X CHAPTER : SAFETY

Nota Bene: much of this chapter has been taken from NASA's SAFETY STANDARD FOR HYDROGEN AND HYDROGEN SYSTEMS. It is meant as an illustration of the various safety aspects that play a role in handling hydrogen. It is by no means a safety handbook !

X.1 PRELIMINARY REMARKS

Hydrogen gas is colorless, odorless, and not detectable in any concentration by human senses. Hydrogen is non-toxic, classified as a simple asphyxiant, and has no threshold limit value (TLV). Hydrogen is not listed as a carcinogen by the National Toxicology Program, International Agency Research on Cancer, or Occupational Safety and Health Administration. For historical reasons hydrogen has a bad reputation, which is not justified as a more recent analysis of the „Hindenburg" air ship catastrophe proves: the air ship caught fire because of a highly flammable skin material in those pre-polymer times and not because of the hydrogen filling gas. The safety of hydrogen relies on its high volatility and non-toxicity.

Hydrogen is not toxic but a very flammable gas. Experiments with hydrogen should only be carried out in well ventilated rooms. As minimum safety precautions one should have an open window and a hydrogen gas detector at the ceiling of the room.

It is the purpose of this Chapter to inform the reader about potential hazards and to provide him/her with indications about the necessary precautions to be taken whenever working with hydrogen or hydrides. **It is, however, by no means be a safety handbook**.

X.2 PROPERTIES OF HYDROGEN

X.2.1 GASEOUS HYDROGEN

General chemical and physical properties of hydrogen have been described in Chapters II and III. Here we are mainly focussing on those properties that are of particular interest for hazard analyses.

Detection.

Hydrogen gas is colourless, odourless, and not detectable in any concentration by human senses. Hydrogen is not toxic but can result in asphyxiation by diluting the oxygen required in breathing air. An atmosphere containing oxygen at a concentration of less than 19.5 percent by volume is considered oxygen deficient.

Variable Density.

Hydrogen gas is lighter than NTP air and tends to rise at temperatures above 23 K. Saturated vapor is heavier than air and will remain close to the ground until the temperature rises. Buoyant velocities are related to the difference in air and fuel densities; therefore, the cold, dense fuel gases produced by LH_2 spills will rise more slowly than standard temperature and pressure fuel gases. The buoyant velocity of hydrogen in NTP air is 1.2 to 9 m/s.

Lack of Flame Color.

A hydrogen-air-oxygen flame is colorless. Any visibility is caused by impurities. At reduced pressures a pale blue or purple flame may be present. Severe burns have been inflicted on persons exposed to hydrogen flames resulting from the ignition of hydrogen gas escaping from leaks.

Flame Temperature in Air.

The flame temperature for 19.6 percent by volume hydrogen in air is 2321 K.

Burning Velocity in NTP Air.

The burning velocity in NTP air, defined as the subsonic velocity at which a flame propagates through a flammable fuel-air mixture, is 2.70 to 3.50 m/s. The burning velocities are affected by pressure, temperature, and mixture composition. The high burning velocity of hydrogen indicates its high explosive potential and the difficulty of confining or arresting hydrogen flames and explosions.

Diffusion Coefficient in NTP Air.

The diffusion coefficient for hydrogen in NTP air is 0.61 cm^2/s.

Limiting Oxygen Index.

The limiting oxygen index is the minimum concentration of oxygen that will support flame propagation in a mixture of fuel, air, and nitrogen. For example, no mixture of hydrogen, air, and nitrogen at NTP conditions will propagate flame if the mixture contains less than 5 percent by volume oxygen.

Table X.1: Properties of hydrogen[1] at normal temperature and pressure (NTP =293 K and 101.3 kPa)

Molecular Weight	2.01594
Density of GH_2	83.764 g/m3
Density of air (for comparison)	1,198 g/m3
Specific heat at constant pressure, Cp	14.89 kJ/kg·K
Specific heat ratio, Cp/Cv	1.383
Enthalpy	4097.7 kJ/kg
Internal Energy	2888.0 kJ/kg
Entropy	64.44 kJ/kg·K
Velocity of sound (adiabatic)	1294 m/s
Viscosity	8.81 µPa·s
Thermal conductivity, k	19.14 µW/m·K
Dielectric constant	1.00026
Compressibility factor, Z	1.0006
Index of refraction	1.00012
Joule-Thomson inversion temperature	193 K
Heat of combustion (low)	119.93 kJ/g
Heat of combustion (high)	141.86 kJ/g
Limits of flammability in NTP air	4.0 to 75.0 vol %
Limits of flammability in NTP oxygen	4.1 to 94.0 vol %
Limits of detonability in NTP air	18.3 to 59.0 vol %
Limits of detonability in NTP oxygen	15 to 90 vol %
Stoichiometric composition in air	29.53 vol %
Minimum energy for ignition in air	0.017 mJ
Autoignition temperature	858 K
Hot air-jet ignition temperature	943 K
Flame temperature in air	2318 K
Fraction of thermal energy radiated from flame to surroundings	17 to 25%
Burning velocity in NTP air	265 to 325 cm/s
Detonation velocity in NTP air	1.48 to 2.15 km/s
Diffusion coefficient in NTP air	0.61 cm2/s
Diffusion velocity in NTP air	<2.0 cm/s
Buoyant velocity in NTP air	1.2 to 9 m/s
Maximum experimental safe gap in NTP air	0.008 cm
Quenching gap in NTP air	0.064 cm
Detonation induction distance in NTP air	L/D~100
Limiting oxygen index	5.0 vol %
Vaporization rates (steady state) of liquid pools without burning	2.5 to 5.0 cm/s
Burning rates of spilled liquid pools	0.5 to 1.1 mm/s
Energy of explosion (theoretical explosive yield)	≈24 (g TNT)/(g H_2) 0.17 (g TNT)/(kJ H_2)

X.2.2 PROPERTIES OF LIQUID HYDROGEN

All of the hazards that exist with gaseous H_2 also exist with liquid H_2 because of the ease with which the liquid evaporates. Characteristic properties of LH_2 also of particular concern for hazard analyses are discussed in this section.

