

Article I. Hydrogen Ignition.....	1
Article II. Introduction.....	1
Basic combustion properties.....	1
Article III. Static Electricity.....	5
Article IV. 3.1.5.3 Electrical Spark.....	7
Article V. Auto-ignition.....	9
Article VI. Mechanical Friction and Impact.....	12
Mechanical Rubbing.....	12
Impact.....	12
Mechanical sparks.....	12
Article VII. Ignition by Explosive.....	13
Article VIII. References & sources.....	14
Article IX. Ignition by Open Flame and Hot Surface.....	14
Article X. Ignition by Hot Surfaces.....	14
Article XI. Miscellaneous.....	15
Microwaves.....	15
Lightning.....	15
Chemical incompatibility/exothermic reaction.....	15
Lasers.....	15
Acoustics.....	15
Article XII. Ignition of Liquid hydrogen and solid oxygen mixtures	15
Article XIII. References & sources.....	16

Article I. Hydrogen Ignition

Contributing author	Main contributions	Organisation	e.mail
Stuart Hawsworth	Chapter coordinator	HSL	
Luc de Broisia	Static electricity	INERIS	

Contributing reviewer	Information reviewed	Organisation	e.mail

Article II. Introduction

There are number of potential ignition sources for flammable mixtures of hydrogen with an oxidant, which include flames, electrical sparks, fused wires, incendiaries, hot surfaces, heating, rapid adiabatic compression, shock waves and catalytic materials. All of these processes heat a portion of the combustible mixture to a sufficiently high temperature such that adjacent un-combusted layers also react, producing a flame, which propagates through out the mixture.

Basic combustion properties

Technical report ISO/TR 15916 (2004) presents basic combustion properties of hydrogen in air mixtures. These are reproduced in the Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-1 below.

Lower flammability limit (% vol.)	Lower detonation limit (%vol.)	Stoichiometric mixture (% vol.)	Upper detonation limit (% vol.)	Upper flammability limit (% vol.)	Minimum Ignition Energy (mJ)	Auto-ignition temperature (°C)
4.0	18.3	29.5	59.0	75.0	0.017	585

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-1 Ignition and combustion properties for hydrogen-air mixtures at 25 °C and 101.3 kPa

The flammability of hydrogen in air with nitrogen as a diluent is presented by Molnárné et al (2003), and flammability diagrams are presented at temperatures from 20°C to 400°C, and pressures from atmospheric to 100 bar. The flammability diagram for 20°C and atmospheric pressure is given in Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-5 below, reproduced from Molnárné et al (2003), with permission.

The limiting oxygen concentration at 20°C and atmospheric pressure can be read from Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-5 as 20.4% air. Since air contains 21% oxygen, the limiting oxygen concentration is $0.204 \times 21\% = 4.3\%$ oxygen. Raising the temperature widens the limits, but the lower limit has the greater ratio of change. The major change is to increase the upper limit, and decrease the limiting oxygen concentration (LOC). The diagram at 400°C and atmospheric pressure is as in Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-6. Note that the limiting oxygen concentration has fallen to 6.2% air, corresponding to a LOC of 1.3%, and the upper limit has risen from 75.6% to 87.6%. The lower explosive limit has fallen from 4.1 to 1.4%.

Similar effects are shown for increases in pressure, with the limits generally falling with pressure, and the limiting oxygen concentration rising. Tabulated data for the effect of temperature at atmospheric pressure is shown below in Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-2, and the effect of pressure at 20°C is shown below in Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-3 and Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-4.

Temperature °C	LEL % volume	UEL % volume	Limiting Air Concentration % volume	LOC % volume
20	4.1	75.6	20.4	4.3
100	3.4	77.6	19.1	4.0
200	2.9	81.3	15.0	3.2
300	2.0	83.9	10.9	2.3
400	1.4	87.6	6.2	1.3

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-2 - Effect of Temperature on Hydrogen Flammability - DIN 51649-1

Pressure bar	LEL % volume	UEL % volume	Limiting Air Concentration % volume	LOC % volume
1	4.3	78.5	21.5	4.5
10	4.9	72.4	27.6	5.8
100	5.8	74.1	25.9	5.4

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-3 - Effect of Pressure on Hydrogen Flammability - 2.7 dm³ Bomb

Pressure bar	LEL % volume	UEL % volume	LOC % volume
1	4.0	95.2	4.5
10	5.0	94.2	5.8
100	5.7	94.9	5.1

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-4 - Effect of Pressure on Hydrogen Flammability - prEN 1839-B

Note that there are small discrepancies between the Tables for 20°C and 1 bar. This is because the limit determinations were carried out using different methods. The preferred method is that of EN 1839-B.

