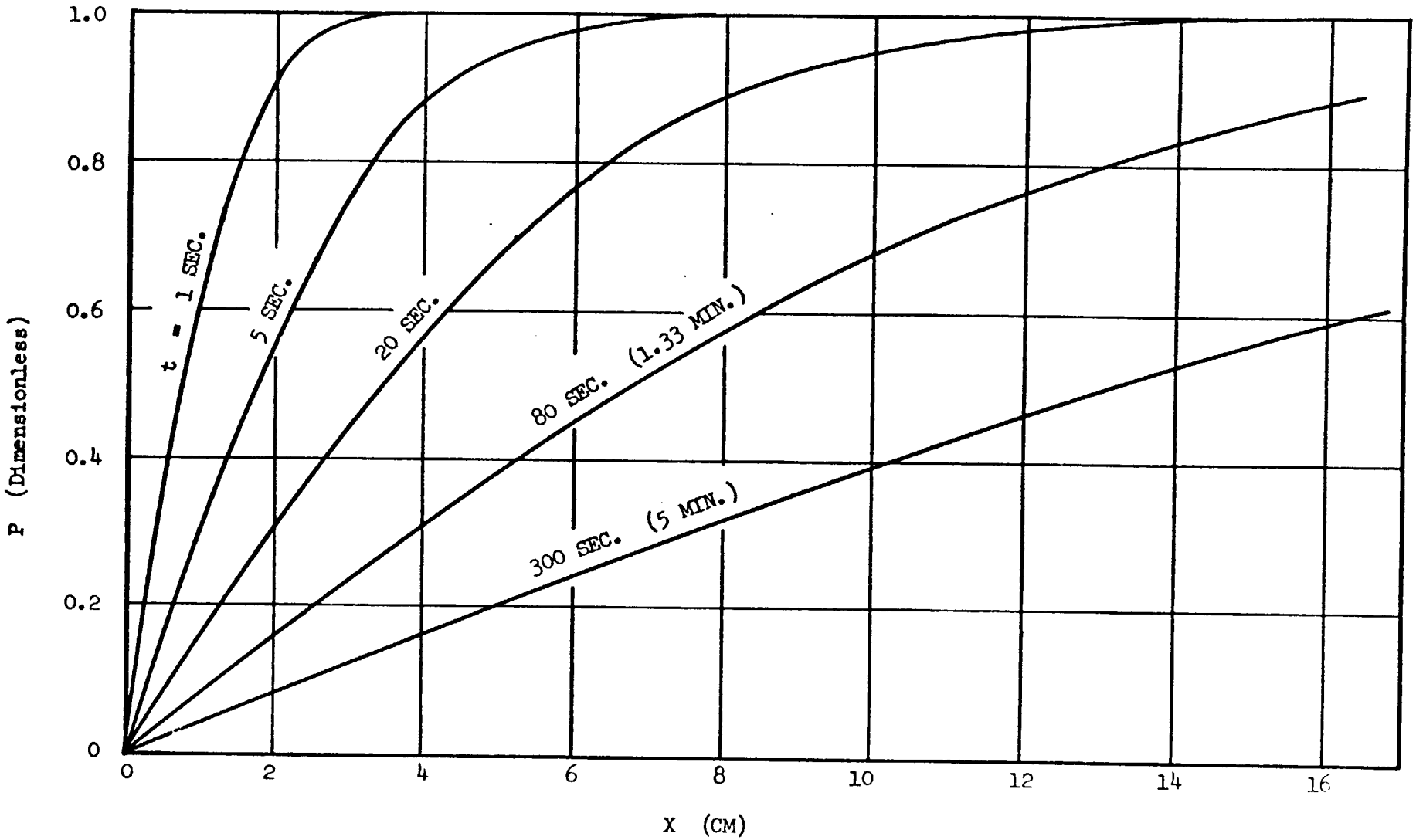


Figure 1

PARTIAL PRESSURE RATIO OF H_2 vs. DISTANCE

TUBE LENGTH = 8 CM. D = 0.634 CM^2/SEC

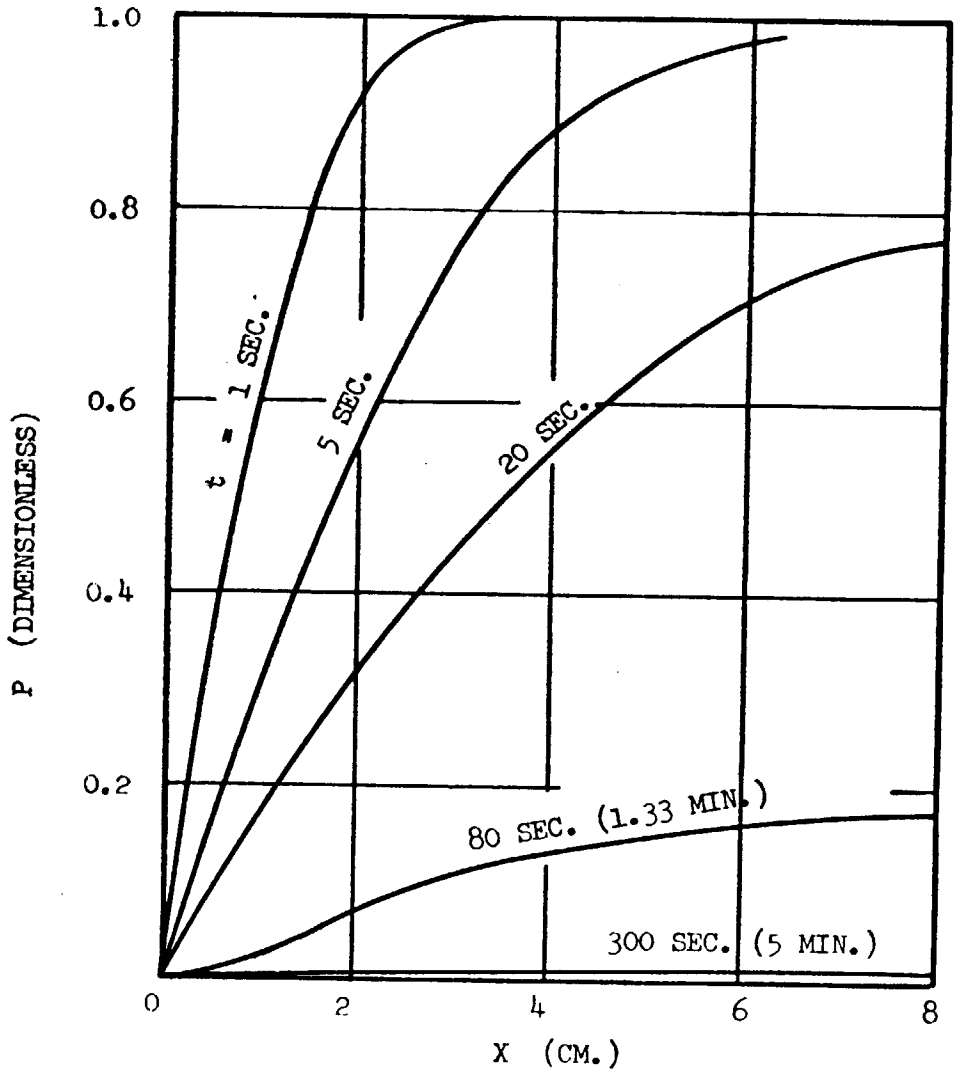


Figure 2

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SECTION III

FLAMMABILITY AND DETONATION HAZARDS

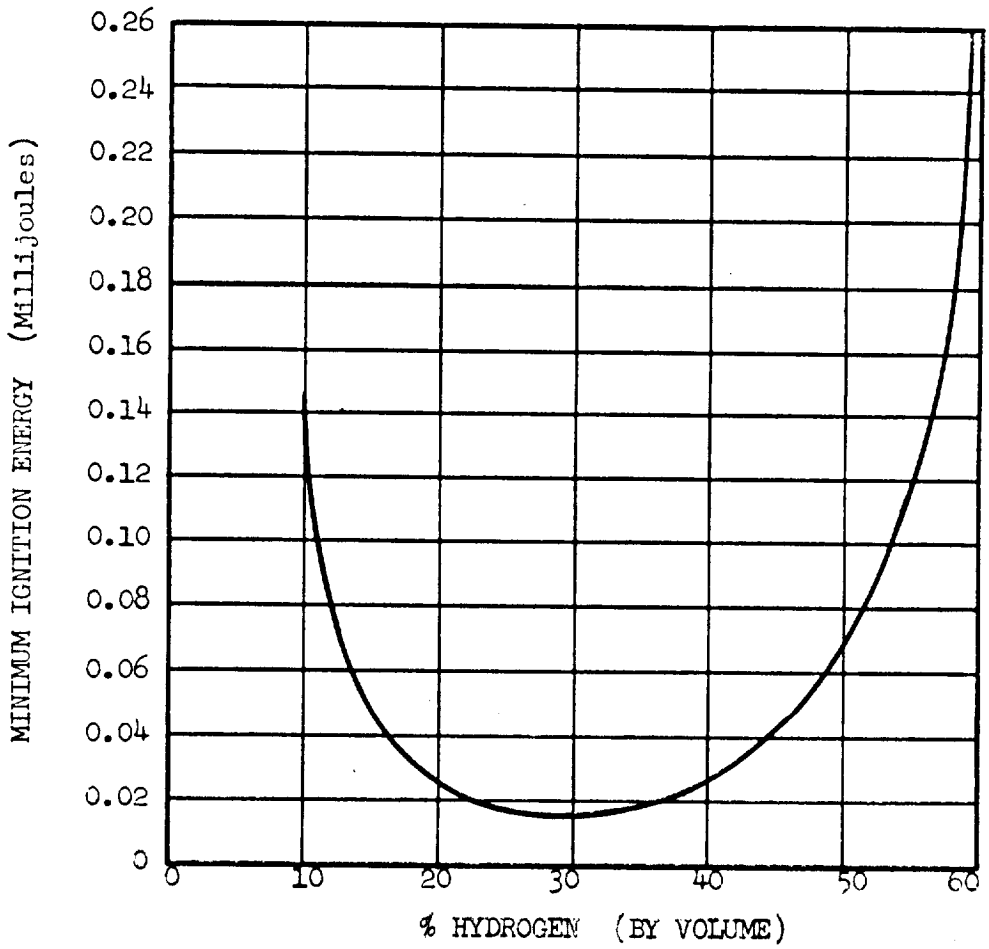
3.1 FLAMMABILITY AND DETONATION OF GASEOUS MIXTURES.

The principal hazard associated with gaseous or liquid hydrogen is its ease of ignition over a wide flammability range in air and oxygen. Detonations can occur although they are more difficult to initiate. Sparks, flames, detonations, and temperatures in excess of 1,000°R will all ignite hydrogen-air mixtures. The combustion limits of hydrogen in air range from 4% to 74% hydrogen by volume. Substitution of oxygen for air raises the upper limit to 94%. The limiting compositions for detonation lie between the upper and lower combustion limits. For confined or unconfined mixtures of hydrogen and air the range is approximately 18% to 59% hydrogen by volume.

Hydrogen-oxygen mixtures can be ignited by minute ignition sources (see Figure 3). For example, the electrostatic spark experienced by a person touching a door knob is 50 to 1,000 times greater than the threshold energy necessary for ignition of hydrogen air mixtures.

When an electric spark is discharged in a mixture containing hydrogen and oxygen, heat and hydrogen atoms generated in the path of the electric discharge similarly ignites the next layer, and so on, so that a combustion wave propagates from the ignition source. The mechanism of spark ignition and combustion wave propagation is in principle the same for all kinds of gaseous fuel-oxidant mixtures; however, hydrogen is unique because of the chain-branching reaction (c)* which has no counterpart in systems such as hydrocarbon-oxygen mixtures. In the latter mixtures, free radicals and atoms are generated only by the effect of high temperature on the fuel molecules, and the flow of heat alone propagates the combustion wave. In hydrogen-oxygen mixtures, flame propagation involves the combined effects of heat flow and multiplication of hydrogen atoms that diffuse from the inflamed layer into the adjacent layer of unignited gas. A hydrogen flame thus propagates much more rapidly than an equivalent hydrocarbon flame; it requires much less peak energy for ignition, and it requires flame traps of much smaller channel width than the width required for stopping a hydrocarbon flame. Comparing, for example, fuel-air mixtures in stoichiometric ratio at atmospheric conditions, one finds that the

*See section II, paragraph 2.2 for equation (a) through (h)



Minimum ignition energies for hydrogen-air mixtures at one atmosphere.

Figure 3

burning velocity (the rate of propagation of the combustion wave relative to the unburned gas) is about 270 cm/sec for hydrogen versus 35 cm/sec for methane; the minimum ignition energy of electric sparks is 0.015 millijoules versus 0.28 millijoules and the quenching distance between plane-parallel plates is 0.063 cm versus 0.23 cm, respectively.

Chain-branching of reaction (c) also explains why detonation occurs much more readily in mixtures containing hydrogen than in mixtures whose fuel constituent is methane or some other hydrocarbon. Detonation waves are initiated by a suitably strong shock, or they develop from flames in pipes in channels due to flame acceleration by the increasing turbulence of the gas flow. They propagate in mixtures of about 17 per cent to 60 per cent hydrogen and air at room temperature and ordinary pressures, but do not propagate in corresponding mixtures of methane and air although these mixtures contain as much or more combustion energy. In hydrogen-air mixtures, therefore, the detonation shock is a sufficient stimulus to initiate combustion at the high rate required to sustain the pressures and temperatures in the detonation wave, whereas in methane-air mixtures, the chemical mechanism does not permit the development of such high rate of combustion. To obtain further insight in this problem, we note that high rates of combustion and heat release require high concentrations of atoms and free radicals in the combustion zone. When a layer of detonatable gas mixture is over-run by the front of the detonation wave and thus suddenly raised to high temperature and pressure, some of the fuel molecules dissociate yielding atoms and free radicals, but when air is the oxidant, the shock strength is too low and the number of atoms and free radicals is insufficient to initiate the required high combustion rate. Hence, when the fuel gas is hydrogen, the concentration of atoms and free radicals increases by chain-branching and the combustion rate accelerates correspondingly. Thus, although there exists a range of mixtures of methane and oxygen which develop sufficient shock strength to sustain detonation, such mixtures are rendered non-detonatable by relatively small additions of diluent gases; whereas hydorgen-oxygen mixtures require large additions of diluents in order to be rendered non-detonatable.

There are sufficient data available to permit a theoretical estimate* of the lowest percentage of hydrogen in air for propagation of detonation. The hydrodynamic theory of detonation yields the temperature and pressure at the front of the detonation wave for any given percentage of hydrogen in air; thus, for 25 per cent hydrogen at room temperature and atmospheric pressure the shock front temperature is 1350°K (2500° F) and the pressure is 23.5 atm., etc. From reaction kinetic theory one obtains the number of hydrogen atoms generated by dissociation of hydrogen molecules in the shock front. Knowing the number of oxygen molecules in the shock front, and knowing that one H reacts with one O_2 via (c), (a) and (b) to generate two H, two H to generate four H, etc., one computes the number of branching cycles of this kind required to convert a substantial fraction, say, 1 to 10 per cent, of the total hydrogen present into H atoms. The calculation is not sensitive to the exact fraction chosen, and it can be readily demonstrated that when branching has progressed to this order of magnitude the combustion reaction goes to completion in an extremely short time, i.e., in less than a microsecond. From recently published data on the rate of reaction (c) one computes the time interval required for completing a branching cycle; and multiplying this time interval with the above number of branching cycles, one obtains the period that elapses between the moment a gas layer is over-run by the shock front and the moment at which combustion is substantially complete. The following table shows calculated periods in microseconds for various values of the shock front temperature, which is the dominant variable in calculations of this type.

T, °K	900	1000	1200	1400	1600
t, microseconds	150	42	9	2	0.65

Experimental observations on the width of reaction zones in detonation waves indicate that a time of the order of 10 microseconds is about the limit for steady-state pro-

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*Unpublished. Data on detonation waves are taken from W. E. Gordon, "Third Symposium on Combustion, "p. 579, Williams and Wilkins, Baltimore, 1949; W. E. Gordon, A. J. Mooradian and S. A. Harper, "Seventh Symposium on Combustion," p. 752, Butterworthe, London, 1959. Data on reaction $H + O_2 - HO + O$ are taken from a paper by F. Kaufman and F. P. Del Greco, presented at the Ninth Symposium on Combustion at Cornell University, Aug. 27 - Sept. 1, 1962. Rate of dissociation of H_2 estimated from collision frequency and dissociation energy (103,000 cal/mole).

pagation of detonation. According to the above table, this corresponds to a shock front temperature between 1000° and 1200°K. Indeed, analysis of data on limits of detonability involving a wide range of hydrogen-oxygen-diluent gas mixtures has shown that the shock front temperature is substantially the same for all these limit mixtures and has a value of about 1100°K (about 2000°F). Theory and experiment are thus in very satisfactory agreement. For hydrogen and air the shock front temperature of 1100°K corresponds approximately to a lean limit of 17 per cent and a rich limit of 60 per cent hydrogen, which are the experimentally observed limit concentrations.

Using nitrogen as a diluent and gases at room temperature and ordinary pressures, inflammation of hydrogen by spark or other ignition source is inhibited at a nitrogen/oxygen ratio of 19:1 by volume. The flame temperature of a mixture containing 1 part of oxygen, 19 parts of nitrogen and hydrogen in stoichiometric amount, i.e., 2 parts by volume, is about 1400°F. This represents roughly the limit of temperature at which the heat flow from the combustion gas into the adjacent layer of unburned gas is sufficiently large to permit chain-branching by reaction (c) to exceed loss of hydrogen atoms by diffusion. A further increase of the nitrogen content of the mixture decreases the flame temperature below the limit, so that inflammation initiated by an extraneous heat source does not propagate, i.e., the mixture is non-flammable. Carbon dioxide or water vapor are more effective than nitrogen because they possess higher heat capacities, so that less diluent is required to reduce the flame temperature. Argon is less effective than nitrogen because it possesses a lower heat capacity. The flame temperature of the limit mixture is roughly the same for the various diluent gases, but not exactly, because physical properties other than the heat capacity are also involved. These other properties are principally the heat conductivity of the gas mixture, which determines the rate of flow of heat into and out of the combustion wave, and the diffusivity, which determines the rate of escape of hydrogen atoms from the combustion wave. Thus, helium as a diluent is considerably more effective than argon because it permits a more rapid dissipation of heat and chain carriers, so that the flame temperature does not have to be decreased as much as with argon.

We mention here that stoichiometric methane + oxygen is rendered nonflammable by nitrogen at a nitrogen/oxygen ratio of 7.4:1, as compared to 19:1 for hydrogen. The corresponding limit flame temperature is about 2,000°F. At this temperature, therefore, the thermochemical process of generation of chain-carriers from methane

molecules and heat liberation in the methane-oxygen chain reaction fails to match the process of loss of heat and chain carriers. Higher hydrocarbons require somewhat larger additions of diluents for non-flammability.

If an additive is not just an inert substance like nitrogen, but is also capable of destroying hydrogen atoms, it is of course more effective than a mere diluent as a flame-extinguishing agent. Chlorinated hydrocarbons, for example, react with hydrogen atoms according to the scheme $RCl + H = R + HCl$, R being the unspecified organic-chemical part of the molecule. The effectiveness of such additives depends very much on the nature of the radical R and its subsequent chemical reactions--in particular, whether or not it regenerates another H atom in the subsequent reaction sequence. In appraising the effectiveness of chemical compounds for flame-quenching purposes, it must be borne in mind that a high flame temperature vitiates any effort of flame-quenching by chemical means alone. If a hydrogen-oxygen mixture is in contact with a heat source comparable, for example, to a fuel-air flame, no chemical additive can compete with the proliferation of hydrogen atoms by reaction (c). It is necessary to introduce a quantity of heat-absorbing material into the combustion zone, sufficient to reduce the temperature to levels at which the chemical component of the quenching agent can be effective.