Low Boiling Point.

LH_2 has an NBP of 20.3 K at sea level pressure. Any LH_2 splashed on the skin or in the eyes can cause serious burns by frostbite or hypothermia. Inhaling vapor or cold gas produces respiratory discomfort and asphyxiation can result.

Ice Formation.

Vents and valving from storage vessels and dewars may be blocked by accumulations of ice formed from moisture in the air. Excessive pressure may then rupture the container and release hydrogen.

Continuous Evaporation.

The continuous evaporation of LH_2 in a vessel generates gaseous H_2, which must be vented to a safe location or temporarily confined safely. Storage vessels and other containers should be kept under positive pressure to prevent air from entering. LH_2 is subject to contamination with air condensed and solidified from the atmosphere or with trace air accumulated during LH_2 production. The quantity of oxygen can buildup during repeated refilling or pressurization of permanent LH_2 storage vessels. This mixture is easily ignited and can then detonate.

Pressure Rise.

LH_2 will eventually warm to the surroundings giving a significant pressure rise if it is confined, as in a pipe between two valves. Considering gaseous H_2 as an ideal gas, the pressure resulting from a trapped volume of LH_2 vaporizing and being heated to 294 K is 85.8 MPa. However, the pressure is 172 MPa when the real hydrogen compressibility is taken into account. A significant pressure increase will occur in a system with only one phase present and the LH_2 experiences a temperature increase.

High Density.

The higher density of the saturated vapor may cause the hydrogen cloud to flow horizontally or downward immediately upon release if an LH_2 leak occurs.

Electric Charge Build Up.

The electrical conductivity of LH_2 is typically 10^{19} $\Omega\cdot$cm at 25 V and varies linearly as a function of applied voltage. This indicates that it is not strictly correct to consider the electrical conductivity of LH_2 in terms of Ohm's Law. Although a current can be passed through LH_2, this current can be explained in terms of charge carriers formed by background radiation. Thus, the current carrying capacity is small and more or less independent of the imposed voltage. Investigation has shown that electric charge build up in flowing LH_2 is not a great concern.

X.2.3 PROPERTIES OF SOLID HYDROGEN

All the hazards that exist with gaseous and liquid H_2 also exist with solid H_2 (SLH_2) Additional system components are required to handle the two-phase SLH_2; therefore, transfer and storage operations become more complex. Characteristic properties of SLH_2 also of particular concern for hazard analyses are discussed in this section.

Vapor Pressure.

The vapor pressure of SLH_2 is 7.04 kPa. Therefore, the SLH_2 system is designed structurally to operate at pressures below atmospheric and greater care must be taken during operations to prevent air leakage into the system.

Ortho-Para-Hydrogen Conversion.

The product is at least 95 percent para-hydrogen in normal production of LH_2. The equilibrium content of para-hydrogen at SLH_2 temperature 13.8 K is 100 percent; therefore, any ortho-hydrogen will be converted to para-hydrogen. The heat generation by this residual ortho-to-para conversion acts as an additional heat leak into the system. This conversion is slow, but finite if no catalyst is present. At 20 K the heat of conversion for normal hydrogen is 525 J/g.

The spontaneous conversion of ortho-hydrogen to para-hydrogen even occurs in the solid state, in which the conversion rate may be even higher.

X.3 FLAMMABILITY AND IGNITION OF HYDROGEN

It is necessary for hydrogen to be mixed with an oxidant, the mixture be within flammability limits, and an appropriate ignition source be present for hydrogen to burn. Leaks and accumulations occur even with the best efforts to contain hydrogen. The safe procedure is to eliminate all likely sources of ignition or place them away from areas of possible hydrogen leakage

Flammability.

(1) Mixtures of hydrogen with air, oxygen, or other oxidizers are highly flammable over a wide range of compositions. The flammability limits, in percent by volume of hydrogen, define the range over which fuel vapors will ignite when exposed to an ignition source of sufficient energy. Flammability limits are dependent on the ignition energy, temperature, pressure, presence of diluents, and size and configuration of the equipment, facility, or apparatus.

(2) A flammable mixture may be diluted with either of its constituents until the mixture concentration falls outside the flammability limits: below the lower flammability limit (LFL) or above the upper flammability limit (UFL). The flammability range for hydrogen-air and hydrogen-oxygen mixtures is broadest for upward flame propagation and narrows for downward flame propagation.

(3) Neither LH_2 or SLH_2 as fuel, and liquid oxygen (LOX) or solid oxygen as oxidizer, are hypergolic. Mixtures of these materials have ignited during the mixing process because the energy required to ignite them is so small. LH_2 and liquid-solid oxygen have been detonated by an externally generated shock wave. Comparable experimental examination of SLH_2 systems does not exist.

(4) The flammability limits of hydrogen in dry air at 101.3 kPa and ambient temperature are 4.1 percent (LFL) to 74.8 percent (UFL). These limits apply for upward propagation in tubes. The flammability limits of hydrogen in oxygen at 101.3 kPa (14.7 psia) and ambient temperature are 4.1 percent (LFL) to 94 percent (UFL). These limits apply for upward propagation in tubes.