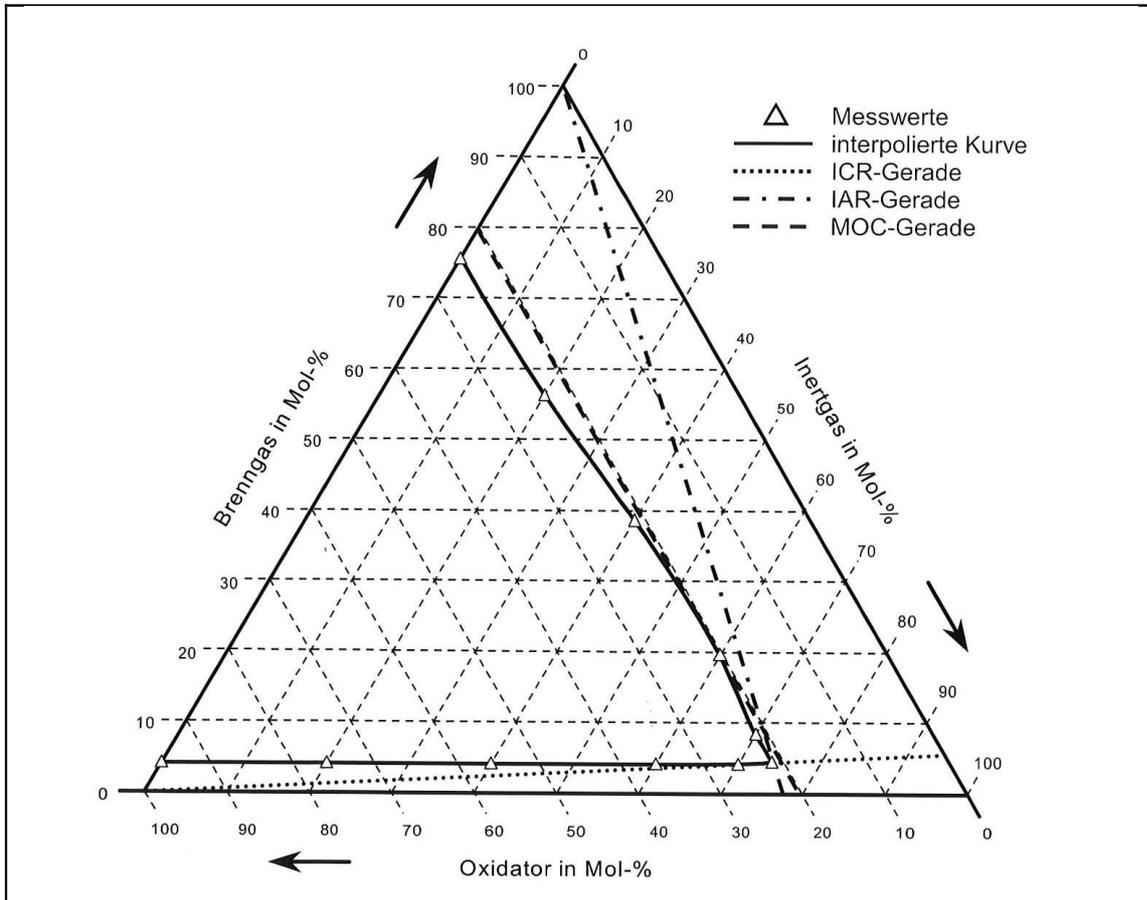


Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-5: - Flammability Diagram for Hydrogen/Air/Nitrogen at 20°C and 1 bar