In this respect dust dispersions commend themselves inasmuch as they provide both a heat sink and a large surface for absorption of hydrogen atoms. The heat-sink properties are determined by the specific heat of the material and in some instances perhaps significantly also by its partial vaporization. The effectiveness of hydrogen atom absorption depends on the degree of dispersion of the dust particles and their ability to retain hydrogen atoms impinging on a particle surface. Various materials differ in the latter respect, but little is known theoretically about such differences of retentive properties.

Certain additives promote the inflammation of hydrogen-oxygen mixtures. These substances generate free radicals and atoms which are capable of chain-branching with oxygen molecules analogous to reaction (c) and in addition are considerably more reactive than hydrogen atoms, so that chain-branching becomes "critical" and the mixture inflames at lower temperatures than corresponds to reaction (c) alone.

One such additive is nitric oxide which in laboratory test vessels may take the ignition temperature down to about 500°F, as compared to roughly 700°F for hydrogen and oxygen alone. The effect is limited to concentrations of nitric oxide between a lower and an upper critical limit, the limit concentrations being functions of temperature, mixture composition and other factors. Traces of nitric oxide in the exhaust of aircraft piston engines are known to be responsible for the exhaust gas flame (which is essentially a hydrogen flame) observed in flight during rich-mixture engine operation. An especially powerful promoter is carbon disulfide which, when added in amounts of a few tenths of one per cent to a stream of hydrogen in air, may cause ignition at temperatures as low as about 250°F.

The slow-burning flames of diluted hydrogen-oxygen mixtures exhibit certain anomalies which are caused by the higher diffusivity of hydrogen molecules as compared to oxygen. Because of the relatively slow propagation of the combustion wave, significant quantities of both hydrogen and oxygen diffuse into the wave from unburned layers farther away, but the depletion of hydrogen caused by this diffusion extends to a greater distance from the flame surface than the corresponding depletion of oxygen. If the combustion wave were perfectly plane, the diffusion process would settle down to an equilibrium in which the concentration gradients of H_2 and O_2 are adjusted so that both species of diffusion molecules arrive at the flame surface in a quantity ratio corresponding to the over-all mixture ratio. But combustion waves in gases are not normally plane in practice; for example, when initiated by a spark they propagate in an expanding, more or less spherical, configuration, and at any stage they are subject to distortion by the movements of the gas. The diffusion equilibrium is therefore not normally established; instead, those areas of the combustion wave that are curved convex toward the unburned gas receive more hydrogen than corresponds to the over-all mixture ratio, and those areas that are curved concave receive less hydrogen. If the over-all mixture ratio is lean, that is, deficient in hydrogen, the convex areas shift closer to stoichiometric ratio and therefore burn and propagate faster than the average, whereas the concave areas become even more deficient in hydrogen and propagate slower than the average. Thus, any convexity and concavity is accentuated, with the result that the flame surface breaks up into little ripples or "cells". The practical consequences of this

behavior are numerous. In a large space, the cellular flame structure may contribute significantly to turbulence generation, which in turn increases the over-all burning rate, thus making an explosion more violent than one would expect from a relatively "mild" mixture. A mixture of only 4 per cent of hydrogen in air and having a theoretical flame temperature of only about 550°F is considered flammable because it is capable of sustaining little disconnected flame "cells" fed by diffusion of hydrogen from the ambient gas. Such mixture does not support a coherent combustion wave because any concave area in the wave becomes so deficient of hydrogen that burning ceases; the convex areas thus become isolated into discrete cells. Since these cells diminish the hydrogen content of the surrounding mixture they cannot grow in size and can only persist if they are carried bodily into fresh mixture. The only force that can do this is buoyancy; that is, the flamelets are supplied with fuel only as long as they are carried upward by gravitational buoyancy. It follows that a 4 per cent hydrogen-air mixture cannot be ignited at the top of a column or at the ceiling of a room.

With respect to the suppression of flammability by admixture of diluent gas, it is evident that what matters is not the over-all hydrogen/oxygen ratio of the test-mixture but the actual hydrogen/oxygen ratio existing in the vicinity of the incipient flame, which is produced by a spark. This flame has a highly convex surface and is therefore richer in fuel than corresponds to the over-all hydrogen/oxygen ratio. If the over-all mixture ratio is stoichiometric, the incipient flame is fuel-rich. It is therefore not as hot as a stoichiometric flame. In order to make the incipient flame stoichiometric and thus to determine a diluent/oxygen ratio which assures non-flammability with hydrogen at any hydrogen/oxygen ratio, the test must be performed with a less-than stoichiometric over-all ratio. For the hydrogen-oxygen-nitrogen system, it has been determined that for an over-all 2:1 (stoichiometric) hydrogen/oxygen ratio of the test mixture flammability is suppressed by a nitrogen/oxygen ratio of about 16:1, whereas for an over-all 1:1 hydrogen/oxygen ratio the required nitrogen/oxygen ratio is 19:1. The lean 1:1 hydrogen/oxygen ratio is thus found to provide the most severe test condition. It should be noted that the flames generated in near-limit mixtures of this kind are discrete buoyant flamelets, as described. They develop little heat and pressure and are therefore only mildly hazardous in themselves, but they can, of course, carry flame to regions of more potent mixture.

Flames of diluted hydrogen-oxygen mixtures such as hydrogen and air are almost invisible because the spectral emission is essentially limited to the infrared bands of H_2O and the ultraviolet bands of OH. The H_2O bands are located roughly between 1u and 20μ, the two principal bands being centered at 6.3μ and 2.7μ. The OH bands are located between about 0.26μ and 0.36μ, the heads of the most intense bands being at about 0.31μ and 0.28μ. Very hot hydrogen-oxygen flames produce a bluish glow whose spectrum does not show a band structure but is continuous and is believed to be generated by unidentified chemical reactions involving atomic oxygen. The bulk of the radiant energy of a hydrogen flame is emitted by the infrared bands at 6.3μ and 2.7μ.

Tests were run (by A. D. Little, Inc.) to determine if dangerous electrostatic charges can be generated in well-grounded systems during storage and transfer of liquid hydrogen. It was found the maximum field strength for two-phase flow was on the order of 10 volts per centimeter. Since the breakdown potential of hydrogen is normally 17,500 volts/cm, the charge was insufficient to cause spark ignition (by three orders of magnitude). Field strengths during single-phase flow were less than 1 volt/cm.

Field strengths build up in a 5,000-gal. tank during liquid hydrogen transfer were even smaller, 0.01 volts/cm. However, because of the extremely low electrical conductivity of hydrogen, these small charges will persist over long periods of time in storage. (The relaxation time is approximately 1,000 times that of jet fuels).

Other tests were made by A. D. Little to determine the consequences of gross spillage of liquid hydrogen, as would be the case if a storage tank or transfer line ruptured. It was found that when liquid is spilled in this manner, initially all heat supplied to the liquid comes from the ground. After approximately three minutes, some heat contribution is made by condensation of air into the hydrogen pool. The evaporation rate of a diked liquid hydrogen pool is on the order of five to seven minutes. It was found that ignition of the vapor does not significantly affect the rate of evaporation of the liquid although a crushed rock bed greatly increases the evaporation rate.

During these spill tests, the voluminous vapor cloud was ignited by a spark or flame prior to, and up to eight seconds after the spill. Upon ignition, the fireball would

consume almost all of the material within the confines of the vapor cloud and the remaining material in the liquid pool would burn within a few minutes. The vapor cloud and the remaining material in the liquid pool would burn within a few minutes. The vapor cloud would remain close to the ground for a few seconds and then rise slowly and drift downwind.

No detonations were recorded in any of the tests. A number of spill tests were also made in which the vapor clouds were ignited by means of explosive igniters such as 2- and 4-gram pentolite charges. In none of these tests did the vapor cloud detonate. It was concluded that nonideal mixing in the spill tests inhibited the detonation.

Hydrogen-oxygen mixtures have a high explosive potential. On a weight basis, a 5-to-1 ratio of liquid oxygen to liquid hydrogen has 3.3 times as much explosive power as an equivalent weight of TNT. Substituting air for liquid oxygen and using a 1-to-5 weight ratio increases the explosive power (f), surprisingly enough, to 6.6 times that of TNT. The maximum overpressures that would be generated by an LO_2/LH_2 explosion at a 5-to-1 weight ratio can be represented by the following equations:

$$\Delta P_{\text{air burst}} = \frac{4{,}120}{Z^3} - \frac{150}{Z^2} + \frac{39.5}{Z}$$

$$\Delta P_{\text{surface burst}} = \frac{4{,}204}{Z^3} + \frac{276.4}{Z^2} + \frac{42.58}{Z}$$

where:

ΔP = overpressure (psi)

$$Z = \frac{R}{(3.3W)^{1/3}}$$

R = slant range (ft.)

W = weight of LO_2/LH_2 (lb.)

For a 1-to-5 weight ratio of air to LH_2,

$$Z = \frac{R}{(6.6W)^{1/3}}$$

Spillage tests have shown that instantaneous ignition prevents a detonation from reaching its full potential, the explosive values being bracketed between 0.05 f and 0.2 f. For delayed ignition, (f) values will increase to a maximum and then decrease with time. Factors that are involved in determining the explosion potential of a spillage as a function of time include amount of spillage, geometry of spillage (confined or unconfined spaces), rate of vaporization, mixing rate, and types of ignition sources.

Experimental work indicates that it takes a strong initiator to detonate an unconfined mixture of hydrogen and air. In tests with a mixture of 32% hydrogen and 68% air, the stoichiometric ratio of hydrogen to oxygen, no detonation occurred when the mixture was ignited with a hot wire, a spark source, or a squib. When ignited with a two-gram charge of pentolite, the mixture detonated.

Tests were also run on mixtures of liquid hydrogen and solid oxygen and liquid hydrogen/solid air. A hot wire would not ignite the solid air/liquid hydrogen mixture unless the oxygen content was enriched. When pure solid oxygen crystals were subjected to impact in liquid hydrogen, they detonated in a manner similar to RDX, a solid explosive. Impact tests on crystals of air in liquid hydrogen produced no explosions. A drop height of 275 cm and a drop weight of 3.3 kg were used.

3.2 DETONATION OF AN UNCONFINED H_2 - AIR MIXTURE

Under some conditions, the hydrogen vented or leaks from the Launch Vehicle exterior surfaces fill and drain and vent line can form a convection current on boundary layer of Hydrogen - air mixture around vehicle skin, caused by the cold walls of cryogenic propellents. Such an interaction could result in propagation of combustion or detonation wave.

Very little information on detonation of unconfined H_2-air mixtures is available in the literature. The only information which was available was a recent article on the subject by Cassutt (1), who determined minimum ignition energies and detonation limits for unconfined, static, hydrogen-air and hydrogen-oxygen mixtures at atmospheric pressure. The author found that detonation in a static, unconfined, stoichiometric air mixture could be obtained with a two-gram explosive charge of pentolite as the

detonation initiator. Neither a squib nor spark source, when used as initiator gave a detonation wave under these conditions. The detonation limits of H_2 - air Mixtures under these conditions were found to be, Lean 20% H_2 Rich, 50% H_2 whereas those reported for Hydrogen-air mixture confined in tube are Lean 18% Rich 59% H_2 at 1 atmosphere pressure.

On the basis of his experimental results, Cassutt arrived at the following conclusions:

(1) Any mixture capable of sustaining a stable detonation wave when confined in a tube will detonate under unconfined conditions if the initiating impulse is sufficiently intense.

(2) Initiation by at least a two-gram explosive charge is needed to fully detonate an unconfined Hydrogen-air mixture <u>under ideal</u> conditions.

(3) The level of energy required for complete detonation rises as the percentage of hydrogen change from stoichiometric and as a nitrogen dilution increases.

Reference:

1. Cassutt, C. H. - Experimental Investigation of Detonation in unconfined Gaseous H_2-O_2-N_2 Mixtures, American Rocket Soc. Journal Vol. #31, 1961 page 1123.

2. U.S. A. System Command, Hazards of Liquid Hydrogen in Research and Development Facilities - Report # ASD-TDR-62-1027 Dec. 1962.

3.3 SUPPRESSION

The problem of hydrogen combustion and the hazard associated with it in a Saturn class vehicle under pre-launch conditions can be changed markedly when the use of suppressants is considered. "Suppressant" is the term given to some material which strongly effects the limits of flammability or detonatability of a hydrogen-oxidizer mixture. The word can also be used to describe those materials added to a combustion already in progress to interrupt it.

Combustion requires an oxidizer, a reducer, a chemical reaction and a source of ignition and can be interrupted or interfered with by removing any one of the major components. Hydrogen combustion is normally a free radical type reaction. One major form of suppressant acts by removing the free radical step in combusion and can greatly decrease the limits of flammability. The free radical removing type suppressant is frequently a finely divided powder of sodium or potassium bicarbonate. The addition of approximately 0.7 pounds of potassium bicarbonate per square foot of burning surface is required to extinguish a liquid hydrogen flame. Since the mechanism is one of trapping of free radicals, another measure is the number of particles per unit volume necessary to interrupt the chain reaction. In the case of hydrogen and oxygen, combustion can be completely inhibited if somewhat more than 10^{10} particles per cubic foot are injected into the combustible mixture.

The use of gaseous suppressants such as iso-butene in relatively low concentration (1%) can materially reduce the combustion hazard of hydrogen. If added to the purge medium upon sensing an excessive hydrogen concentration, the total amount of such control material would be relatively small.

3.4 CONTAMINATION

Any air trapped in the system will solidify when cooled down to liquid hydrogen temperature. Experimental work and test were performed with solid air and solid oxygen - nitrogen mixtures in liquid hydrogen. Test results indicate it is very difficult to ignite hydrogen and solid air of normal composition. If the mixture was enriched with oxygen, however, ignition sometimes did occur.

Work directed at measuring impact sensitivity confirmed these observations. When pure solid oxygen crystals were subjected to impact in liquid hydrogen, they detonated

in a manner similar to RDX, a solid explosive. However, the addition of nitrogen to the oxygen reduced the sensitivity sharply. With the impact test machine employed, which had a drop height limited to 275 cm, it was not possible to detonate solid air in liquid hydrogen. Indications were that the sensitivity was quite low. As a point of reference, the system solid oxygen-liquid hydrogen is significantly less sensitive than the physical similar system, solid acetylene-liquid oxygen. The critical drop conditions for the explosion of solid oxygen in liquid hydrogen in this testing machine were a 3300-gram weight dropped from a height of 160 cm.

3.5 COMBINED PROPELLANTS

While gaseous phase hazards result from the combination of hydrogen and oxidizer emanating from leaks, an additional hazard results when RP-1 is added to a hydrogen and oxygen leakage mixture. RP-1 is a stable liquid at room temperature and will freeze in liquid oxygen or liquid hydrogen. The gell formed by the liquid oxygen/ RP-1 mixture is impact sensitive and can detonate producting high overpressure. Therefore, RP-1 and O_2 can provide an ignition source for hydrogen. A greater detonatable yield is probable from a combination of hydrogen, oxygen, and RP-1 than from a combination of either fuel with oxygen.

Consideration should be given in the design of vehicle areas where these propellants might mix due to leaks or propellant system failure. Confined compartments such as an intertank adapter should be of particular concern. In an intertank section between LO_2 and RP-1 tanks, hydrogen may enter from leaks external to the vehicle. Consideration should be given to the purge of such compartments with dry nitrogen or air and excluding particularly hazardous ignition sources from that environment.

SECTION IV

MATERIAL

4.1 PROPERTIES OF STRUCTURAL MATERIALS IN LIQUID HYDROGEN SERVICE

In designing components for use in liquid hydrogen service, the designer must consider both the compatibility of materials with liquid hydrogen, and the mechanical properties of materials at the temperature of liquid hydrogen.

Compatibility concerns the deterioration of the materials as a result of chemical action of the liquid or gas in contact with the solid. Because hydrogen is a reducing agent, and most structural materials are in the reduced state, it is not likely that there will be a compatibility problem between hydrogen and any of the metallic or non-metallic structural materials which might be employed in hydrogen service.

On the other hand, the mechanical properties are often severely affected by the temperature of liquid hydrogen. The designer must, therefore, take into account the changes in properties that occur as structural materials are cooled to the liquid hydrogen temperature.

The following mechanical properties are considered to be important from the standpoint of strength and endurance.

1. Yield strength
2. Tensile strength
3. Fatigue strength
4. Impact strength
5. Notch sensitivity
6. Hardness

Other properties which must be considered are the thermal expansion coefficient, and the thermal diffusivity, which affect the stress due to thermal shock.

4.2 METALLIC MATERIALS

The following generalization can be made: as the temperature of a metallic materials is lowered, the yield strength, tensile strength, hardness, and fatigue strength all increase. There are numbers of exceptions to this statement; the most notable is ordinary carbon steel, which undergoes a transition to a

brittle phase as the temperature is lowered to the cryogenic range. An example of this is shown in Figures 4 and 5. This brittle behavior at low temperatures occurs even though the yield and tensile strengths increased by a factor of 2 to 3 or more as the metal was cooled from room temperature to the temperature of liquid nitrogen (77 deg K).

On the other hand, the impact energy of 6061 aluminum increases slightly as it is cooled from room temperature to that of liquid hydrogen. See Figures 6 and 7. The tensile and yield strengths of this alloy increase considerably as it is cooled to liquid hydrogen temperatures. See Figure 8.

Some of the aluminum alloys show a slightly more brittle behavior at liquid hydrogen temperature than at liquid nitrogen temperatures. For example see Figures 9 and 10 for 1100 aluminum.

The impact energies of many of the austenitic stainless steels do not change much between room temperature and liquid hydrogen temperature (Reference 7), but the impact energies of the ferritic and hardenable stainless steels generally decrease through the same temperature range (Reference 7).

Figure 11, reproduced from Reference 8, gives ranges of tensile and yield strengths of some common metals and alloys down to liquid hydrogen temperature.

It is impossible in a short review to give enough data to be of value to the design engineer, because there are so many exceptions to the sweeping generalizations that could be made regarding low temperature metal properties. The designer should possess several good handbook type references on low temperature properties, such as References 7, 11, and 17. Some of these references have collected and condensed data from many sources. Reference 17 lists a bibliography of 1,114 references.

4.3 NON-METALLIC MATERIALS

The non-metallic materials to be considered for use in liquid hydrogen handling systems are polymers; plastics, rubbers, glasses, synthetic fibers, etc. All polymers exhibit a transition from a rubber-like material to a glass-like material as the temperature decreases. The characteristic hardening takes place at

different temperatures for different materials, and the shape of the modulus-temperature curve may be somewhat different due to variations in crystallinity, polarity, chain length, and other structural variations. [1]* This transition is known as the glass-transition. Most polymers exhibit this behavior at room temperature and above, but some hydrocarbon rubbers have transitions at temperatures well below 0°C such as natural rubber -73°C, and GTR-S at -61°C. Liquid hydrogen temperature is well below the glass-transition temperature of all polymers. Polymers will behave similar to that of glass at room temperature having low toughness although withstanding mechanical shock better than glass [3], elongations ranging from 0 to 4%[5], yield stresses 2 to 4 times that at room temperature, and a lower thermal coefficient of expansion. Also at cryogenic temperatures polymers have a higher compressive strength than tensile strength and may be sensitive to surface scratches that start propagation of fatigue cracks when subjected to strain. Polymers should be designed for slightly compressive pre-stress to avoid tensile stresses similar to concrete designs, should be free of surface flaws, and subjected to small deflections.