(5) Autoignition Temperature. Hydrogen is only slightly more difficult to ignite in air than in oxygen. Ignition temperatures are dependent on gaseous H_2 concentration and pressure and the surface treatment of containers. The reported temperature is very dependent on the system and values selected should be applied only to similar systems. At 101.3 kPa the range of reported autoignition temperatures for stoichiometric hydrogen in air is 773 to 850 K; in stoichiometric oxygen it is 773 to 833 K . At pressures from 20 to 50 kPa gaseous H_2-air ignitions have occurred at 620 K.

(6) Minimum Spark Energy for Ignition. Minimum spark energy for ignition is defined as the minimum spark energy required to ignite the most easily ignitable concentration of fuel in air and oxygen. The minimum spark energies of hydrogen in air are 0.017 mJ at 101.3 kPa, 0.09 mJ at 5.1 kPa, and 0.56 mJ at 2.03 kPa. The minimum spark energy required for ignition of hydrogen in air is considerably less than that for methane (0.29 mJ) or gasoline (0.24 mJ); however, the ignition energy for all three fuels is sufficiently low that ignition is relatively certain in the presence of any weak ignition source; such as, sparks, matches, hot surfaces, or open flames. Even a weak spark caused by the discharge of static electricity from a human body may be sufficient to ignite any of these fuels in air.

Note: Major emphasis should be on containment, detection, and ventilation because the minimum energy of GH$_2$ ignition in air at atmospheric pressure is about 0.02 mJ and experience shows that escaped hydrogen is very easily ignited.

Table X.2: Flammability limits for hydrogen in air and in a mixture[2]

	Upward Propagation		Downward Propagation		Horizontal Propagation	
Limit	Lower	Upper	Lower	Upper	Lower	Upper
Hydrogen Content (vol %)						
Hydrogen in air and oxygen at 101.3 kPa: H_2 + air:						
Tubes	4.1	74.8	8.9	74.5	6.2	71.3
Spherical Vessels	4.6	75.5	---	----	---	----
H_2 + oxygen	4.1	94.0	4.1	92.0	---	----
Hydrogen plus inert gas mixtures at 101.3 kPa:						
H_2+He+21 vol% O_2	7.7	75.7	8.7	75.7	---	----
H_2+CO_2+21 vol% O_2	5.3	69.8	13.1	69.8	---	----
H_2+N_2+21 vol% O_2	4.2	74.6	9.0	74.6	---	----

Ignition Sources.

There should be no sources of ignition, such as from open flames, electrical equipment, or heating equipment in buildings or special rooms containing hydrogen systems

(1) The ignition of GH_2-air mixtures usually results in ordinary deflagration. Table A2.1 gives potential ignition sources for hydrogen systems. The potential hazards are significantly less than if detonation results. It is possible that in a confined or partially confined enclosure a deflagration can evolve into a detonation. The geometry and flow conditions (turbulence) have a strong effect on the transition from deflagration to detonation.

(2) Electrical sparks are caused by sudden electrical discharges between objects having different electrical potentials, such as breaking electrical circuits or discharges of static electricity. The sparks may dissipate tremendous amounts of energy in comparison with friction sparks.

(3) Static electricity can generate sparks that will ignite hydrogen-air or hydrogen-oxygen mixtures. Static electricity is caused by many common articles, such as hair or fur when combed or stroked or a leather belt operating on a machine. People generate high-voltage charges of static electricity on themselves, especially when walking on synthetic carpet or dry ground, wearing nylon or other synthetic clothing, sliding on automobile seats, or combing their hair. Flowing GH_2 or LH_2 can generate charges of static electricity. This is true also for all nonconductive liquids or gases. Flow in SLH_2 has the potential for generating static electricity, although such an effect has not been confirmed. Turbulence in containers as well as laminar flow in systems has the same effect. Static charges may be induced during electrical storms

(4) Friction sparks are caused by hard objects coming into shearing contact with each other, such as metal striking metal, metal striking stone, or stone striking stone. Friction sparks are particles of burning material that have been sheared off as a result of contact. The particle initially is heated by the mechanical energy of friction and impact. Sparks struck by hand tools are considered to have low total energy. Mechanical tools such as drills and pneumatic chisels can generate highenergy sparks.

(5) Impact sparks are also caused by hard objects coming into forcible contact with each other. Impact sparks are produced by impact on a quartzitic rock such as the sand in concrete. As with friction sparks, small particles of the impacted material are thrown off.

(6) Hot Objects and Flames.
   (a) Objects at temperatures from 773 to 854 K can ignite hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure. Substantially cooler objects, about 590 K, can cause ignition under prolonged contact at less than atmospheric pressure.
   (b) Open flames easily ignite hydrogen-air mixtures.

(7) Provisions should be made to acceptably contain any resulting deflagration or detonation if ignition sources are a required part of a hydrogen use. As an example, a combustor or engine should not be operated in hydrogen-rich atmospheres without well-dispersed water sprays in its exhaust. Experience indicates that multiple bank sprays will partially suppress the detonation pressures and reduce the number and temperature of ignition sources in an exhaust system. Water sprays should not be relied on as a means of avoiding detonations. Carbon dioxide may be used with the water spray to further reduce hazards.

Table X.3: Potential ignition sources[3]

Thermal Ignition	Electrical Ignition
Personnel smoking	Electrical short circuits, sparks, and arcs
Open flames	Metal fracture
Shock waves from tank rupture	Static electricity (two-phase flow)
Fragments from bursting vessels	Static electricity (flow with solid particles)
Heating of high-velocity jets	Lightning
Welding	Generation of electrical charge by equipment operations
Explosive charges	
Friction and galling	
Resonance ignition (repeated shock waves in a flow system)	
Mechanical impact	
Tensile rupture	
Mechanical vibration	
Exhaust from thermal combustion engine	

Note: Ignition sources must be eliminated or safely isolated and operations should be conducted as if unforeseen ignition sources could occur.

Detonation

The worst-case event resulting from release of all forms of hydrogen into the ambient environment is mixing of the hydrogen with an oxidizer (usually air), reaching detonable concentrations, and subsequent ignition producing a detonation of the mixture. The positive buoyancy and rapid molecular diffusion of gaseous H_2 means that any release will quickly mix with the surrounding gases. Rapid vaporization occurs and subsequent mixing with the surrounding gases can lead to a detonable mixture if LH_2 or SLH_2 leaks. Should a detonation occur, the resulting reaction zone is a shock wave and the accompanying blast wave has much greater potential for causing personnel injury or equipment damage.

Detonation Limits.

Lower and upper detonation limits vary considerably with the nature and dimensions of the confinement and cannot be specified for any fuel-oxidizer mixture unless the nature and dimensions of the confinement are also specified.

(1) Fig. X.1 shows the minimum dimensions of hydrogen-air mixtures for detonation in three types of confinement at 101.3 kPa. The figure shows a significant effect of confinement type on detonation limits. The ignition energy for detonation also becomes large for lean or rich mixtures; however, it is possible to produce overdriven detonations when large ignition energy is introduced. Therefore, detonation limits found in the literature should be used with caution.

(2) While values of lower and upper detonation limits for gaseous H_2-gaseous O_2 of 15 and 90 percent hydrogen, respectively, are cited, the values suffer from the same shortcomings noted for hydrogenair and should be used with caution.

(3) No specific detonation limits for LH_2 and air or GOX are available. The rapid volatilization of LH_2 to GH_2 and subsequent mixing with air or GOX would result in detonable mixtures as described above.

(4) Mixtures of solid oxygen in excess (with respect to stoichiometry) and LH_2 is shock sensitive. A stimulus (shock) of 100 to 250 MPa will detonate such mixtures. For comparison, nitroglycerin is detonated by 250 to 500 MPa shocks.

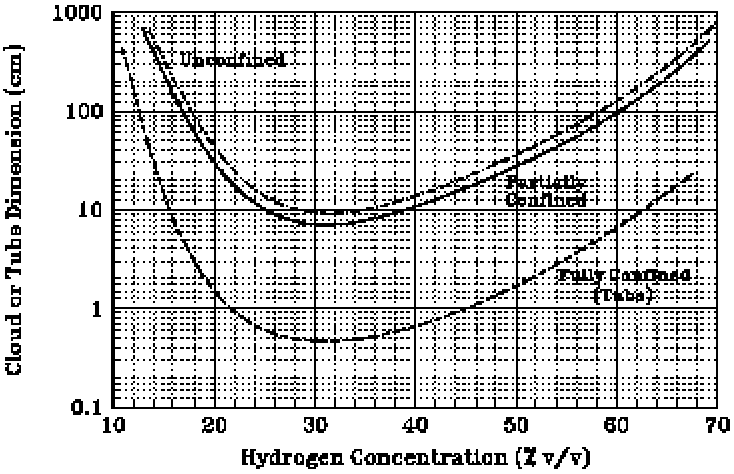

Fig. X.1: Minimum dimensions for detonation[4] of gaseous hydrogen – air mixtures at 101.3 kPa and 298 K .

Detonation Cell Size.

A detonation wave is not a single planar wave front but has a three-dimensional structure consisting of cells. The size of the cell, as measured through the pattern left by a detonation on a smoked plate, is of considerable value in predicting the onset of detonation and describing the conditions for stable detonation waves. The cell size has been shown to relate to several key parameters in assessing a potential hazard, including critical energies and dimensional characteristics of structural confinement of the detonation.

The length (a) of a detonation cell is one to two times its width (b). The aspect ratio (a/b) increases with decreasing initial pressure. Detonation cell lengths for stoichiometric gaseous H_2 air/ gaseous O_2 at 101.3 kPa are 15.9 mm and 0.6 mm, respectively. The measurements are specific to the system configuration used. Figure A2.8 gives the variation of detonation cell widths for gaseous H_2-air mixtures at 101.3 kPa. Ignition energy requirements depend on the concentration of the detonable mixture.

Energy of Explosion.

The explosive yields for hydrogen-air follow:

- NTP GH_2-air: approximately 24 g TNT/g GH_2 or 2.02 kg TNT/m^3 GH_2 or 0.17 g TNT/kJ GH_2

- NBP LH_2-air: 1.71 g TNT/cm^3 LH_2 (107.3 lb TNT/ft^3 LH_2)

It should be emphasized that only a fraction of this theoretical explosive yield will be realized in an actual open air mishap. It is virtually impossible to spill or release a large quantity of fuel and have all of it mix in proper proportions with air before ignition.

Deflagration-to-Detonation Transition.

A hydrogen-air combustion can start as a detonation, or it can start as a deflagration and then transit to a detonation after the flame has traveled for some distance. The composition rangein which a detonation can take place is narrower than that for deflagration. The commonly quoted range for detonation in a hydrogen-air mixture is from 18.3 to 59 percent hydrogen.

However, with higher energy ignition sources, the limits can be extended. The factors that influence whether hydrogen-air combustion will occur as a detonation, rather than a deflagration, include the hydrogen percentage, the strength of the initiator, complete or partial confinement of the reaction, and the presence of structures that can induce turbulence in the flame front. An energetic source of initiation is required for combustion to start as a detonation. A mechanism toaccelerate the flame velocity is necessary for a deflagration to transit to detonation. Factors that favor this transition include the composition being within the detonation range, a degree of confinement, and anything that can induce turbulence in the flame front as it travels through the combustible mixture. The latter tends to stretch out the flame front and increase its velocity.