The coefficient of thermal expansion of polymers is 10 to 20 times higher than that of metals. Plastics below the glass-transition temperature have a thermal expansion of 1/2 to 1/3 as high as above the transition temperature, but still higher than metals. The large coefficient of thermal expansion affects polymers used for transfer piping, storage vessels, and seals. Unfilled polymers, when subjected to cryogenic fluids, will crack and fail unless the polymer is carefully lowered to the cryogenic temperature. Because of the low coefficient of thermal conductivity and the high coefficient of thermal expansion, there will exist when subject to sudden temperature changes a thermal gradient across the polymer which causes a large variation in strain across the section. Below glass-transition polymers are unable to withstand large strains without failure. Thus temperature gradients must be kept small in polymers below glass-transition temperature. Polymers without fillers are not suitable for structural members subjected to thermal shocks. Fiberglass filled polymers have exhibited better thermal shock properties, but have not yet been completely evaluated in this environment. Separating of fiber and resin has been reported during thermal shocks [2].

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* refers to references

Above the glass-transition temperature, the discrepancy between the thermal expansion of a metal flange and a polymer seal was not serious, since the polymer readily distorted to conform to the gland. However, as the joint is cooled below the glass transition temperature of the polymer, the capacity of the polymers to deform to match the metal flange diminishes and is practically non-existent at liquid hydrogen temperatures. Assuming a seal held in place by metal compressing elements at top and bottom surfaces and cooled to low temperature after compression, the reactive forces by the polymer against the compression elements will begin to decrease as soon as the temperature drops through the glass transition. It may actually decrease to zero and the polymer seal may shrink away from the compressing faces if some provision is not made. With elastomers (Viton, natural rubber, and neoprene) it is possible to initially compress them 80 to 90% [3] compression before cooling to insure positive sealing. If the polymer cannot be initially compressed sufficiently, the seals may be either spring loaded or the joint heated [4] to prevent excessive contraction of the polymer.

Other properties which should be considered in seal design are stress relaxation and fatigue strength. Unfortunately, experimental data is difficult to obtain and its publication limited.

Teflon FEP (Fluorinated Ethylene Propylene) is preferred to Teflon TFE (Trifluorochloroethylene) because of its better toughness and elongation at -420°F. Teflon cold flows when under a force and must be confined to limit the flow. Filled teflon with glass particles has added strength, reduced thermal contraction, and inhibited cold flow. Also filled Teflon does not seem to become appreciably harder when cooled to cryogenic temperatures. Edges, however, tend to shed and flake [3]. Composite materials in cryogenic environment are under investigation.

Viton, an elastomer at room temperature, behaves similar to Teflon and cryogenic temperatures having an elongation less than 4%.

Silicone rubber should be avoided at liquid hydrogen temperature because its elongation approaches zero and therefore has low toughness.

Laminates and glass filled resins improve the properties of these resins at cryogenic temperatures, but the resin has a tendency to separate from the filler. This concept is in research and shows the most promise for the future.

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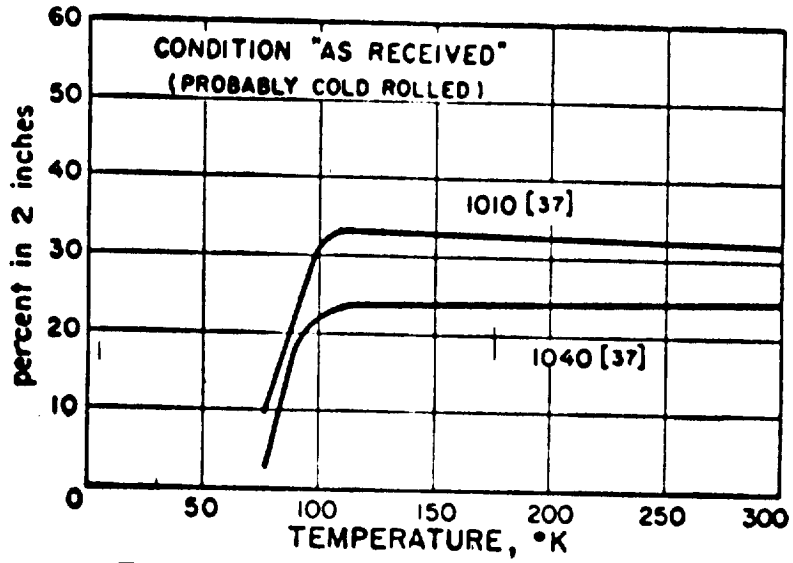
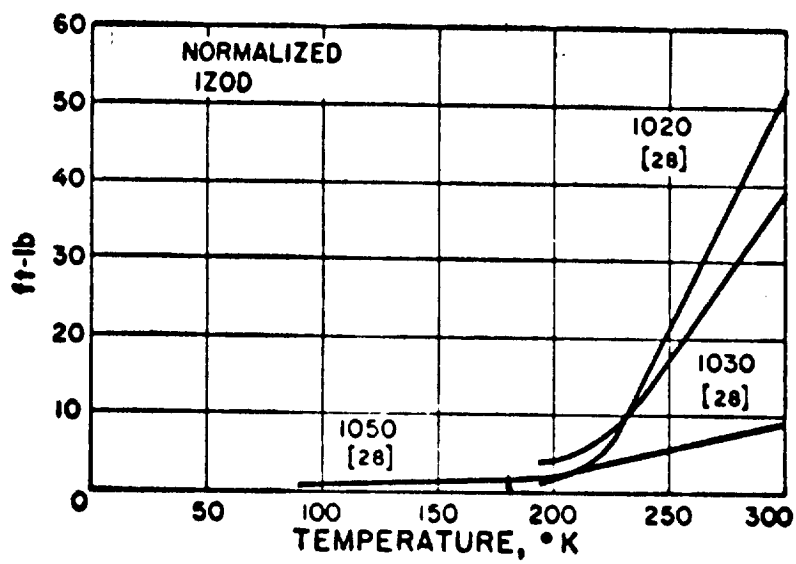


ELONGATION OF SOME AISI-SAE PLAIN CARBON STEELS

Figure 4



IMPACT ENERGY OF AISI-SAE PLAIN CARBON STEELS

Figure 5

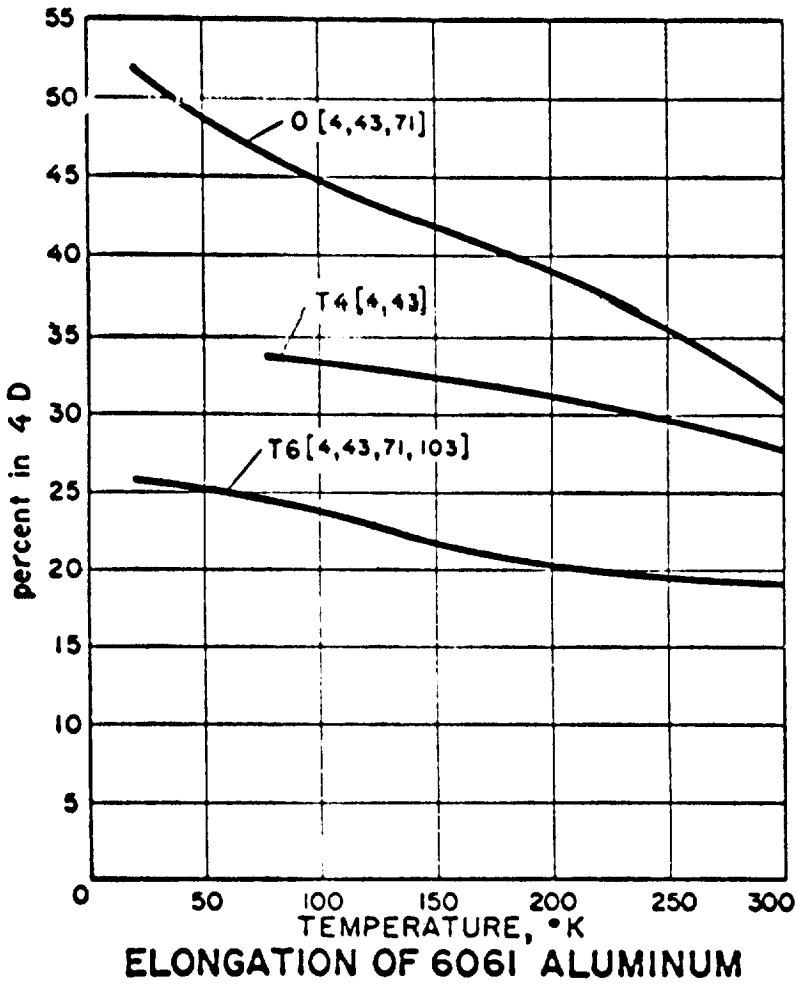


Figure 7

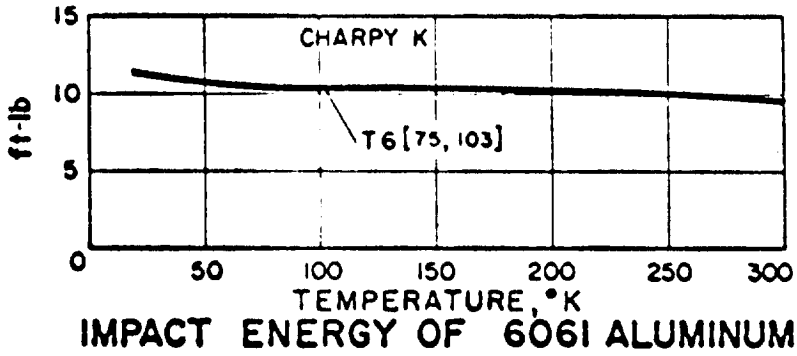
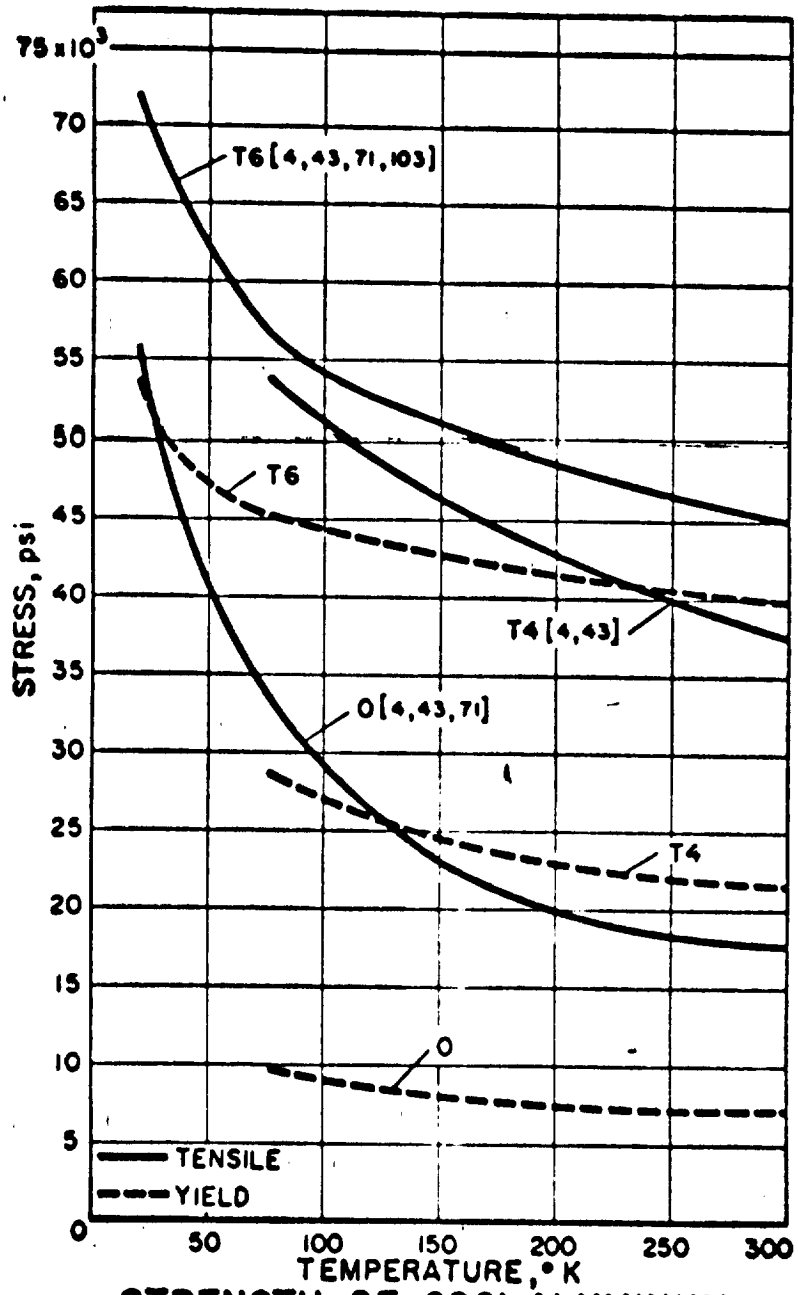


Figure 6



STRENGTH OF 6061 ALUMINUM

Figure 8

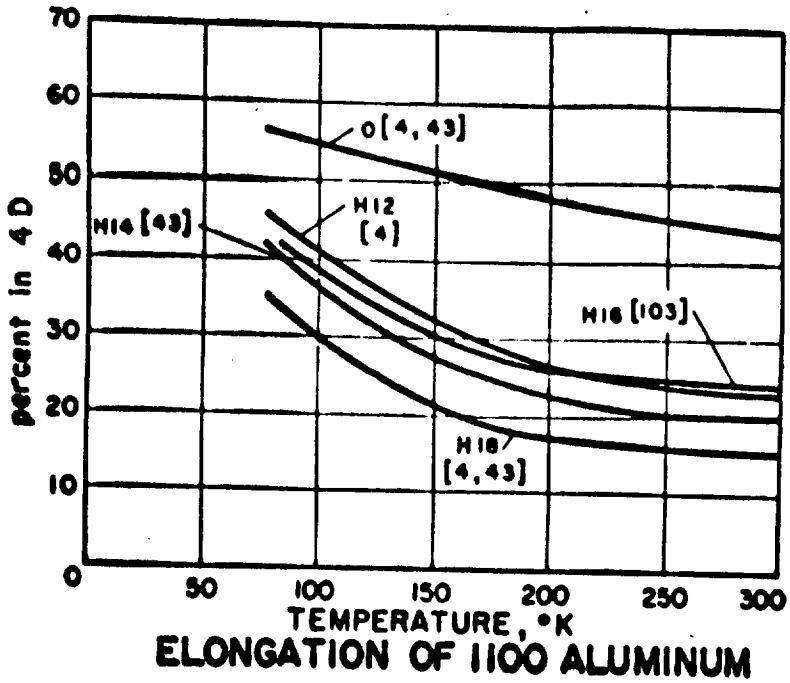


Figure 9

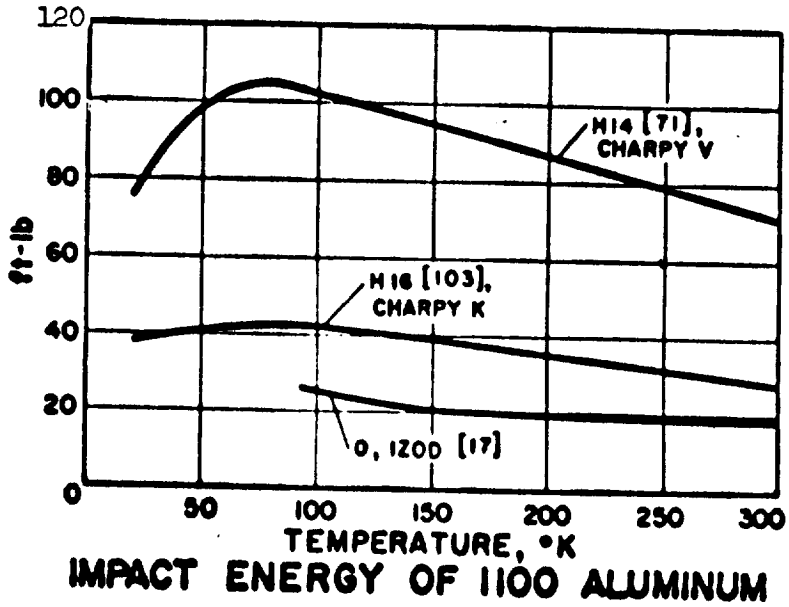
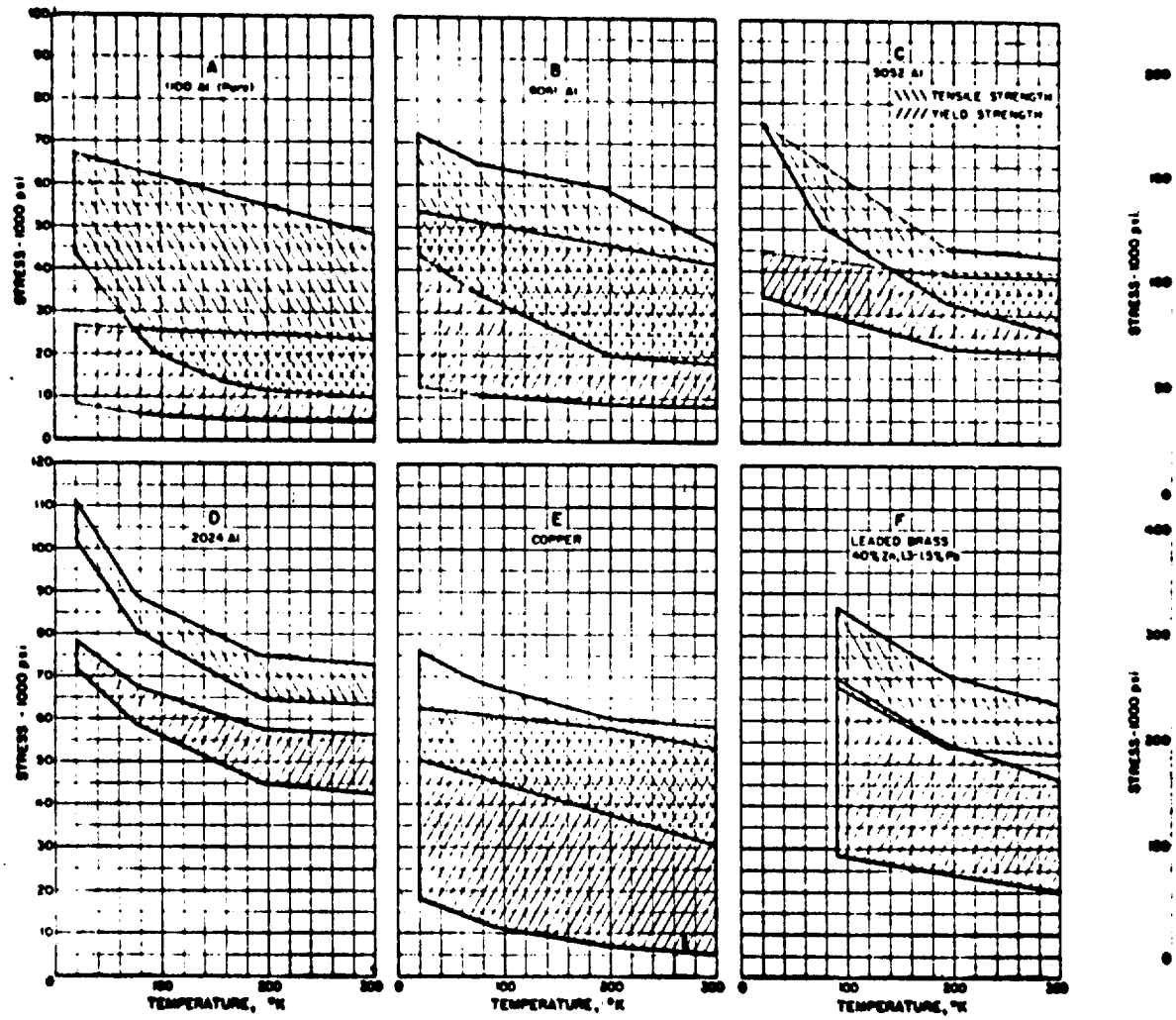


Figure 10



Tensile and yield strengths of some common metals and alloys.