X.4 TYPES OF HAZARDS ASSOCIATED WITH HYDROGEN

The hazards associated with the use of hydrogen can be characterized as physiological (frostbite, respiratory ailment, and asphyxiation), physical (phase changes, component failures, and embrittlement), and chemical (ignition and burning). A combination of hazards occur in most instances. The primary hazard associated with any form of hydrogen is inadvertently producing a flammable or detonable mixture, leading to a fire or detonation. Safety will be improved when the designers and operational personnel are aware of the specific hazards associated with the handling and use of hydrogen. Hazards of hydrogen use are discussed below.

X.4.1 IGNITION.

Fires and explosions have occurred in various components of hydrogen systems as a result of a variety of ignition sources. Ignition sources have included mechanical sparks from rapidly closing valves, electrostatic discharges in ungrounded particulate filters, sparks from electrical equipment, welding and cutting operations, catalyst particles, and lightning strikes near the vent stack. Table A2.1 lists additional ignition sources.

X.4.2 FIRE AND EXPLOSIONS.

A potential fire hazard always exists when hydrogen is present. The following situations can occur:

- H_2 diffuses rapidly with air turbulence increasing the rate of H_2 dispersion. Evaporation can rapidly occur in an LH_2 spill; resulting in a flammable mixture forming over a considerable distance. Although ignition sources may not be present at the leak or spill location, fire could occur if the movement of the flammable mixture causes it to reach an ignition source.

- A deflagration could result if a mixture within flammability limits is ignited at a single point.
- A detonation could occur if the gaseous H_2-air mixture is within detonability limits and an appropriate energy source is available. A deflagration could transform into a detonation if there is confinement or a mechanism for flame acceleration.
- Flash fires or boiling liquid expanding vapor explosions

X.4.3 HYDROGEN DISPERSION.

A property of hydrogen that tends to limit the horizontal spread of combustible mixtures from a hydrogen spill is its buoyancy. Although saturated hydrogen is heavier than air at the temperatures existing after evaporation from a spill, it quickly becomes lighter than air, making the cloud positively buoyant. The dispersion of the cloud is affected by wind speed and wind direction and can be influenced by atmospheric turbulence and nearby structures. A nice illustration of the rapid dispersion of hydrogen in air is given in the series of photographs in Fig. X.2. The much faster dispersion of hydrogen limits drastically the seriousness of the hazard. More information about hydrogen , methane and gasoline can be found in Table X.4. Although hydrogen has a much higher calorific value and a very low ignition energy, its high dispersion is clearly reducing its hazardous character.

Table X.4 : Comparison of various properties of hydrogen with those of methane and gasoline

Properties	hydrogen H_2	methane CH_4	gasoline $(\text{-CH2-})_n$
Lower caloric value [kJ/g]	120	50	44.5
Ignition temperature [°C]	585	540	228 - 501
Flame temperature [°C]	2045	1875	2200
Ignition range in air [Vol%]	4 - 75	5.3 - 15	1.0 - 7.6
Ignition energy [mJ]	0.02	0.29	0.24
Flame front velocity [m/s]	2.65	0.4	0.4
Detonation range [Vol%]	13 - 65	6.3 - 13.5	1.1 - 3.3
Detonation velocity [km/s]	1.48 - 2.15	1.39 - 1.64	1.4 - 1.7
Detonation energy [kg TNT/m^3]	2.02	7.03	44.22
Diffusion coefficient in air [cm^2/s]	0.61	0.16	0.05

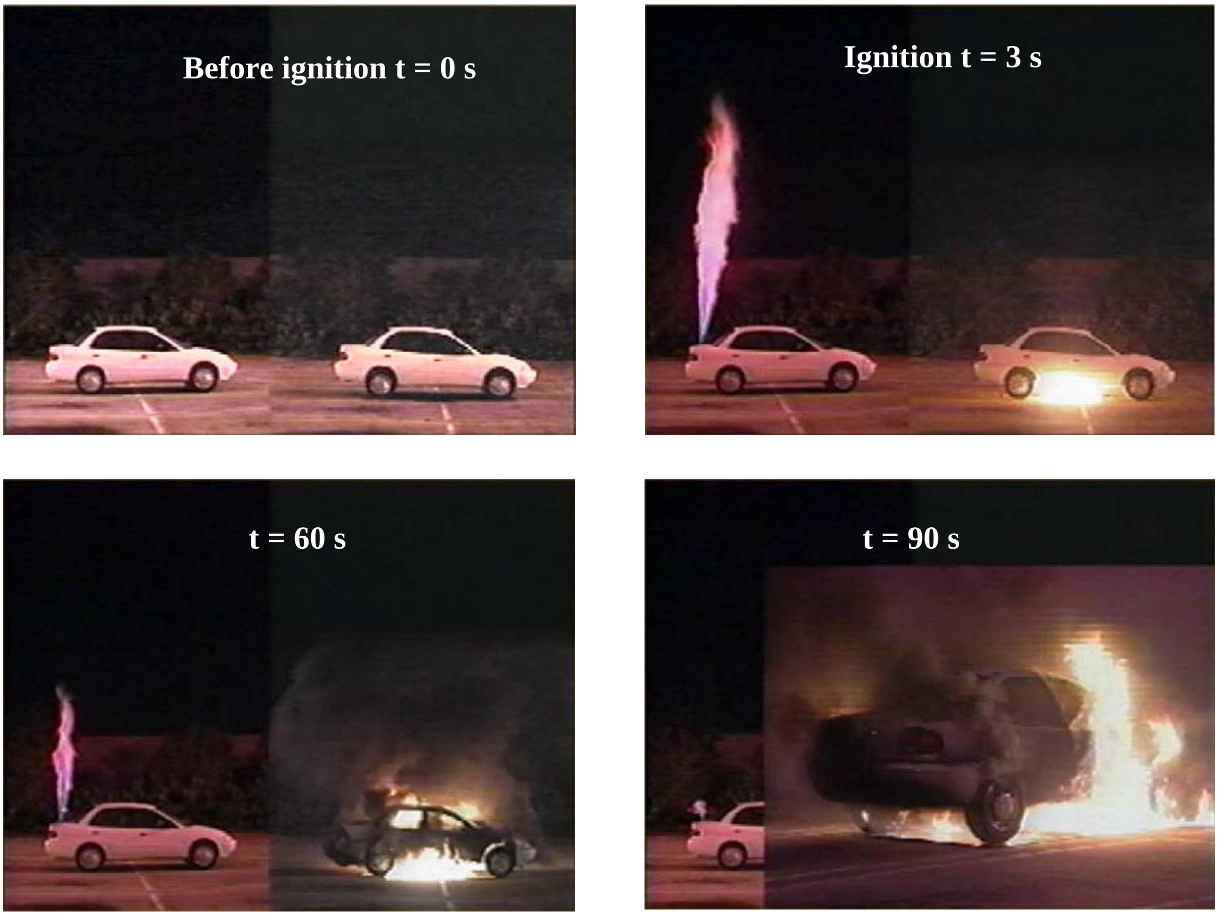

Fig. X.2: Comparison of hazard with a hydrogen powered vehicle on the left and a gasoline powered vehicle on the right. At time t=0 ignition of both fuels occur. After 3 s the hydrogen flow rate is 0.18 m^3/min while that of gasoline is 680 cm^3/min. After 60 s the hydrogen flow is almost finished. The view of gasoline powered vehicle in the last panel has been expanded to show the size of the gasoline fire[5].

X.4.4 PHYSIOLOGICAL HAZARDS.

Personnel present during leaks, fires, or explosions of hydrogen systems can incur several types of injury.

- Asphyxiation is a hazard when someone enters a region where hydrogen or a purge gas has displaced the air, diluting the oxygen below 19.5 percent by volume. The following stages of asphyxiation (at ground level) have been noted based on the oxygen concentration:

Volume percent of oxygen	Stages
15-19 percent by volume	Decreased ability to perform tasks; may induce early symptoms in persons with heart, lung, or circulatory problems
12-15 percent by volume	Deeper respiration, faster pulse, poor coordination
10-12 percent by volume	Giddiness, poor judgment, slightly blue lips
8-10 percent by volume	Nausea, vomiting, unconsciousness, ashen face, fainting, mental failure
6-8 percent by volume	Death in 8 min; 50 percent death and 50 percent recovery with treatment in 6 min, 100 percent recovery with treatment in 4 to 5 min
4 percent by volume	Coma in 40 s, convulsions, respiration ceases, death

- Blast waves from explosions will cause injury as a result of overpressure at a given location (eardrum rupture and worse)
- Cryogenic burns result from contact with cold fluids or cold vessel surfaces.
- Exposure to large LH2 spills could result in hypothermia if proper precautions are not taken.

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X.5 HYDROGEN DETECTION AND SENSORS

GH_2 is colorless and odorless and normally not detectable by human senses. Means shall be provided to detect the presence of hydrogen in all areas where leaks, spills, or hazardous accumulations may occur.

GH_2 Detection Specifications

(1) Detection and alarm at 1 percent by volume hydrogen concentrations in air, equivalent to 25 percent of the LFL, is required for enclosed areas in which GH_2 buildup is possible. Detection and alarm at 0.4 percent by volume hydrogen concentrations in air (equivalent to 10 percent of the LFL) is required for permit-required confined spaces.

(2) It may be necessary to conduct a gas sample through a sensing line to the sensor under conditions in which the sensor cannot be located at a leak source. The response time under such conditions depends on the length of the sensing line. Response times should be 1 s or less if possible.

(3) A 1 percent by volume hydrogen concentration in an exhaust purge should generate an alarm. A higher hydrogen concentration at a purge exhaust indicates a major leak or a fire hazard after the purge is exhausted in air.

(4) A 1 percent by volume hydrogen concentration should generate an alarm in a vacuum chamber when it is not evacuated and at anytime in the evacuation duct.

(5) A 1 percent by volume hydrogen concentration at any point 1 m from the hydrogen equipment should generate an alarm in areas around hydrogen facilities. The performance of the detectors depends on the location of sensors and the leak and wind directions, and they may fail to indicate a leak. A larger number of sensors may be necessary to survey the area of concern.

(6) Specifications for hydrogen sensors should include requirements for the following:

- (a) Minimum gas concentration detection requirements
- (b) Full scale range of the detector system
- (c) Level of concentration for which alarm detection is required
- (d) Response time of the detector system
- (e) Accuracy of sensors
- (f) Reliability and recalibration frequency
- (g) Interface to facility safety and shutdown systems

Detection Technologies.

(1) Bubble testing is one of the simplest methods of leak detection; however, it is not a continuous monitoring system, needs to be applied directly on the source of the leak, can only be used with inert gases at low pressure, and is limited to temperatures above freezing. Bubble solutions can detect very small leaks but do not measure concentrations.