Figure 11

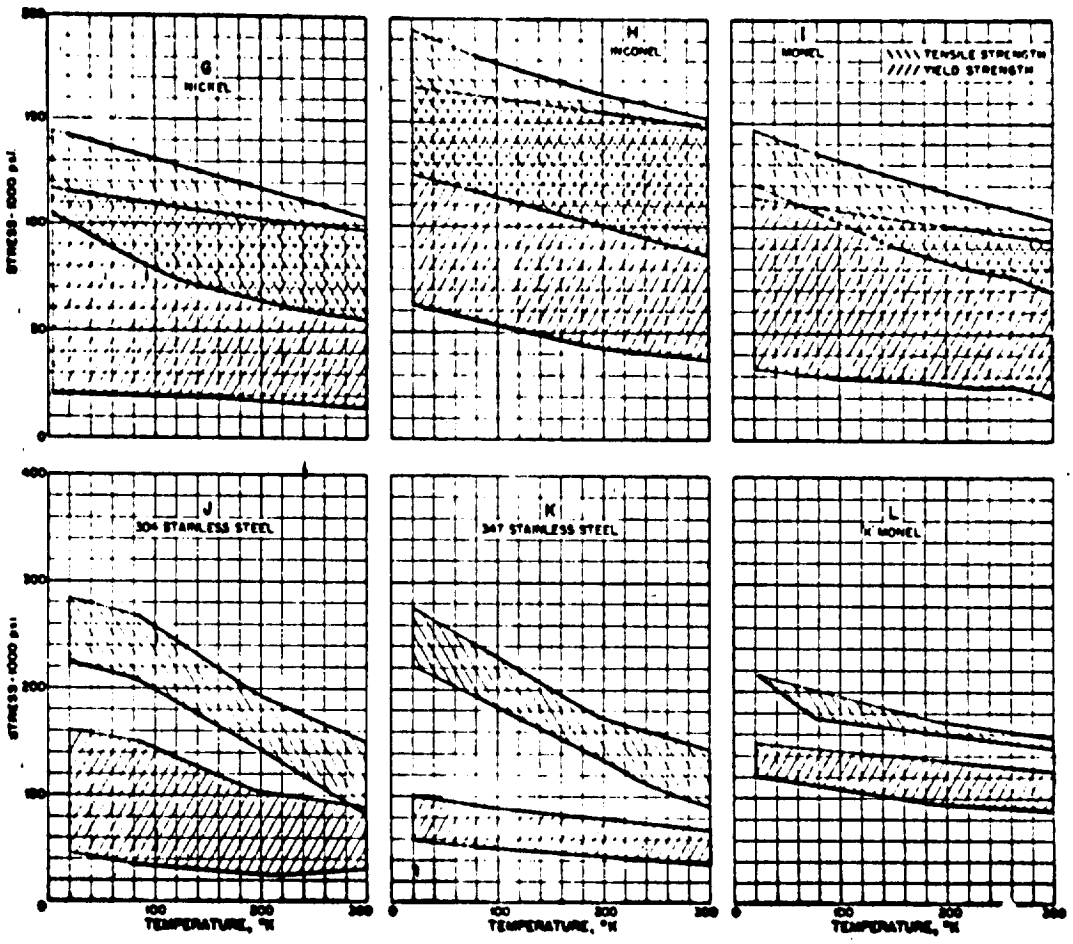


Figure 11 (Continued)

SECTION V

DESIGN CONSIDERATION

5.1 VENTILATION - COMPARTMENT

The principal danger from Hydrogen spills or leaks is fire. Proper ventilation in confined areas and provisions for enhancement of evaporation will help to reduce the fire danger.

The main purposes of a launch vehicle compartment interstages ventilation to maintain are good thermal control and prevent potential hydrogen hazards. In the cases where liquid hydrogen can evaporate into a confined area, steps shall be taken to assure that the area is adequately ventilated to prevent the accumulation of excessive gaseous hydrogen concentration in the confinement. The vent system must have sufficient vent area to relieve a buildup of compartment/interstage pressure differential during boost phase and prevent air inflow resulting from winds. Confined areas should be ventilated at the highest and lowest point so that hydrogen will not accumulate.

5.1.1 Compartment Arrangements

Hydrogen gas diffuses rapidly through a compartment in a non-uniform pattern. Vehicle design should consider the need for purging and locating components such as valves. Pockets and dead ends should be avoided. The area of intersection of bulkhead and adapter sections and any flexible seal between them should receive special attention. The seal around tubes and harnesses in the systems tunnel is another example. It must be remembered that the seals placed in such areas to prevent the entrance of hydrogen also obstruct purge gases.

Since oxygen and nitrogen are constituents in air, consideration should be given to the fact that oxygen has a higher freezing point than nitrogen; therefore, condensation on hydrogen lines or vessels will be oxygen rich. Insulation will tend to trap the oxygen if separation or gaps are present in the insulation.

5.1.2 Venting of Boil-off Gas

Decisions regarding particular venting procedures depend on a number of factors such as venting rate, continuous versus intermittent venting, temperature of

vent gases, vent-stack environment, etc. The following practices merit consideration:

a. Boil-off gas should be vented in an area distant from operating and inhabited areas.

b. Pressurization of the vent line with inert gas and utilization of a check valve at the discharge end are very desirable to prevent air-in leakage. Check valves at the ends of vent lines are frequently designed to operate at pressures on the order of 0.5 psig. For intermittent operations where no positive pressure system is employed, a purge with an inert gas prior to and accompanying venting is desirable.

c. Flaring of vent gases for burning is desirable if considerable flow is anticipated. A quantity level of 30 pounds per minute of continuous flow has been suggested as an arbitrary criterion; i.e., quantities in excess of this amount should be flared. However, other factors of terrain, environments, etc., must be considered. Continuous burning igniter systems such as propane burners provide suitable ignition on flared vent stacks. At some locations where large quantities of boil-off gas are vented, the vent gases are passed through a water bubbler designed to prevent air-in leakage. The boil-off gas is then flared above the water bubbler.

d. On vent systems that are not flared, it should be noted that a sudden release of hydrogen boil-off gas can result in spontaneous ignition. Any device that prohibits flow such as sudden pressure buildup and rapid venting can be used to substantially reduce the probability of a spontaneous ignition.

In venting systems pressure relief devices are usually used on all equipment where an excessive pressure may build up. This is especially important in systems where trapped residual liquid hydrogen may vaporize with explosive force if the insulation is faulty, as in a transfer line between valves. As an example, the pressure rise due to one cubic foot of liquid hydrogen vaporizing and warming to 68°F in a volume of ten cubic feet is 1154 PSI.

Rupture discs and relief devices are normally used on vehicle containers, vent and transfer lines. The rupture discs are designed or set to handle the worst possible conditions.

5.2 PURGE

5.2.1 Purging of Interstage Compartment

While the Saturn vehicle is on the launching pad, a danger may arise due to the leaking of H_2 into the interstage compartment. There are two purge conditions involved. First: initiate inert purge to clear air prior to hydrogen tanking; secondly: continuation of inert purge to remove after H_2 tank drainage. In order to avoid potentially hazardous condition the interstage compartment is purged continuously while the vehicle is tanked to ensure that H_2 concentrations are kept below dangerous levels. A study was performed in the program to determine general requirements associated with the purging operation..

The analysis considered H_2 leak rates as a parameter. O_2 leak rates were not considered. While maintenance of concentrations of O_2 below a certain limit (4.9%) does render any mixture of H_2, N_2, and air non-combustible, use of such a criterion as a measure of safety is not practical. The possibility of air seepage providing the necessary O_2 to support combustion is too great. The only practical limits which can be relied upon are those which are imposed on the fuel portion of the mixture.

If it is assumed that the O_2 leak rates are of the same order of magnitude as the H_2 leak rates, the amount of O_2 entering the compartment would be small compared to the purge medium. As such, this leakage of O_2 would have only a second order influence on the properties of the mixture. Consequently, O_2 leak rates could be ignored in the analysis.

With hazard level based upon H_2 concentration, it is immaterial to the mechanics of purging whether air or N_2 is used as the purging medium.

Since the molecular weights of air and N_2 are so close, only a very small difference in the results would be noted if separate analyses were performed. Because of this, only N_2 was considered as the purging medium in this analysis. The results can be applied to air purge considerations with very little error.

It may be noted that on the basis of H_2 concentration alone, the purging of the interstage compartment could be accomplished with about equal effectiveness by either N_2 or air. On a cost basis, use of air should certainly be the more economical. Use of N_2, of course, provides an extra margin of safety by lowering the O_2 concentration along with H_2 concentration so that both would be below their respective lower limits for combustion of the mixture. In addition, if an unanticipated surge of H_2 occurred, a dangerous concentration of H_2 and O_2 could result with air as the purge medium. With N_2 as the purge medium, this high concentration of H_2 would not be dangerous since no additional oxidant would be involved.

The purging analysis was based on H_2 leakage and N_2 purging. The analysis is a simple and straightforward treatment of the flow of gases through a volume at conditions of constant pressure and constant temperature. Four parameters were considered in this analysis. These were H_2 leak rate, N_2 purge rate, maximum permissible concentration of H_2 and lowest concentration of H_2 achieved by purging. The data obtained as functions of these parameters have been presented in forms which should be useful in either devising purging design requirements and procedures for a given leak rate or for evaluating the suitability of existing procedures.

The results of the purging analysis are presented in Figures 12 through 18. Figure 12 presents the time required for the H_2 concentration of the mixture to rise from a lower limit achieved by a preceding purge cycle to the maximum permissible concentration. The concentration of 4% has been used as the upper limit to the maximum permissible since this is the actual lower limit for combustion of mixtures of H_2, N_2 and O_2 (varying from 3.9% for H_2 and O_2 alone, to 4.1% for H_2 in air). Various upper and lower operating limits within these bounds have been considered.

Figures 13, 14, and 15 present the duration of the purge required as a function of H_2 leak rate and operating limits for H_2 concentration. Three purge rates are considered 2000 ft^3/min. 3500 ft^3/min. and 5000 ft^3/min. It is to be noted that the purge duration is relatively insensitive to the H_2 leak rate at the lower leak rate values. An abrupt increase in purge duration occurs as the leak rates are approached for which continuous purging is necessary to maintain selected concentrations. The vertical lines on the plots represent the conditions under which the leak rate is the given percentage of the total gas flow rate. These are, in effect, continuous purge results for which steady-state conditions are maintained.

Figures 16, 17 and 18 present, as functions of H_2 leak rate and operating limits of H_2 concentration, the N_2 use rates averaged over the entire purge-no purge cycle. These data can be employed to determine the quantities of the purge medium required for the purging operation simply by multiplying the average use rate by the time duration of the operation. As can be seen, for a given width of the operating limits, more N_2 is required if the concentrations involved are lower. For example, for an H_2 leak rate of 0.01 lb/min and an N_2 purge rate of 2000 ft^3/min the data of Figure 16 shows that about 4 lbs. of N_2 per minute would be required to operate between the limits of 2 and 1%. Similarly, N_2 requirements are greater if wider operating limits are maintained. For the same example, about 7 lbs. of N_2 per minute are required for operation between the limits of 4% and 1% as compared to 4 lbs/min for limits of 4% and 3%.

The general conclusions which can be drawn from the N_2 use rate data of Figures 16, 17, and 18 are that, keeping the H_2 concentration operation limits as narrow and as high as permissible, represents the most efficient purging operation. Safety requirements, of course, should always take precedence over efficiency.

Efforts were also directed in the purging investigation to the requirements for continuous purging. Results are presented in Figure 19 in which the purge rate required to maintain a desired H_2 concentration is given as a function of leak rate. These data may also be considered to show how large a leak can be tolerated for a given continuous purge rate.

TIME REQUIRED FOR H_2 CONCENTRATION TO REACH UPPER LIMIT AS A FUNCTION OF H_2 LEAK RATE AND LOWER LIMIT

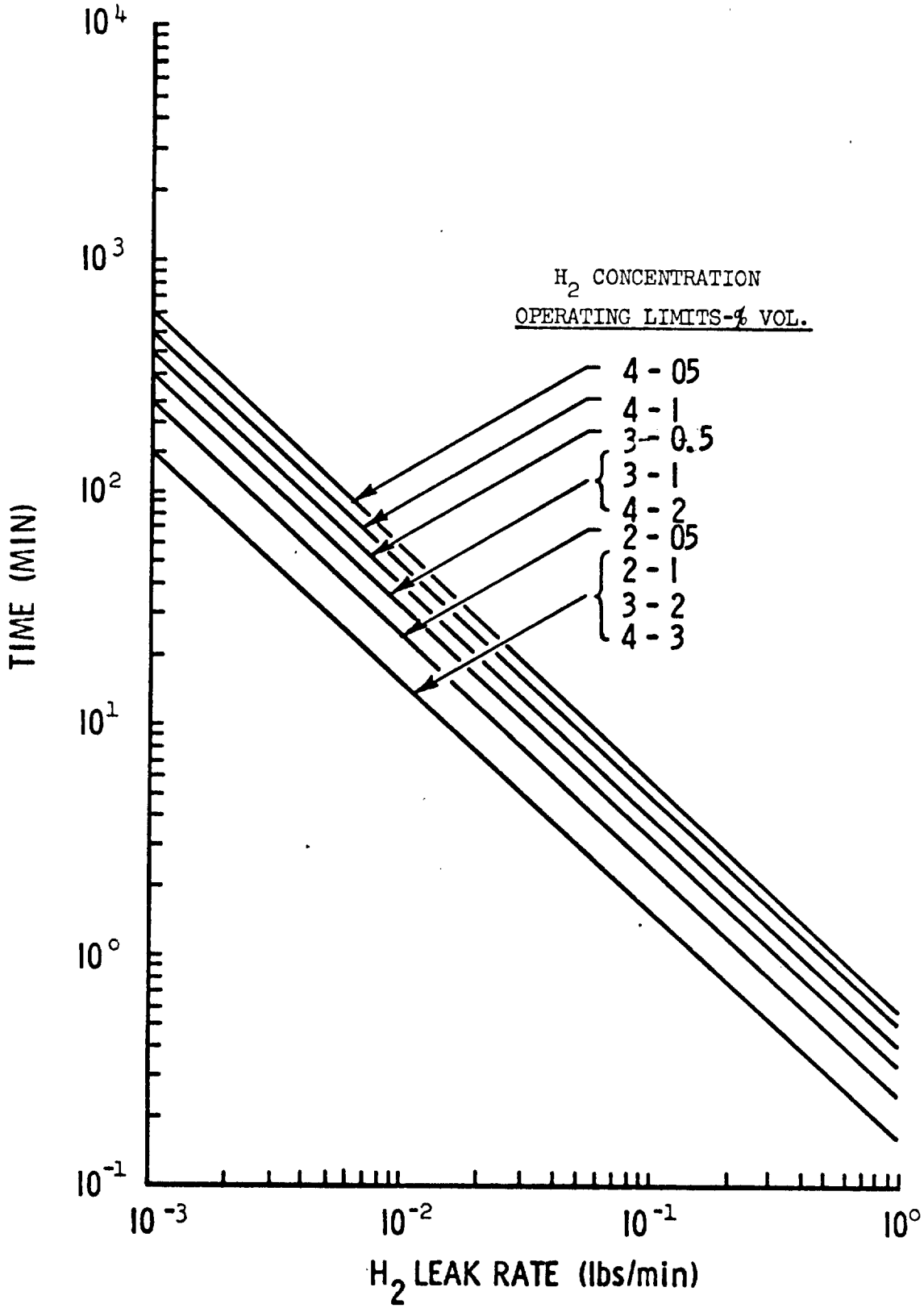


Figure 12

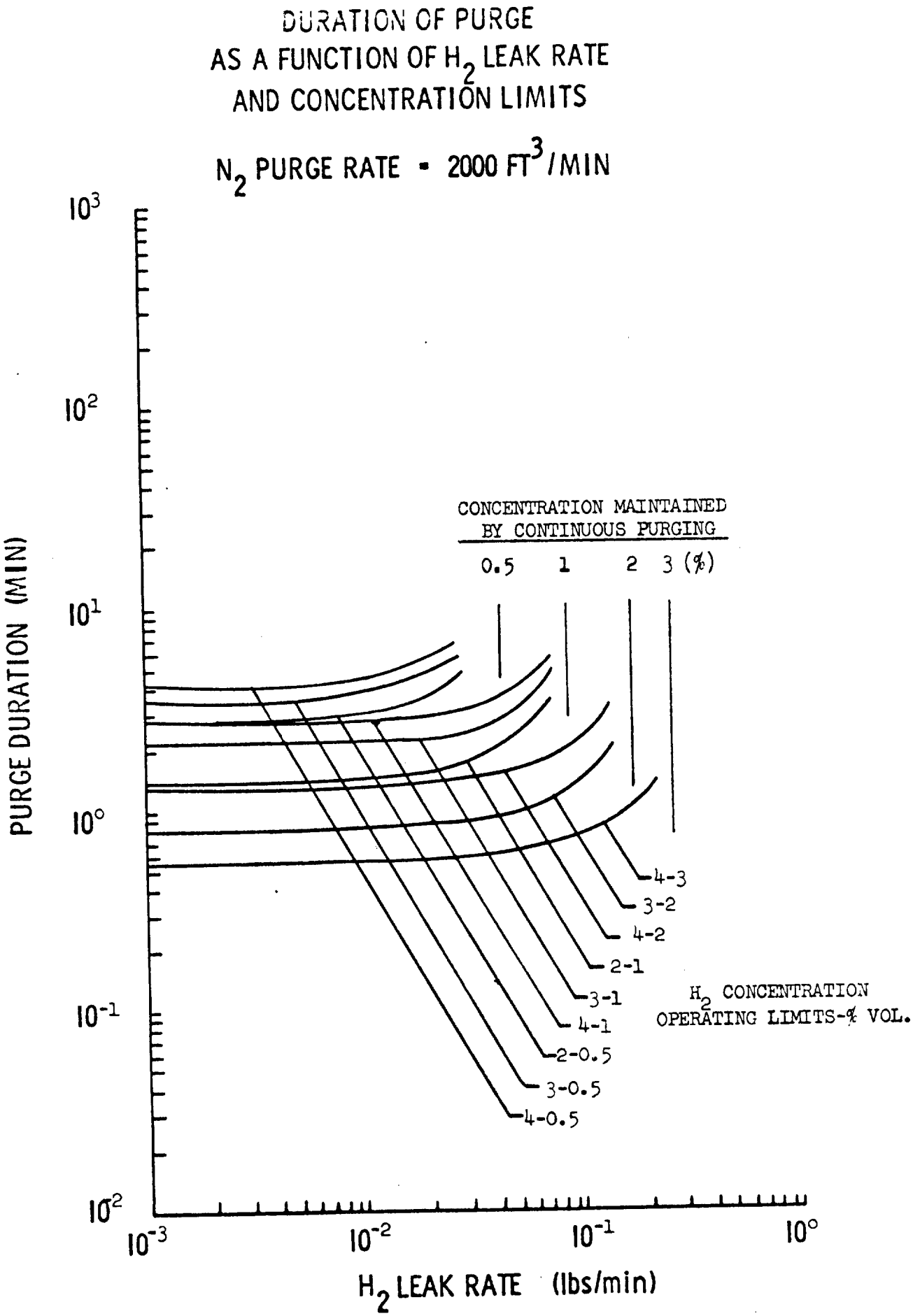

DURATION OF PURGE
AS A FUNCTION OF H_2 LEAK RATE
AND CONCENTRATION LIMITS
N_2 PURGE RATE = 2000 FT^3/MIN
PURGE DURATION (MIN)
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-2}
10^{-1}
10^0
H_2 LEAK RATE (lbs/min)
CONCENTRATION MAINTAINED
BY CONTINUOUS PURGING
0.5 1 2 3 (%)
4-3
3-2
4-2
2-1
3-1
4-1
2-0.5
3-0.5
4-0.5
H_2 CONCENTRATION
OPERATING LIMITS-% VOL.