(2) Catalytic combustion sensors detect hydrogen gas by sensing the heat generated by the combustion of hydrogen and oxygen on the surface of a catalytic metal such as palladium or platinum. The sensors work well for detection of hydrogen in the 0 to 4 percent by volume (0 to 100 percent LFL) in air but do not operate in inert environments or 100 percent by volume hydrogen. Sampling systems can be designed to mix air in with the sample before exposure to the catalytic sensor for operation in inert environments; however, this results in a longer response time. Catalytic sensors such as sintered bronze utilize a heated filament and need to be enclosed in flame arrests to prevent the sensors from becoming ignition sources. Also, catalytic sensors are not hydrogen specific and will respond to other combustible gases such as methane.

(3) Thermal conductivity sensors work well in stable environments with minimal temperature variations and a constant background gas. Thermal conductivity sensors work well in background gases that have a thermal conductivity that varies significantly from hydrogen, such as air or nitrogen. However, they do not work in helium backgrounds; a significant drawback for LH_2 systems because helium purges are often required because helium does not solidify at LH_2 temperatures. Thermal conductivity sensors can go from 0.02 to 100 percent by volume hydrogen detection.

(4) Electrochemical sensors typically utilize a liquid electrolyte and require a gas permeable membrane for the hydrogen to reach the electrolyte. The sensors are low power and canoperate from 0.02 to 100 percent by volume hydrogen. Exposure of the membrane to cryogenic or time-varying temperatures greatly affects the gas diffusion and can make the sensor unreliable.

(5) Semiconducting oxide sensors rely on surface effects with a minimum oxygen concentration present and do not work in inert environments. Semiconducting oxide sensor can operate at lower powers than catalytic sensors, but performance at lower temperatures is degraded. Semiconducting oxide sensors are relatively new and not as common as the older catalytic based systems.

(6) Mass spectrometers are extremely sensitive (1 ppm), very specific to the gas being detected, linear over a wide dynamic range, and provide continuous monitoring. The complexity and high cost of mass spectrometers requires skilled operators and the use of sampling systems to monitor multiple locations with one instrument. The use of long sample lines can significantly reduce the response time.

(7) Gas chromatographs are similar to mass spectrometers in their sensitivity and accuracy; however, measurement times are extremely slow. Gas chromatographs typically are used in alaboratory to analyze the gas collected in the field with sample bottles.

Table X.5: Typical Hydrogen Gas Detectors[6].

Type of Detector	Description
Catalytic	A palladium and/or platinum catalyst is used to facilitate the combustion of hydrogen with oxygen.A sensing element detects the heat of combustion.
Electro chemical	Liquid or solid electrolytes surrounding a sensing electrode and a counter electrode. Reaction with hydrogen product produces a current. The hydrogen gas must flow through a gas permeable membrane to reach the electrolyte.
Semi conducting Oxide	Hydrogen gas reacts with chemisorbed oxygen in a semiconductor material, such as tin oxide, and changes the resistance of the material.
Thermal Conductivity	The rate of heat conduction from a heat source into the surrounding environment is dependent on the thermal conductivity of that environment.
Mass Spectrometer	The gas is ionized and then accelerated through an electric field along a curved path. The amount of curvature induced by the electric field is dependent on the mass of the particle and is used to separate the particles by mass. A detector is placed in the path of the desired gas to be measured.
Sonic	Leaking gas can produce acoustical emissions in the range of 30 to 100 kHz, with 40 kHz being the most common.
Optical	The differences in the refractive index of various gases can be used for detection in sensors using optical interferometry.
Glow Plugs	Glow plugs are not a true gas detection technique. When a combustible gas mixture exists, the glow plug ignites the mixture and then the fire is detected with heat sensors.

(8) Ultrasonic leak detection can be used when hydrogen specificity is not required and there is minimal background interference noise. Ultrasonic systems typically are used to pinpoint the source of a leak, and cannot measure whether a combustible mixture is present.

(9) LH_2 leaks can be detected through loss of vacuum and by observing the formation of frost, the formation of solid air, or a decrease in outer wall temperature on vacuum-jacketed equipment.

(10) Glow plugs and heat sensors are a less common technique used for rapid leak detection. The glow plugs ignite any combustible mixture present and, a heat sensor detects the fire and provides rapid shutdown of the process. The theory is it is better to burn the hydrogen gas rather than letting a combustible mixture accumulate, and the facility can shut down before the fire can do significant damage if a fire is started

Table X.6: Sensitivity Limits of Hydrogen Detectors[6] (Minimum Detection Limits, Average Values).

	In Air			In Nitrogen		
Principle	atm-cc/s	% Hydrogen	% LEL	atm-cc/s	% Hydrogen	Distance (m)
Catalytic Combustion	8.0	0.02	0.5	80	0.2a	600 (b)
Bubble Testing	1 x 10-4	NA	NA	1 x 10-4	NA	NA
Sonic-Ultrasonic	1 x 10-2	NA	NA	1 x 10-2	NA	30 (c)
Thermal Conductivity	1 x 10-3	5 x 10-4	0.01	1 x 10-3	5 x 10-4	----
Gas Density	1 x 10-2	5 x 10-3	0.1	1 x 10-2	5 x 10-3	NA
Hydrogen Tapes	0.25	1.5	35	---- -	---	(d)
Scott-Draeger Tubes	----	0.5	13	----	----	NA
Electrochemical	----	0.05	1.2	----	0.05	300b
Optical Interferometer	----	0.2	5	----	0.2	NA

a) Only one commercial catalytic instrument has claimed to detect hydrogen in nitrogen.
b) The sensing head is remote from readout.
c) For pressure differential of 25 psi with orifice of 0.20 inch.
d)Tape can be placed on suspected leak site and visually checked periodically.
Dashes indicate information is not available.