Figure 13

DURATION OF PURGE
AS A FUNCTION OF H_2 LEAK RATE
AND CONCENTRATION LIMITS
N_2 PURGE RATE = 3500 FT^3/MIN

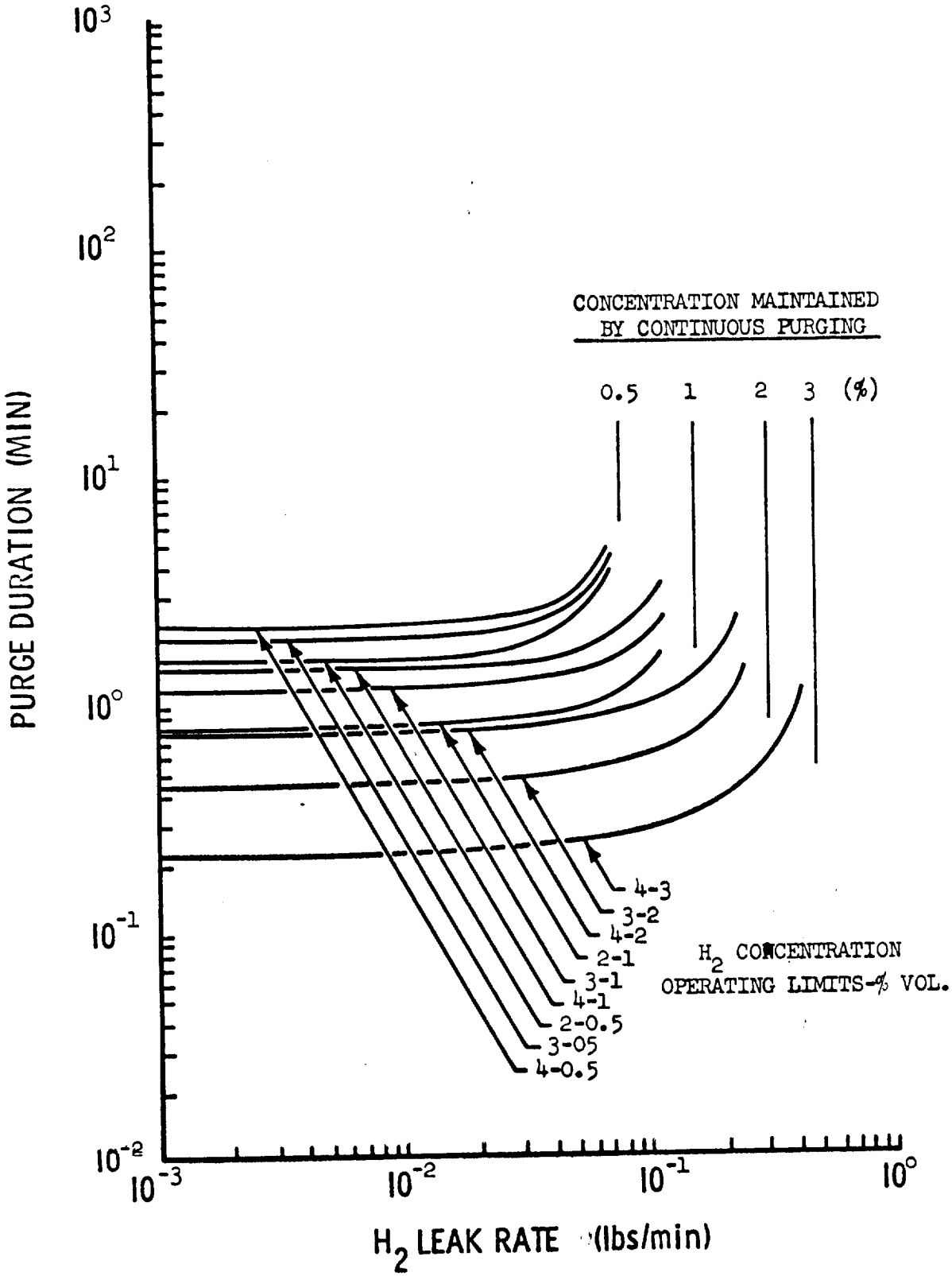


Figure 14

DURATION OF PURGE
AS A FUNCTION OF H_2 LEAK RATE
AND CONCENTRATION LIMITS
N_2 PURGE RATE = 5000 FT^3/MIN

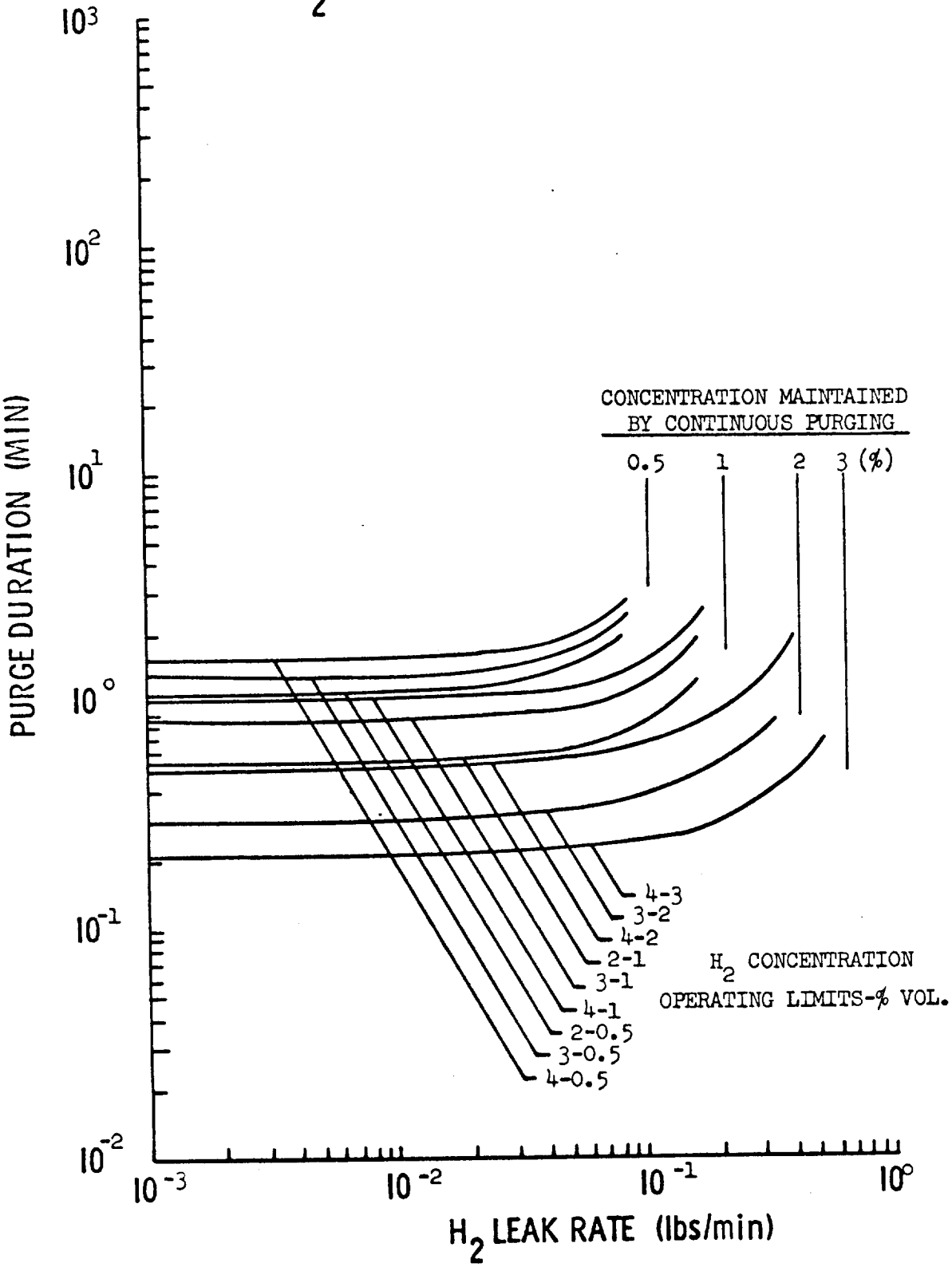


Figure 15

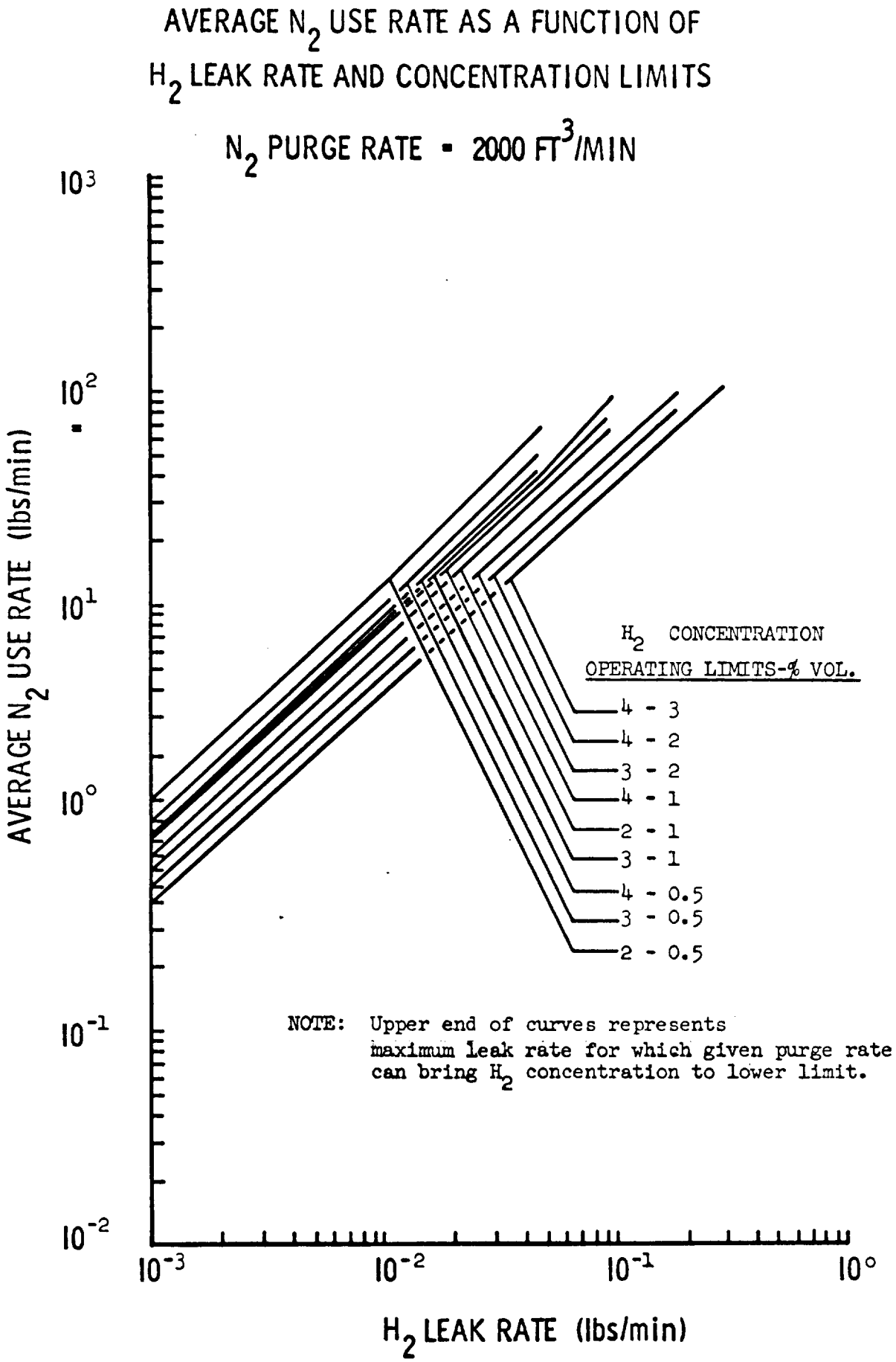

AVERAGE N_2 USE RATE AS A FUNCTION OF
H_2 LEAK RATE AND CONCENTRATION LIMITS
N_2 PURGE RATE = 2000 FT^3/MIN
AVERAGE N_2 USE RATE (lbs/min)
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
H_2 CONCENTRATION
OPERATING LIMITS-% VOL.
4 - 3
4 - 2
3 - 2
4 - 1
2 - 1
3 - 1
4 - 0.5
3 - 0.5
2 - 0.5
NOTE: Upper end of curves represents maximum leak rate for which given purge rate can bring H_2 concentration to lower limit.
10^{-3}
10^{-2}
10^{-1}
10^0
H_2 LEAK RATE (lbs/min)

Figure 16

AVERAGE N_2 USE RATE AS A FUNCTION OF
H_2 LEAK RATE AND CONCENTRATION LIMITS

N_2 PURGE RATE = 3500 FT^3/MIN

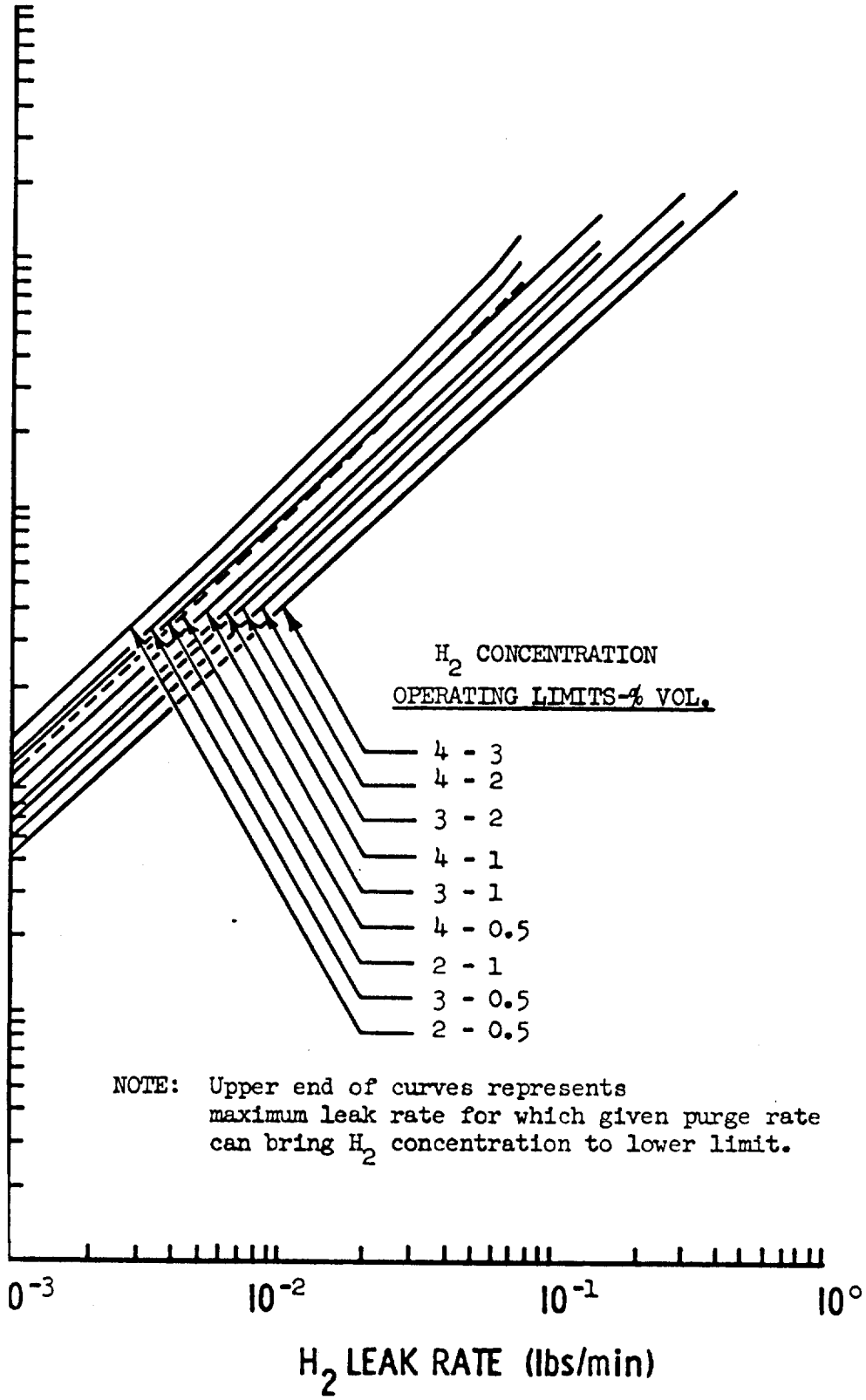


Figure 17

AVERAGE N_2 USE RATE AS A FUNCTION OF
H_2 LEAK RATE AND CONCENTRATION LIMITS
N_2 PURGE RATE = 5000 FT^3/MIN

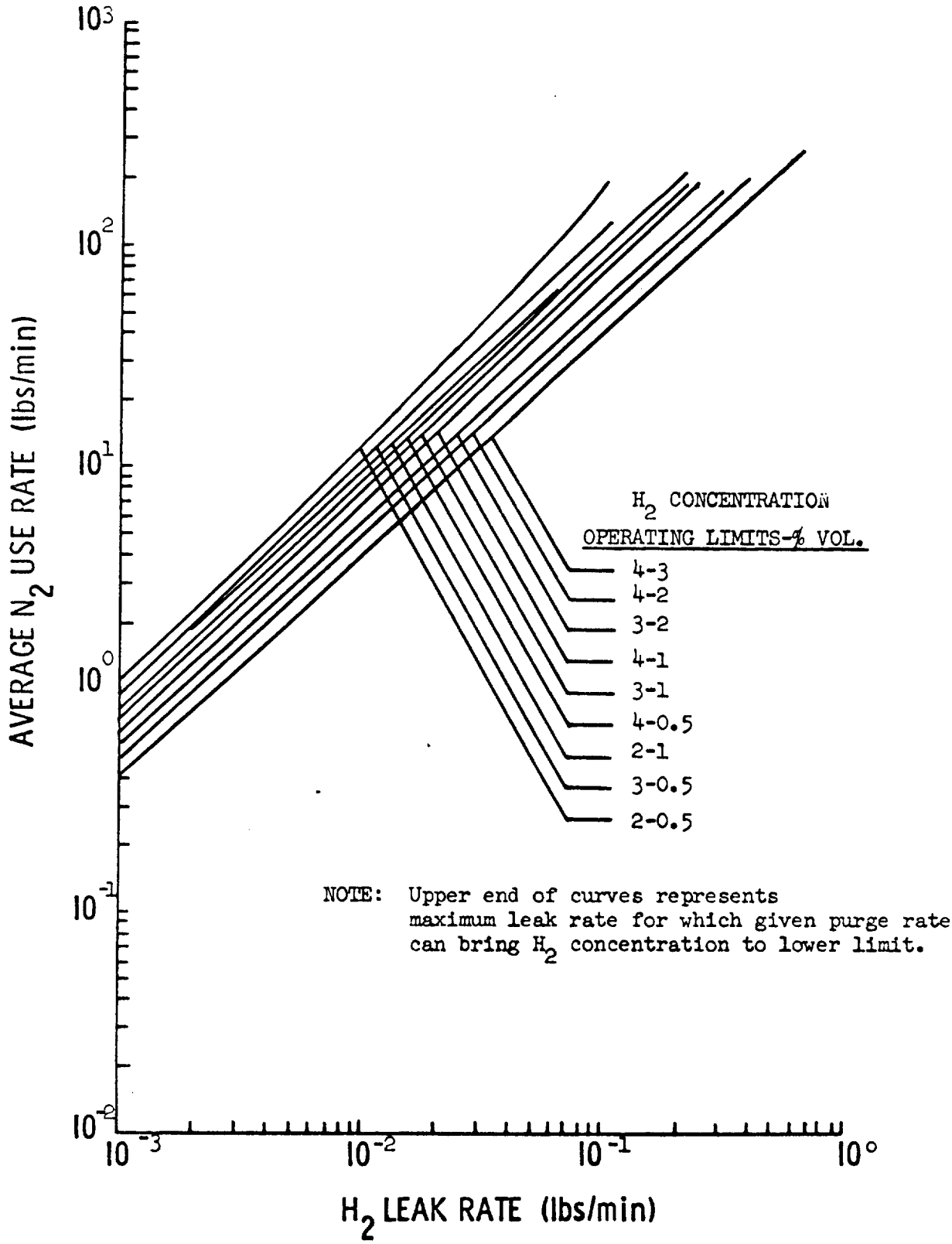


Figure 18

Concentration Maintained by Continuous Purge as a Function OH_2 Leakage

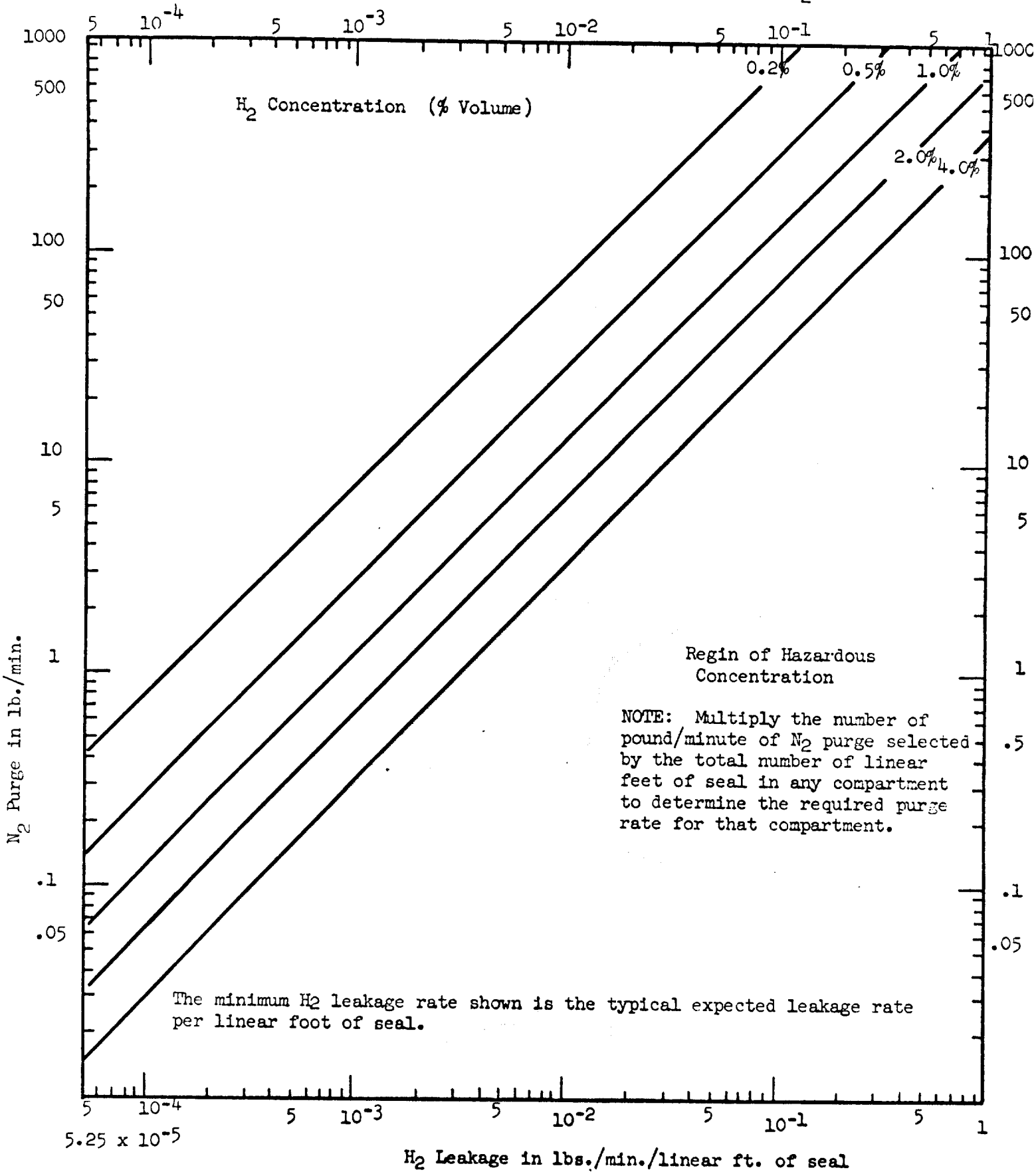


Figure 19

Throughout the analysis, perfect mixing within the compartment has been assumed. In reality, however, some regions may be purged more or less effectively than calculations show because of imperfect mixing. To ensure safe practice in the purging operation, consideration should be given to purge inlet design to minimize the possibility of stagnation regions occurring in which dangerous concentrations of H_2 may accumulate.

5.2.2 Purging - Hydrogen Propulsion System

Prior to the introduction of liquid hydrogen into vehicle containers and the propulsion system, potentially hydrogen hazardous situations may exist. A purging of the hydrogen propulsion systems is required, and must be accomplished, to avoid the following:

1. Combustible mixtures within the systems
2. Contamination of liquid hydrogen
3. Gases which may freeze into particles during propellent loading
4. Combustible mixtures upon dismantling the system.

Most purge techniques employ helium, nitrogen, or hydrogen gas.

Helium is the best choice if cost is not a major factor. Nitrogen is an effective purge gas, however, it solidifies at liquid hydrogen temperatures. Therefore, if nitrogen is used, a hydrogen gas purge must be achieved before liquid hydrogen is introduced.

If hydrogen is used as a purge gas, care must be taken to insure that combustible mixtures are not formed. Nitrogen may be used as an intermediate purge to reduce the probability of forming a flammable mixture.

5.3 GAS LEAK DETECTORS

There are several gas analysis methods currently in use industrially to detect leakage of hydrogen and other combustible gases into normal ambient air. Current design approaches for hydrogen detectors are based on:

1. A difference in thermal conductivity between the leaking gas and ambient gas.
2. Temperature rise due to catalytic combustion of the leaking gas at a solid interface.

Leakage of oxygen into ambient air could conceivably be detected using gas analysis methods sensitive to oxygen. However, the situation is somewhat different in that a high background of oxygen ($\sim$ 20%) is normally present and some normal variation could be expected even in the absence of leakage. Where only moderate sensitivity was sufficient, or in situations were the ambient was oxygen-free or depleted of oxygen several oxygen analysis methods might be useful.

5.3.1 Detecting Hydrogen Leakage into Air by Thermal Conductivity Difference

At room temperature, the thermal conductivity of hydrogen is about 7 times that of air. This fact can be utilized in rather simple equipment which measures the relative thermal conductivity values of gas sampled from the monitored region and a reference gas sample. This is done by determining heat loss from an element which is heated above the ambient gas temperature. Heat loss due to radiation and other non-conductivity sources renders the device useless as an absolute measure of conductivity, but placement of a second heated element in a known gas provides a reference heat loss to which the analyzer heat loss may be compared.

In the more common forms of the device, the heated elements are either fine wire filaments or thermistors, which serve both as a heater and temperature detector. Two such elements and two fixed resistors are connected to form a Wheatstone bridge; one element is sealed into a volume of reference gas and the other exposed to the gas under test. The excitation voltage impressed upon two diagonally opposite corners of the bridge causes power to be dissipated in the elements with a resulting temperature rise above the ambient. An output potential then appears across the remaining two diagonals which is a function of the differential temperature of the elements, and may be related to thermal conductivity by calibration against known standards. Should both elements be in air, the temperature and therefore the resistance of both elements will be the same, resulting in a "balanced" bridge. Upon exposure to H_2, for example, the greater heat loss from the analyzer element will reduce the temperature of this element, the resulting resistance change unbalancing the bridge and causing an output signal. Replacement of the two fixed bridge arms with two more active arms will essentially double the usable signal, but seldom warrants the additional expense.

Indirect methods of determining heat loss, such as thermocouples attached to the heated elements, are also commonly used. Higher sensitivity and greater precision can be achieved by using a servo system to maintain a given temperature relationship. The power required to maintain the balance may then be related to thermal conductivity.

Selection of circuit approach and type of element depends on the load and stability requirements. A low impedance ($\sim$ 10 ohms) hot wire bridge can be used to best advantage to drive a conventional D'Arsonval meter movement and supply as much as 20-30 mv./percent H_2. Similarly, a high impedance (10-100 K ohm) thermistor bridge can supply a proportionally higher voltage to a high impedance amplifier input. A typical thermistor bridge may supply 5 times as much output voltage as a hot wire bridge at room temperature, but will supply the same output at approximately 200°F due to its large temperature coefficient. Ambient temperature is therefore an important consideration in bridge element selection. Where the application requires low power consumption, the thermistor bridge is more suitable.

For application to H_2 leak detection a a compartment or hooded area, it is only necessary to allow the compartment atmosphere to diffuse into the chamber containing the unsealed sensing element.

The thermal conductivity approach is not specific to hydrogen as it will detect other gases present when their thermal conductivity differs from that of air. However, sensitivity to hydrogen is much higher than other gases normally encountered. A thermal conductivity detector capable of detecting 0.1% H_2 in air would also be slightly affected by normal humidity variations.

The list below of the thermal conductivities relative to air of some common gases gives an indication of possible interfering gases:

Hydrogen	7.01
Helium	5.93
Neon	1.92
Methane	1.13
Air	1.00
Ethane	.88
Ethyl Alcohol	.71
Methyl Alcohol	.59
Carbon Dioxide	.59
Propane	.50
Benzene	.37

Those above air in the table would cause a high indication of hydrogen, those below a low indication.

5.3.2 Detecting Hydrogen Leakage into Air by Catalytic Combustion on a Filament

In this type of detector, any hydrogen or other combustible gas in an air sample reacts catalytically on a platinum filament. The heat of reaction raises the temperature of the filament and therefore its resistance. By incorporating such an element as one of the members of a Wheatstone bridge, and employing an identical element sealed in air as a reference arm of the bridge, it is possible to use the bridge output signal as an indication of the combustibles content of the gas sample.

The method is not specific to hydrogen but responds to any combustible gas. It is not a useable approach in an oxygen-free atmosphere. The response of the instrument to various materials is related to their heat of combustion, and the activity of the catalyst employed. In some cases certain materials present in the atmosphere as contaminants can interfere with proper operation of the method by poisoning the catalyst.

5.3.3 Hydrogen Leak Detection Using the Palladium Window

In this method, use is made of the high specific permeability which heated palladium exhibits toward hydrogen. The sample gas is brought into contact with the window under such conditions that hydrogen diffuses through into an enclosed space where it is detected by various means. The method is most useful in a non-oxidizing atmosphere. It will work with air but threshold sensitivity is reduced to the order of several percent of hydrogen, probably because hydrogen is destroyed by catalytic combustion on the Palladium.

5.3.4 Halogen Type Hydrogen Detector

This detector operates by aspirating a sample of air between the electrodes of a diode-type sensitive element. The positive electrode is a heated metallic surface and the negative electrode is a relatively cool metallic surface surrounding the positive member. At correct operating temperatures a faint positive ion current flow is detectable for random air samplings. However, when the air is contaminated with very slight amounts of vapor from the halogen compounds, there

is substantial increase in ion current flow. This type of detector is well suited for H_2 detection.

This type of hydrogen detector is being developed by General Electric Company of Daytona Beach, Florida

5.3.5 Polarographic Hydrogen Detectors

A relatively new type of detector which has not yet seen industrial service utilizes an electrochemical cell which produces an output current proportional to the hydrogen content of the sample gas. A typical cell consists of a zinc sulfate cathode and a platinum plated gold anode contained in a gel of electrolyte such as potassium chloride. Hydrogen diffusing through a thin teflon barrier, produces a related current in a properly biased cell.

Such cells tend to be rather temperature sensitive and are useable over a rather narrow ambient temperature range.

5.3.6 Polarographic Oxygen Detectors

This sensor is geometrically similar to the hydrogen detector described above. It differs in that a platinum cathode and silver anode are used and the bias level and polarity are different. It is subject to the same limitations mentioned for the hydrogen detector.

5.3.7 Paramagnetic Oxygen Detectors

This method makes use of the fact that oxygen is one of the few para-magnetic gases, i.e., it is attracted by a magnetic field. This property is pronounced at room temperature but decreases as temperature increases. It is utilized in various ways in instrumental gas analyzers. In one approach, a heated analyzer filament is positioned in a strong magnetic field and connected as one member of a Wheatstone bridge. A similar reference filament is connected in the bridge, but outside the magnetic field. Sample gas containing oxygen introduced in the vacinity of the analyzer filament causes a temperature change due to oxygen movement relative to the filament. Cold oxygen attracted into the field is heated by the filament and becomes diamagnetic. In this state it is displaced by additional cool oxygen. The net result is a cooling "wind" of oxygen proportional to the oxygen content of the sample which results in a corresponding output signal from the bridge.

The method will also detect other paramagnetic gases, the most common being NO and NO_2.

5.4 IGNITION SOURCES

5.4.1 General

Likely sources of ignition in the hydrogen area shall be eliminated.

a. Very minute sparks are ignition sources.

b. All electrical connections must be tight.

c. No open flames or sparking equipment are permitted.

d. Internal sources of ignition must be eliminated. In plumbing containing Pearlite insulation, the Pearlite may cause ignition.

5.4.1.1 Friction and Impact Sparks

These ignition sources are glowing bits of metal or stone and may be caused by hand or mechanical tools.

5.4.1.2 Tools

(Ref. "Sparking Characteristics and Safety Hazards of Metallic Materials", Tech. Rpt. NGF-T-1-57 NAVORD Rpt. 5205)

Tests and experience have shown that so-called "spark-proof" tools are not spark-proof, and do cause ignitions.

Further, with hydrogen, the energy required for ignition is so small that the so-called "spark-proof" tools reduce the hazard ineffectively and give a false feeling of security.

Therefore, "spark-proof" tools are not required.

However, all tools shall be used with caution to prevent slipping, glancing blows, or dropping, all of which would cause sparks.

5.4.1.3 Static Electricity

Flowing liquid or gaseous hydrogen causes charges of static electricity. The same is true of most liquids or gases.

Turbulence in liquid hydrogen transfer and storage equipment should be avoided as much as possible. For example, liquid falling into a partially filled vessel will create more static charge than if it is piped to enter beneath the liquid surface.

All equipment containing liquid or gaseous hydrogen should be properly grounded to prevent accumulation of a static charge which would cause a static spark.

People generate high voltage charges of static electricity on themselves. Especially, walking on dry ground, wearing nylon or other synthetic clothing or combing the hair will cause static charges. Operators must remember to ground themselves before touching hydrogen couplings and joints so as not to cause ignitions in hydrogen-air atmospheres.

5.4.1.4 Electrical Equipment

Electrical equipment sparks are caused by breaking live circuits, as at switches, commutators, loose connections, or breaking wires.

"Explosion-proof" equipment is equipment that is strong enough to contain an explosion of specific combustibles. However, there is little equipment made which is strong enough to contain a hydrogen explosion.

Instead of requiring expensive and complicated "explosion-proof" equipment it is better to have plentiful ventilation and that electrical installations be:

1. spark and ignition-proof, or that
2. spark or ignition hazard equipment be enclosed and pressurized with clean dry air or nitrogen at low pressure to prevent infiltration of hydrogen, or that
3. sparking or ignition-hazard equipment be placed at a safe distance from the hydrogen area.

5.4.1.5 Open Flames, Smoking, Hot Objects

Open flames or smoking shall not be permitted in or around hydrogen areas. The usual distance requirement is not less than 50 feet. Conditions may require a larger distance.

Objects at temperatures of approximately 1075° will cause ignitions of hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure. At less than atmospheric pressure.prolonged explosure to temperatures as low as 650° will cause ignitions.

Protective guards shall be in proper place on light fixtures if the lights are used while hydrogen is in the area.

Before welding care must be taken that no hydrogen is in or will be in the area.

5.4.2 Ignition Energies and Quenching Distances

Table 2 lists minimum ignition energies and quenching distances for mixtures of hydrogen and air at room temperature and atmospheric pressure[i]. The quenching distances represent distances between two parallel plates below which flame propagation is inhibited by the flow of heat from the flame gas to the channel walls. The minimum ignition energies refer to ignition by electric sparks with spark gaps approximately equal to the quenching distances.

TABLE 2

Minimum Ignition Energies and Quenching Distances for Hydrogen-Air Mixtures at Room Temperature and Atmospheric Pressure

Hydrogen percent	Minimum Ignition Energy millijoule	Quenching Distance inches
7	0.60	.11
10	0.17	.067
15	0.047	.036
20	0.027	.028
30	0.019	.025
40	0.029	.030
50	0.070	.043
60	0.30	.08
65	0.70	.14

A spark passing between two plates that are separated by less than the quenching distance does not cause ignition even if the energy is large. If the spark electrodes do not provide effective quenching surfaces (for example, if the electrodes are wires), ignition is possible but the spark energy is larger than the minimum. This is also the case whenever the spark gap is substantially larger than the quenching distance.

An undiluted stoichiometric mixture of hydrogen and oxygen at room temperature and atmospheric pressure has a quenching distance of .0075 inches[2]. The minimum ignition energy has not been measured but may be estimated from theoretical considerations to be between 10^{-3} and 10^{-4} millijoules. Such mixture is therefore initiated by an extremely small spark. Furthermore, the flame develops readily into detonation, particularly when the mixture is confined in a channel exceeding a width of about 0.01 inches.