Note: The system design should ensure that detection occurs immediately and operating personnel are notified as appropriate if hydrogen leaks into the atmosphere or a hydrogen fire occurs.

X.6 HANDLING, STORAGE AND TRANSPORT OF HYDRIDES[7]

X.6.1 HANDLING

The alkali- and the alkaline-earth- hydrides as well as the complex hydrides of the bor-group are extremely reactive, moisture sensitive bases (only $NaBH_4$ und KBH_4 are to some extent resistant to hydrolysis). On human skin and in lungs (in the form of powders) they are strongly aggressive.

Eyes and lungs are especially sensitive to these materials. For more details on these hydrides one should consult the specialised literature.
When handling hydrides such as LiH, CaH_2 $NaBH_4$, $LiAlH_4$ one should systematically wear protective glasses, a mask, a protection helmet with face protection and rubber gloves. In some cases wearing a protective coat might even be advisable.
In case hydrides are inadvertently brought in contact with your skin, you should immediately wash the skin with ample water followed by a second wash with a dilute solution of acetic acid. If some of these hydride came in contact with your eyes, wash them first with a lot of water and then with a l,2% solution of boric acid. Then go immediately to a physician.

The greatest source of hazard in the handling of hydrides is their large content of hydrogen. For hydrolyse sensitive hydrides (for example CaH_2) contact with water leads to a violent reaction and large production of hydrogen. This can lead to a dangerous pressure increase in closed containers. In presence of air hydrogen leaks can lead to the formation of explosive H_2-O_2 mixtures.
An additional hazard during the handling of some hydrides is that as powders they can react spontaneously with humid air and start to burn. They can then act as a potential ignition source for eventual explosive hydrogen-mixtures in the surrounding. To reduce this danger to acceptable level one should systematically

- exclude water in the immediate surrounding (by using for example other inert liquids in peripheral heating and cooling equipment)
- carry out all experiments in inert atmospheres
- use only explosion protected electrical equipment
- avoid any electrostatic charging that could lead to the formation of sparks
- arrange for adequate ventilation
- use gas reactors with safety valves to prevent sudden pressure built-up
- install backfire equipment.
- have dry-powder fire extinguishers (preferably based on sodium-chloride)), Asbestos covers and respiratory safety equipment within reach; a dry-powder shower might also be advisable. Under no circumstances should water-, carbondioxide or tetrachlorincarbon fire extinguishers be used to fight a fire.

X.6.2 IMPLICATIONS FOR CONSTRUCTION MATERIALS

Hydrogen can cause a significant deterioration in the mechanical properties of metals. This effect is referred to as hydrogen embrittlement. Hydrogen embrittlement involves a large number of variables such as the temperature and pressure of the environment; the purity, concentration, and exposure time of the hydrogen; and the stress state, physical and mechanical properties, microstructure, surface conditions, and nature of the crack front of the material. There are several types of embrittlement that can occur in one or a combination of the following three forms:

(a) Environmental hydrogen embrittlement that has been observed in metals and alloys plastically deformed in a H_2 environment. Deformations under such conditions lead to increased surface cracks, losses in ductility, and decreases in fracture stress. Cracks start at the surface.

(b) Internal hydrogen embrittlement caused by absorbed hydrogen. Small amounts of hydrogen may cause premature failures in some metals; the failures may occur with little or no warning. Cracks start internally.

(c) Hydrogen reaction embrittlement that occurs when the absorbed hydrogen chemically combines with one or more of the constituents of the metal to form a brittle hydride. This reaction occurs more readily at elevated temperatures. Hydrogen has formed methane with the carbon in steels.

For the construction of apparatus one should therefore take into consideration that :

- at room temperature most elastomere are inert with respect to hydrogen

- hydrogen is non corrosive at modest temperature and modest hydrogen pressures. This implies that virtually all metals used for construction can be safely used.

- at high pressure steels (especially cold worked ferritic steels) can suffer from hydrogen embrittlement. Metals with a face-centered cubic structure, such as, austenitic stainless steels, aluminum alloys, copper, and copper alloys, generally are satisfactory for hydrogen service. Nickel, a face-centered cubic material, is an exception and generally is not used because it is subject to severe hydrogen embrittlement. Unstabilized austenitic stainless steel (some of the 300 series) can revert to a martensitic structure when stressed above the yield stress at low temperature, reducing the ductility of the steel.

- at high temperatures one should use austenitic steels (AISI 316 or 304) to avoid segregation of carbon at grain boundaries. Above 300 ^{0}C one should use steels such as AISI 316L or 304L or, when possible, aluminium, siliconcarbide or siliconnitride.

- at low temperatures materials should remain sufficiently ductile. Steels such as AISI 316L or 304L, as well as aluminium and aluminium alloys, and furthermore, Teflon (PTFE, Polytetrafluorethylen) und Kel-F®.satisfy this condition

X.6.3 STORAGE AND TRANSPORT

All hydrides can be stored indefinitely as long as they are not in contact with air or humidity. Since they belong to the category of dangerous materials[8,9] their storage and transport should comply with existing rules.

The alkaline- and alkaline-earth hydrides, as well as the bor- and aluminum-complex hydrides (boranates and alanates) are Ie/2b hazardous materials, Titan- and Zirconium-hydride are II/6e hazardous materials. Consequently the following transport regulation apply: max. 50 kg of NaH in oil, of $NaBH_4$ or of KBH_4; 40 kg of NaH powder; 10 kg of LiH, MgH_2, CaH_2, $LiBH_4$, $LiAlH_4$ and substituted boranates and alanates. Transport by regular mail is not allowed.

X.7 REFERENCES

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