There is a lack of data on mixtures at pressures other than atmospheric and temperatures other than room temperature. It is probable that over a wide range of pressures the quenching distances are approximately proportional to the inverse of the pressure, and minimum ignition energies are roughly proportional to the inverse of the cube of the pressure. Furthermore, it is certain that minimum ignition energies and quenching distances decrease with increasing temperature, but the magnitude of the effect is not accurately known. The trend of the data below room temperature is likewise unknown experimentally and not readily predictable. Whereas a temperature decrease would tend to increase the values of ignition energies and quenching distances, the associated density increase at constant pressure may very well reverse the trend and cause a net reduction in the values of these quantities. At temperatures well below the boiling point of oxygen, flammable gaseous mixtures cease to exist. Possible explosive cryogenic combinations comprise hydrogen gas in contact with liquid or solid oxygen, and liquid or solid hydrogen in contact with solid oxygen. Ignition of any such system requires vaporization of some small quantity of the condensed phase and formation of a hydrogen-oxygen mixture of sufficient temperature and volume to propagate the formation and inflammation (or detonation) of explosive gas mixture. The energy requirements of such processes are ill-defined and may

be expected to vary randomly in experimental tests. However, it is certain that ignition energies are always very much larger than the minimum ignition energy of the stoichiometric gas mixture. It is also probably that on a statistical average there is little difference between a solid O_2 - solid H_2 and a solid O_2 - liquid H_2 system, and perhaps little difference even between any such totally condensed system and a system comprising gaseous H_2 in contact with liquid or solid O_2. It is certain that the sensitivity of a hydrogen-oxygen system is greatly decreased when the temperature is below the range of existence of flammable gaseous mixtures (see below).

Some experiments are on record in which liquid hydrogen-solid oxygen systems have been detonated by heat sources such as fused wires [3,4,5] and by shock [4,5].

With regard to the latter mode of initiation the observations have been seemingly inconsistent and erratic. In one test[4] a brass punch over 2 pounds in weight was dropped from some height into a metal Dewar vessel containing liquid hydrogen and solid oxygen at the bottom. A violent explosion occurred. In several subsequent tests the same brass punch was placed into the liquid so that it rested on the solid oxygen covering the vessel bottom, and was struck in this position by a heavy hammer. No explosion occurred even though the energy expended in these blows was greatly in excess of the drop energy expended in the former test that gave a positive result. This may seem to be paradoxical; actually, however the test conditions were not comparable. In the former case the brass punch was at room temperature and in the latter case it was at the temperature of liquid hydrogen. The warm punch would instantaneously generate a thin gas film or small gas bubbles at the hydrogen-oxygen interface, whereas the cold punch had no such effect. It is well-known that a small amount of adiabatically compressed gas plays an important role in impact-induced explosions of condensed explosives. Thus, a microscopic gas bubble sensitizes an explosive such as nitroglycerin to detonation by slight impact, whereas absolutely gas-free nitroglycerin is resistant to heavy impact. The quoted test suggested an analogous behavior of condensed hydrogen-oxygen systems. Conventional impact tests have yielded an impact sensitivity comparable to RDX[5] which is a high explosive of medium sensitivity.

5.4.3 Electrical Insulation Exposed to Gaseous or Liquid Hydrogen

5.4.3.1 Introduction

This discussion is limited to combustion or operational hazards involving the electrical insulation of electrical or electronic devices (i.e., motors, transformers, hook-up wire, etc.) which may be exposed to gaseous or liquid hydrogen in a Saturn class vehicle. Only normal atmospheric air pressure is assumed, although it should be recognized that partial atmospheric pressures at moderate altitudes may introduce a potentially more hazardous situation with electrical insulation.

It is recognized that prior to hydrogen exposure the electrically insulated devices may have been subjected to electrical test and operational check-out of varying time duration and severity and exposed also to environmental ambients such as dirt, high relative humidity and high storage temperatures. It is assumed that such test and ambient exposure have been held to reasonable values and within accepted design limits.

Moreover, it must be realized that operational failure and combustion hazards with electrical insulation are often complex and depend upon many factors which may be difficult to isolate and analyze. This discussion is limited to the hazards which may come about when a hydrogen ambient is superimposed upon the other operational and environmental conditions.

The type and size of the electrical device, the nature of the insulating material, and the physical and electrical stress imposed upon the insulation all effect normal insulation performance and hence also may effect performance in a hydrogen ambient as well. A wide variety of electrical devices and associated insulating materials are incorporated in the complex structure of a Saturn class vehicle. It is necessary, therefore, to discuss the insulation problem in a somewhat general fashion with specific reference to recognized or potentially hazardous materials, designs, or situations. Unfortunately very little investigation is known to have been directed to the specific problem of electrical insulation exposed to hydrogen (as contrasted to that of oxygen, for example). The problem of hook-up wire exposed to liquid hydrogen has been investigated in NASA Contract No. NAS-8-2442 and provides a basis for some of the discussion to follow. For many years large

turbine-generators have been operated in a very pure hydrogen atmosphere and considerable insulation experience has been accumulated.

Since oxygen has been carefully excluded, no combustion hazards have been encountered.

In many cases operational failure in electrical insulation, which in itself is a hazard, may also prove to be the "trigger" for the combustion hazard in a hydrogen ambient. In other cases, operational failure may not occur, but the performance of the electrical insulation may still be responsible for a combustion hazard in hydrogen. Both types of situation will be considered.

5.4.3.2 Operational Hazards Caused by Gaseous Hydrogen

Chemical Interactions - The many years of experience for several types of turbine-generator insulations operating at high voltage with some corona in a pure hydrogen atmosphere have indicated no undesirable chemical interaction. In fact the life and performance capability of these insulating materials in hydrogen gas is generally superior to that in air.

It is possible to conceive of hydrogenation reactions which could occur with unsaturated organic insulating materials to cause cross linking and embrittlement, but the reaction kinetics would not normally be favorable. Some ceramic oxide insulations theoretically might be reduced by hydrogen but the required temperatures would be above those normally encountered in operation. However, electrical devices with ceramic insulation which operate at high temperatures (i.e., above 300°C) should be considered suspect and specific investigation made.

Environmental Problems - The electrical breakdown voltage of pure hydrogen is about 70% that of air at atmospheric pressure. (except for very small spacings). The minimum sparking potential is 273 volts in hydrogen as compared to 327 volts in air*.

*"Gaseous Conductors Theory and Engineering Applications", Cobine, Dover Books, 1958.

The electrical breakdown voltage of hydrogen-air mixtures will be intermediate between the values of the pure gases. (The explosion hazard will be considered later.) While the reduction in breakdown voltage in hydrogen is not large, it might in marginal cases contribute to failure in the high voltage test of high voltage devices. If the flashover voltage of an electrical devices has been drastically reduced by contaminent and/or moisture in field exposure as is possible, than a hydrogen atmosphere might tip the balance to cause failure even at operating voltage or perhaps with voltage surges produced by switching etc. Admittedly such situations would be unusual and normally limited to high voltage equipment. For example, failure under such circumstances would never be experienced with transistors or similar low voltage equipment.

The problem of electrical corona in ambients with a partial pressure of hydrogen must also be considered. Some high voltage electrical and electronic equipment does operate normally with both internal and external corona. The presence of hydrogen will lower the corona inception voltage and increase the intensity of the corona. If even a small amount of air is present, both ozone and nitrous oxides will be formed and these can chemically attack insulation and cause corrosion of metals. Corona causes other types of degradation as well. A particularly insidious type of attack produces deep cracks in some types of elastomers, particularly when they are mechanical stretched. Such attack may occur not only on rubber used in electrical insulation but also on adjacent parts such as gaskets. Fortunately, a few elastomers such as the silicones are resistant to this type of attack. Since hydrogen diffuses very rapidly into organic insulations corona in internal voids will be increased. In such situations hydrogen alone without air may cause damage to organic insulations.

5.4.3.3 Operational Hazards Caused by Liquid Hydrogen

Chemical Interaction - Unlike liquid oxygen, liquid hydrogen is not known to react with either organic or inorganic insulating materials. Even when electrical breakdown measurements have been made on a variety of electrical insulations immersed in liquid hydrogen (with air excluded of course) no interactions have been noted.

Environmental Problems - Liquid hydrogen causes serious environmental problems with insulation mounted in thermal contact with storage tanks or exposed to liquid leaks. The cold temperature and not the liquid hydrogen itself is important. Two problems, embrittlement and moisture condensation, are involved.

All organic insulating materials become more rigid as the temperature is decreased. Some, like many elastomers, lose the ability to elongate quite rapidly below a more or less arbitrarily established temperature called the brittle point. For most elastomers the brittle temperature lies between 0 and -100°C. At very low temperatures many insulating materials fail mechanically when elongated from 1 to 2% or even less. However, appreciable differences do exist in the brittle characteristics of insulating materials at very low temperatures as described in the reports of NAS 8-2442. Polyimide polymers and Teflon exhibit relatively good low temperature characteristics.

Organic insulating materials also contract considerably as the temperature decreases and much more than metals do. Considerable strain may be set up by differential contraction between different materials or even in a homogeneous material if it has a thick section or is cooled quickly so that considerable temperature differential can exist. The internal strains in organic insulating materials set up by cooling may cause cracking up of the cold brittle structure. An example, a 1/2 inch thick section of polyethylene will often crack if immersed quickly in liquid nitrogen or if liquid nitrogen is allowed to flow over it. The same specimen can be cooled slowly without cracking. While such investigations have been performed with liquid nitrogen, similar results would be expected with the colder liquid hydrogen although the situation might be ameliorated to some extent by differences in specific heat and perhaps by the "wetting" characteristics.

Of course, the performance of cold insulating materials depends to a great extent upon the mechanical design and the strain imposed by operational requirements. In general, free, thin films (i.e., Mylar) will not crack even when flexed at cryogenic temperatures unless several layers are bonded together or tensile as well as flexural strain is imposed. In contrast even thin enamel films on wire fail when flexed because considerable strain is imposed as the wire bends at cryogenic temperatures.

When electrically insulated devices in warm moist air become cold, frost or moisture will be deposited on them depending upon the temperature. If one part of the device is warmer than another, a line may develop with frost on one side and melted water from the frost on the other. Frost, particularly when cold, has relatively good electrical properties but the melted and condensed water sometimes can produce disasterous effects on electrical insulation. If cracks exist in the insulation structure (for example as a result of cryogenic cooling), moisture will be deposited deep within the crack and tend to be trapped there even if the surface dries off. More serious problems may be encountered if the insulation surfaces have been contaminated with dirt or salt so that ionizable material can dissolve in the melted or condensed water.

Condensed moisture will be absorbed by some insulating materials and also may penetrate imperfections and at the interfaces between different materials. Sometimes moisture will cause mechanical swelling or warping of electrical insulation which can in itself interfere with the operation of the electrical device (i.e., contact spacing in relays).

By far the most serious potential threat from condensed moisture results from the degradation of electrical properties.

1. Leakage resistance may decrease by many orders of magnitude (leakage current increases).
2. Electrolytic corrosion may be induced in the fine wire of DC coils such as relays.
3. The dielectric loss may increase so that the Q is decreased which in turn may upset resonant circuits, sensitivity, amplication, etc.
4. Volume voltage breakdown may occur.
5. Voltage failure may occur over surfaces in two ways.
   a. by flashover which will dry the surface off,
   b. by tracking which will produce permanent failure of the insulation surface.

Of course, such effects of moisture can be expected from more usual conditions of service and are normally guarded against. However, moisture from exposure to cyrogenic liquids is more serious than usual atmospheric exposure in that larger quantities of water may be involved, the moisture tends to deposit deep within imperfections in the insulation structure instead of just on the surface and worst of all the cryogenic exposure itself may have produced cracks or failed moisture seals in and around the insulated structure. Consequently, exposure to cold temperatures or spillage of liquid hydrogen can cause severe operational hazard in the electrical insulation of electrical and electronic devices.

5.4.3.4 Combustion Hazards in Gaseous Hydrogen

For the purpose of this discussion a combustible mixture of hydrogen and air will be assumed. Moreover, it will be assumed that any luminous electrical discharge in the gas - no matter how small the energy* - will initiate combustion. On the other hand, even overheated insulation in a defective electrical device (i.e., from shorted turn insulation) will seldom attain a temperature sufficient in itself to ignite the hydrogen - air mixture (about 580°C) unless one of the components reaches its ignition temperature and bursts into flame. This flame of course could then ignite the hydrogen. In the following, only the conditions resulting from electrical discharge will be considered since these are believed to constitute the major combustion hazard.

It should be recognized that electrical discharges associated with electrical insulation may cause combustion in a surrounding hydrogen-air mixture without necessarily causing operational failure in the device itself.

Electrostatic Discharges - Any insulated structure with components for which the voltage to ground is not controlled (floating) may under certain conditions build up an electrostatic charge which will produce an electrical discharge if the flashover voltage of the dielectric spacing is exceeded. The factors which can cause the build up of such a charge are many and often complex.

In example: The charge may be induced by another high voltage component even if the latter is adequately insulated. Even water droplets blowing by an insulated conductor may induce a charge on it. Sometimes, an isolated metal band around

* Obviously some lower limit exists but even very low energy corona is known to have initiated combustion in gas mixtures.

the center of an insulator can build up an electrostatic potential and spark to ground. When one electrostatic discharge occurs, operation failure usually does not result, but combustion of a surrounding hydrogen - air mixture is essentially inevitable. The hazard can be avoided only by making sure that the potential of every conducting member of every insulated device is definitely established so that an electrostatic potential cannot build up.

Voltage Breakdown - If for any reason, as described in previous section, a voltage breakdown occurs through the space or insulation surface in the hydrogen air moisture, then combustion will occur. In power (stiff) circuits, safety-factors are usually sufficient so that voltage crackdown in the air spacing is not likely unless a defect has developed such as a crack induced by exposure to cryogenic temperatures. In contrast, low-current, high-voltage equipment sometimes has marginal insulation spacings, since in normal operation it is recognized that a voltage discharge can occur without causing permanent operational failure. Devices with such marginal insulation will produce a grave hazard if operated in a combustible gas mixture. It is particularly important to remember that the presence of hydrogen actually decreases the voltage breakdown. Moisture condensation on insulation surfaces may also drastically reduce the flashover voltage.

Voltage breakdown through the volume of the insulation is perhaps not quite as dangerous as voltage flashover, but can also cause ignition of a combustible gas mixture. While voltage breakdown is not likely in the insulation system of adequately designed and appropriately tested new electrical equipment, the situation becomes moreproblematical after exposure to severe checkout operations and environmental ambients. Unfortunately, voltage breakdown is most likely to occur overvoltage tests are used in the attempt to prevent such failure in subsequent use. Overvoltage tests should consequently be avoided while electrical devices are exposed to a hydrogen gas ambient.

Corona - Corona may be defined as a limited electrical discharge from a high voltage electrode (usually a point), or at the junction of a metal electrode and insulation or within voids and discontinuity in the insulation structure. Internal corona probably does not constitute an appreciable combustion hazard. External corona, however, will ignite combustible gas mixtures. Unfortunately,

high voltage equipment and the connections to it are likely to exhibit external corona. The absence of corona must be demonstrated by test if high voltage equipment is to be used in a hydrogen atmosphere. In contrast, corona is seldom a problem in low voltage circuits of 600 volts and lower and at 220 volts or less does not occur.

Surface Tracking and Scintillation - Under the influence of a combination of moisture and ionizable or carbonaceous contaminant (dirt), electrical stress can produce multiple tiny arcs on insulation surfaces. Voltages as low as 100 volts have been shown to produce such surface scintillation. Even with very conservative insulation spacings, scintillation may occur under adverse ambient conditions (i.e., over a 10-inch spacing at 1000 volts). Such surface scintillation has been shown capable of igniting combustible gas mixtures.

Surface scintillation, if continued over a sufficiently long time, can lead to permanent tracking and failure of insulation surfaces. While such tracking accentuates the scintillation problem, the scintillation by itself may cause ignition even if no tracking has occurred.

5.4.3.5 Combustion Hazards in Liquid Hydrogen

As described earlier, exposure to the cryogenic temperatures associated with liquid hydrogen increases the danger of insulation failure and the resultant ignition of the gaseous hydrogen phase. Such dangers are particularly important under the influence of surface tracking and scintillation.

Whether or not additional combustion hazards exist if air becomes mixed with the liquid nitrogen as it spills on an insulated structure is not known to have been demonstrated, but seems quite possible if electrical discharge is likely to occur.

5.4.3.6 Means for Evaluating and Preventing Operational and Combustion Hazards

Insulation failure has always been a hazard in the operation of electrical and electronic equipment.* The failure hazard is compounded by operation in hydrogen-

* Insulation failure is estimated to cause from 85 to 95% of electrical equipment failure.

air mixtures and by a liquid hydrogen ambient as described in the foregoing. No truly adequate means have yet been developed for evaluating the probability or imminence of insulation failure even though attempts to do so have been made for at least 80 years. Unfortunately, some dielectric testing in itself may be hazardous if conducted in a hydrogen-air atmosphere.

Dielectric Tests - It is not possible here to write a complete treatise on dielectric testing and only aspects related to the hydrogen problem can be dealt with briefly and rather incompletely. Voltage withstand tests to ground (often 2 x rated + 1000 volts) have been traditionally used on electrical equipment for acceptance as manufactured. After field service, voltage withstand tests have also been used but the test voltage has usually been lowered to 1.75 times rated voltage. Such tests may be of limited value in air, but should not be made in hydrogen-air mixtures because of the ignition danger. D-c resistance, dielectric absorption, power factor and repeated surge tests** have been used to evaluate electrical equipment in the field with some success. Such tests may be suitable for use in hydrogen also, if the test voltage is kept well below the operating voltage. Unfortunately, these dielectric tests require considerable and skilled interpretation and are most significant if used repetitively at intervals during installation and operational check out. In this way the presence of moisture and dirt contamination can often be detected. Insulation degradation such as cracking sometimes will be indicated also. Unfortunately, acceptable dielectric test cannot assure complete reliability.

Tests for Corona and Scintillation - Since corona and surface scintillation are important factors in contributing to combustion hazard, special attention should be directed to their detection. These tests must not, of course, be made in a hydrogen atmosphere but should be used in preparation for hydrogen exposure. Corona inception voltages may be determined by several methods but the appropriate technique depends upon the type of equipment involved and the suggestions of the manufacturer should be considered. Unfortunately, considerable skill may be needed to separate dangerous external corona from relatively less dangerous internal corona. In some instances, visual observation in a completely darkened room may be useful but not completely conclusive.

** See AIEE Publication #62, Nov. 1956, "Proposed Recommended Guide for Making Dielectric Measurements in the Field."

The problem of detecting surface scintillation is more difficult in that it will occur only under adverse conditions with wet and contaminated insulating materials. Component manufacturers are not generally familiar with the problem. If ambient conditions are right, scintillation will be detected with corona measuring equipment and it also can usually be seen in a darkened room if accessible to observation. The conditions which might produce scintillation may sometimes be detected indirectly by other tests such as insulation resistance.

Hazard Prevention - It is trite but true to point out that experienced, conservative design and intelligent care in installation and check out provide the greatest safeguard against insulation failure. Techniques which increase reliability in usual operating situations will tend to decrease the hazard associated with hydrogen exposure. The prevention of moisture ingress with seals, potting, the use of conformal coatings on printed circuitry, etc., may be particularly important.

Nevertheless, the specific factors involved in hydrogen exposure may invalidate some of the more normal approaches used to avoid operational problems. For example, spillage of liquid hydrogen may crack conformal coatings away from a printed circuit board to provide an even worse moisture problem than if no coating had been used at all. If spillage of liquid hydrogen is possible, each insulated component should be type tested to evaluate the likelihood of failure under such conditions. Of course, all insulated components should be evaluated also in a moisture environment and such test might well follow cryogenic shock exposure.

Design selection also can be used to decrease or eliminate hazards. For example, if the maximum voltage can be kept below 300 volts many types of insulation hazards will be eliminated. Even when high voltages must be used, the hazard problems can be alleviated by careful control of voltage at all points (i.e., elimination of "floating elements"), by decreasing or preventing voltage surges and in general by conservative design with adequate insulation spacing and the use of the best insulating materials.

5.4.4 Elimination of Ignition Sources

Even with the best of efforts concerning hydrogen containment, accidental leaks and accumulations may occur.

Therefore, the philosophy is to eliminate likely ignition sources or place them away from the hazard area.

5.4.4.1 Friction Sparks*

Friction sparks are caused by hard objects coming into forcible contact with each other. That is, metal striking metal, metal striking stone, or stone striking stone.

A friction spark is a particle of burning metal which has been sheared off as a result of contact. Initially, the particle is heated by mechanical energy of friction and impact converted into heat. The freshly exposed surface of the particle may oxidize at the elevated temperature to cause an increase of temperature until the particle is heated to incandescence.

Sparks struck from hand tools are considered as having low total energy. Sparks from mechanical tools such as drills and pneumatic chisels generate high energy sparks.

5.4.4.2 Impact Sparks *

Impact sparks are also caused by hard objects coming into forcible contact with each other.

Impact sparks are produced by impact on a quarzitic type rock. Quartz is piezo-electric and can convert mechanical into electrical energy. As in the case of friction sparks, small particles of the impacted material are thrown off. These particles, however, do not oxidize and therefore, lose heat after the initial impact.

* (Reference: Sparking Characteristics and Safety Hazards of Metallic Materials Technical Report No. NGF-T-1-57 NAVORD Rpt. 5205)

5.4.4.3 Electrical Sparks*

Electrical sparks are caused by sudden electrical discharges between contacts having different electrical potentials, for example, breaking electrical circuits or discharges of static electricity. These sparks may carry tremendous amounts of energy in comparison with friction sparks. The discharges are hazardous but usually can be prevented by proper grounding.

Static electricity - will generate sparks which will ignite a hydrogen-air or hydrogen-oxygen mixture. Static electricity is caused by many common articles such as hair or fur when combed or stroked or by a leather belt when operating on a machine. People generate high voltage charges of static electricity on themselves, especially, when walking on dry ground, wearing nylon or other synthetic clothing, sliding on automobile seats or combing the hair. Flowing liquid or gaseous hydrogen causes charges of static electricity. This is true also for all non-conductive liquids or gases. Turbulence in containers as well as laminar flow in systems has the same effect.

Therefore, in hydrogen areas special care must be taken to prevent static sparks from the above or any other sources. It is necessary to:

1. Ground all metal parts of the test rig and structure enclosing it.
2. Make sure machinery belts are spark-free.
3. Avoid using combs to comb the hair.
4. Avoid wearing nylon or other synthetic clothing.
5. Be sure personnel ground themselves before touching or using a tool on dewars or vents.
6. Keep furred animals out of hydrogen areas.

However, in spite of precautions, static sparks may occur from unknown sources.

5.4.4.4 Electrical Equipment and Wiring

Electrical sparks are caused by breaking live circuits, as at switches, commutators, loose connections, or breaking wires. Hot wires or parts are also ignition sources.

All circuit-switching equipment shall be prevented from sparking in the hydrogen environment by hermetically-sealing the contacts.

* (Reference: Sparking Charactertistics and Safety Hazards of Metallic Meterials Technical Report No. NGF-T-1-57 NAVORD Rpt. 5205)

If the electrical equipment has rotating or moving parts such as motors, solenoids, etc., provisions shall be made to prevent electric sparking and metal to metal friction sparking. Hermetic-sealing or explosion proofing is required if purging is not used.

Disconnecting of electrical connectors exposed to the hydrogen environment shall be prohibited, except in the case of de-energized circuits. Floodlights and aircraft obstruction lights are not available in explosion-proof construction and shall therefore be disconnected before hazardous operations begin.

Wiring in hazardous areas shall be protected mechanically from liquid spillage and also to prevent accumulation of hydrogen.

5.4.4.5 Conduit

Threaded, rigid, metal conduit is not required except as judged necessary for protection of wiring against mechanical damage. If used, the ends should be sealed if the conduit could conduct leaked hydrogen to a non-hazard area.

Liquid-tight, flexible conduit may be used and the ends sealed as above.

5.4.4.6 Wiring (Without conduit)

Flexible heavy-duty rubber-covered cable may be used without conduit. The ends must be sealed, as with cord grips to prevent hydrogen infiltration.

5.4.4.7 Starters, Relays, Breakers

Equipment of this nature shall be located remotely from the hazard area, or pressurized, or continuously scavenged of any combustible.

5.4.4.8 Solenoid Valves

Solenoid valves, e.g., the Skinner Electric Valve, are considered sparkfree and need not be pressurized with inert gas nor sealed.

If desired, a fuse or other protection may be used to prevent overheating.

5.4.4.9 Bonding

The term bonding as used in this document means an electrical connection between adjacent metallic parts. Bonding shall be used to assure that no electrical

potential exists between metallic parts in the vehicle that could cause ignition of a hydrogen mixture.

Single point bonding is generally sufficient for low-frequency circuits, such as audio and power. Electrical equipment which may produce radio frequencies, desired or undesired, shall be so installed that there will be a continuous low-impedance path to the ground. Multiple bonding will be applied, as required, to reduce the possibility of resonant loops. In radio frequency circuits the skin effect must be taken into consideration in the design of the bonding strap, to assure a low-impedance path. Figure 20 shows the variation of skin depth with frequency for copper, and can be used as a guide for determining the bonding strap configuration.

5.5 LEAKAGE

5.5.1 Modes of Leakage

When containing liquid hydrogen in a duct or piping system in which connectors of some sort exist, leakage through three separate modes is possible - permeation through the component materials, flow through the component materials having porosity, and flow through the interface between the mated components. Leakage flow through porous materials can be ruled out only by proper quality control. It is generally not a problem in properly designed systems. The problem of permeation, however, is much more severe. Hydrogen is known to permeate some structural materials which may be used either for piping or tubing or the fluid connector itself. To preclude this possibility, the proper materials must be chosen such that the calculated permeation rate of hydrogen through the required material thicknesses will be within tolerable limits.

Where elastomeric materials or plastics are used for gasketing materials, permeation can be a limiting factor in the over-all design. The amount of expected permeation flow is easily calculatable when the geometry of the containing material is known, the pressure differential is established and a permeation constant for that material and hydrogen is available.

By far the most serious mode of leakage in a system having fluid connectors is that of leakage flow through the interface between the mated components of the connector. In general, permeation flow and porosity are quite small in relation to this potential leakage model. Whether the hydrogen contained is in liquid form or in gaseous form, the flow rate through the interface will ultimately depend on the rules governing gaseous flow, since even if the fluid is liquid when it begins leaking, by the time it reaches the exterior of the leak it is a gas.

Where dimensions descriptive of the cross-sectional area of the leak path are extremely small in comparison with the mean free path of the gas leaking through the path, the flow will be molecular in nature. Molecular flow exists generally for extremely low flow rates. During the molecular flow regime, the leakage rate is proportional to the pressure difference existing across the leak path. Where the leakage path is somewhat larger, indicating a larger flow

rate, then viscous flow will exist. During this regime, the flow rate is proportional to the difference between the internal pressures squared and the external squared.

5.5.2 Expected Leakage Rates

Where the problem is one of limiting the percentage of hydrogen gas in a cavity, the allowable leakage rate through the fluid connectors must be established on the basis of the volume of the cavity and operational life of the system. Under normal design practices, it is possible to achieve leakage rates for approximately 10^{-6} atm cc/sec leakage rates. This rate is roughly equivalent to one liter per 30 years. Detection of such a leak requires tests more sophisticated than the normal liquid immersion bubble test (which will indicate leakage rates down to 10^{-4} atm cc/sec).

NAA reports* that the approximate extent of seal leakage for the S-II engine compartment will be 1.33 SCIM per linear inch of seal circumference.

5.5.3 Elimination of Leakage

5.5.3.1 Material and Hardware

In general, permissible materials of construction for liquid hydrogen systems include aluminum, copper, monel, inconel, austenitic stainless steels (types 304, 304L, 308, 316, and 321) and brass and bronze. Stainless steel of type 347 is very sensitive to cracking during welding and should not be used. The actual selection of materials depends on requirements of the specific application such as thermal conductivity, strength, porosity, weight, and cost.

Typical Recommended Material for LH_2 Service

Valves	Forged 304 Stainless Steel or Brass Body with Extended Bonnet	Conventional
Fittings	Stainless Steel Bayonet Type for Vacuum Jackets	Conventional
O-rings	Stainless Steel Type (or Kel-F)	Conventional
Gaskets	Soft Aluminum, Lead, or Annealed Copper between Serrated Flanges	Conventional
Hoses	Flexible Type 316 Stainless Steel	
Burst Disc Assembly	304 or 304L Stainless Steel Flanges	Forged Steel Flanges
Piping	304 or 304L Stainless Steel	Uncoated Wrought Steel or any 300 series stainless

*SID 62-142 Saturn S-II Engine Compartment Conditioning Subsystem Report 15 November 1963

5.5.3.2 Piping

Threaded joints are acceptable for use on gaseous hydrogen systems with conventional thread seal such as "Expando". Threaded joints are to be avoided on liquid hydrogen systems. If they must be used, the male and female threads should be tinned with a 60% lead-40% tin solder, then heated to provide a soldered joint with pipe thread strength.

Cryogenic liquid piping should be vacuum jacketed for low heat leakage. Material preferred is type 304L stainless.

High pressure gas manifolds are to be constructed of heavy-walled 304L stainless tubing and are to be welded construction wherever possible. Where metal pigtails are used, they are to be clamped so as to minimize stresses at the welds.

In vent piping a check valve shall be located near the atmospheric discharge to prevent back-flow of air. If over one-inch in diameter, the vent piping shall be purged (with nitrogen preferably) immediately before, and immediately after flowing hydrogen. Purging during hydrogen flow or of a vent pipe of one-inch diameter or less is not required.

A burst diaphragm or a relief valve should be installed in every section of a line where liquid can be trapped. This condition exists most often between two valves in series. A burst diaphragm or relief valve may not be required if at least one of the valves will, by its design, relieve safely at a pressure less than the design pressure of the liquid line. This procedure is most appropriate in situations where bursting of the diaphragm could create a serious hazard.

Important equipment should not be placed over hydrogen containers or systems where a hydrogen leak-fire would cause damage.

Flared stainless tubing should be used up to 3/4 inch diameter. Use flanged or welded joints for steel tube sizes greater than 3/4 inch and pressures greater than 50 psig.

5.5.3.3 Seals

Seal materials suitable for low temperature and vacuum service are required. Natural rubber freezes, hardens, and loses its seal at low temperatures. Synthetic rubber, Teflon, Kel-F, copper, brass, and stainless steel, for example, may be used as low temperature seals.

Avoid pipe threads because they are more subject to leaking. Use welded fittings or flanged connections of approved types.

The problem of ensuring that an extremely low leakage rate exists across a seal is one of ensuring that the two surfaces pressed together to effect the seal have few enough and small enough voids between them to render the leak rate desired. The resulting leak rate will be a function of the pressure differential across the seal, the materials being used as seals, the original surface finish of those components, and the stress applied to the seal.

Where metal seals are used, the resultant leakage rate is extremely sensitive to the surface finish of the mating components. Empirical results gained from many tests show that, should the surface finish be omitted, a design parameter, then a normal stress equal to 2.75 x the yield strength of the softer material in contact must be applied in order to effect a seal (leakage less than 10^{-6} atm cc/sec).

Should extreme quality control be used and particular surface finishes be utilized, the stress level may be dropped to as low as 1.7 x the yield strength. Where a normal stress lower than 2.75 times the yield stresses is used, the problem of random scratches caused by improper handling during the first assembly or any successive reassembly must be faced.

In the case of metal gaskets or direct metal-to-metal sealing, the presence of a sealing stress equal to 2.75 times the yield strength of the softer material causes the metal to flow plastically. Hence, the response of the system upon reassembly will certainly be different than its response during initial assembly since any tolerances on which the initial response are predicated will no longer exist. Thus, where metal seals are used, it is general practice to utilize new metal gaskets upon each reassembly. In this case, the structural components, being stronger than a soft metal gasket, will

not be injured in any way and the response of the system will, in general, be repeatable.

Metal O-rings have proven satisfactory for sealing flanges on liquid hydrogen piping and vessels only when coated with a soft material and when used on smooth surfaces.

Type 321 stainless steel O-rings, with a coating of teflon or silver, should be used in stainless flanges with stainless bolting.

Likewise, teflon coated aluminum O-rings should be used in aluminum flanges with aluminum bolting. Using similar materials avoids the leakage possibility from unequal contraction of dissimilar metals.

Surface finishes in the O-ring groove and contact area should be at least 32 microinches r.m.s. All machine or grind marks must be concentric.

Where elastometers are used as gasketing materials, the resulting leakage is much less sensitive to surface finish. Extremely low stresses are adequate to effect a seal. Elastomers deform grossly elastically and hence, have in general adequate reuseability qualities. A problem which must be faced when elastomers are used is that under extremely hard vacuums such as are found in outer space, the sealing characteristics of elastomers degenerate quickly.

Plastic gaskets such as Kel-F or Teflon deform visco-elastically and are time dependent in their behavior. In general, extremely low stress levels will effect seals. The problem generally encountered when plastics are used is that the stress applied to them relaxes over a period of time and interface leakage flow may result.

In all separable fluid connectors, the major problem facing the designer is that of stress relaxation during the operational life of the connector. While a certain stress is necessary to effect the seal, thereafter, during the life of the connector, it is possible to allow the stress to drop off somewhat. In most cases, a safe relaxation of stress will be approximately 40% loss of initial stress. A loss greater than that will usually cause voids to become present at the interface and the leakage rate to increase. Where thermal-cycling, high temperatures, or vibration are present during operational life of the system,

stress relaxation is quickened. The structural design of such connectors must take into consideration the allowable loss in stress and insure this is minimized.

Seal and Gasket Material

Teflon (polytrifluorochloroethylene) or Kel-F (polytetrafluoroethylene) can be used in liquid hydrogen systems for:

1. Valve seat materials on liquid hydrogen use to 300 psig. Kel-F is first choice and teflon second. Kel-F has a higher tensile strength and is less brittle at cryogenic temperatures. Both should be shrouded to avoid plastic flow. Valves for liquid service over 300 psig should use metal-to-metal seat because the pressure requires excessive seating force for the Kel-F and Teflon.
2. Soft coating on metallic O-rings to provide more positive seal.
3. Flat-thin gaskets for tongue-and-groove type flanges where gasket is shrouded on four (4) sides.
4. Spacers in vacuum area between liquid flow tube and vacuum pipe.
5. Gland packing or seal only if it is maintained near ambient temperature as in an extended bonnet of a shutoff valve. The contraction or shrinkage of teflon when cooled from ambient to cryogenic temperatures allows leakage.

For gaseous hydrogen at ambient temperature, the valve seat materials can be the conventional composition type.

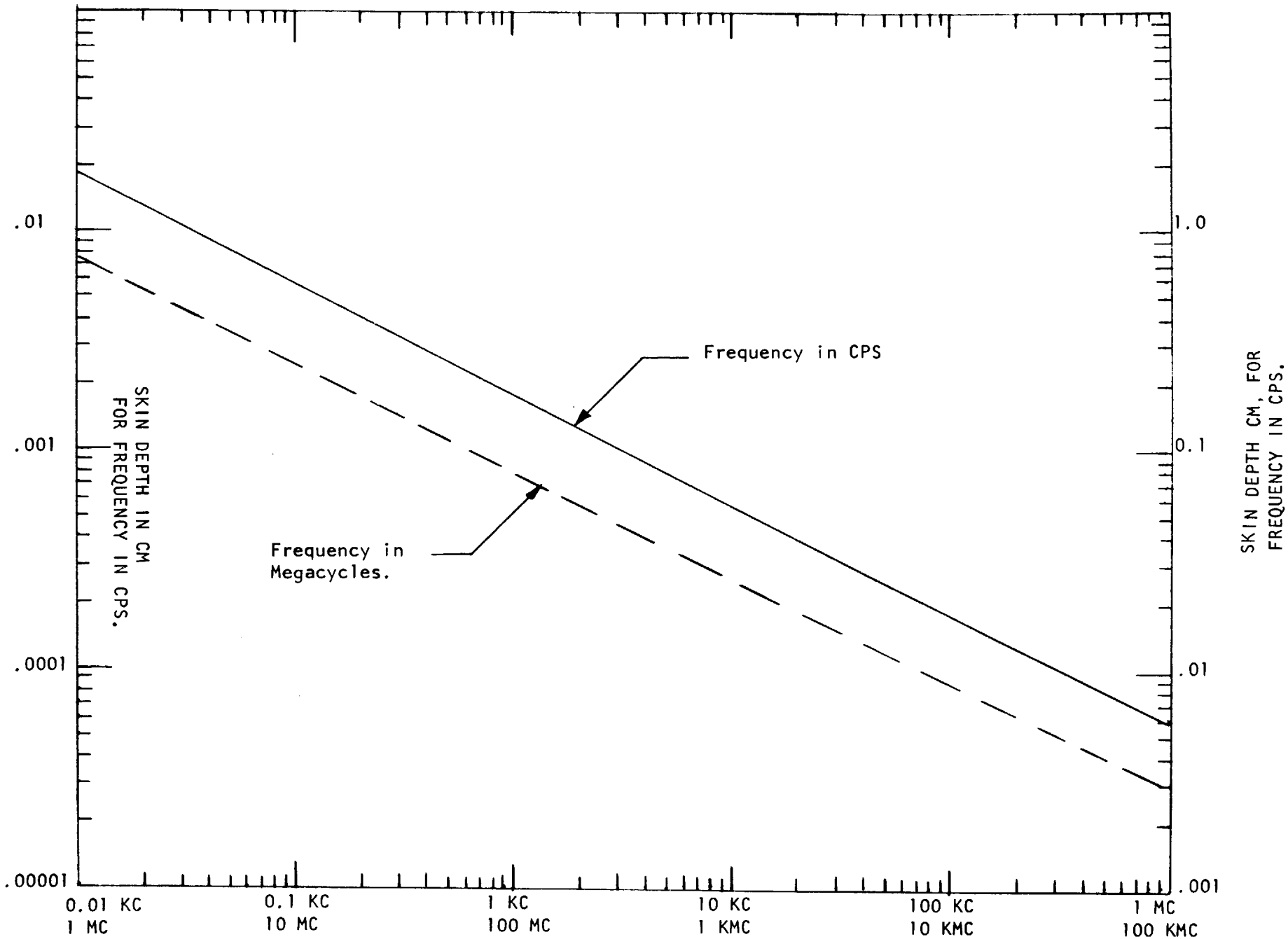
5.5.3.4 Thermal Contraction

Thermal contraction of a liquid hydrogen system of stainless steel is usually calculated from ambient to minus 420°F as 0.35% of the original length.

5.5.3.5 Dissimilar Metals

Dissimilar metals in systems or containers are to be avoided. They cause:

1. Corrosion by electrolysis
2. Electrical charges and high electrical resistances which make grounding more difficult, and
3. Structural weakness, as a result of corrosion, which causes equipment breakages.



SKIN DEPTH VS. FREQUENCY FOR COPPER
FIGURE 20

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