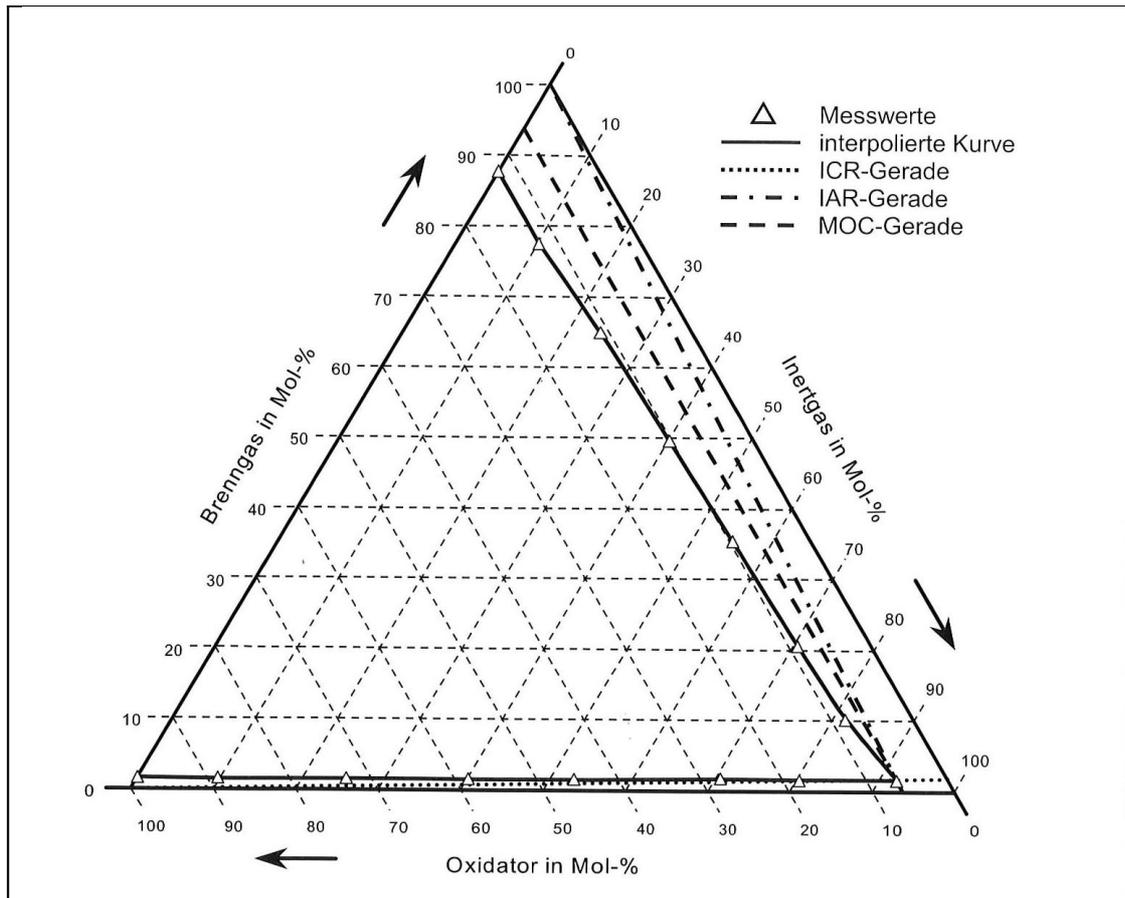


Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-6: Flammability Diagram for Hydrogen/Air/Nitrogen at 400°C and 1 bar

For hydrogen, the minimum ignition energy is low at 0.017 mJ for mixtures with air (ISO, 2004), and even lower at 0.0012 mJ for mixtures with oxygen (Kuchta, 1986). Hydrogen has a such a low minimum ignition energy that it is often difficult to determine the exact mechanism and cause of an ignition when it occurs. In some incidents where hydrogen has been involved in an explosion or fire, it has not been certain as to the source of ignition and the mechanism of the release. Some incidents have had obvious ignition sources such as flames or grinding sparks, but other incidents had releases of hydrogen where all obvious sources of ignition had been excluded, and self ignition had been blamed. The propensity of hydrogen to ignite in this fashion for no apparent reason has been reported several times previously, by Reider (1965), Lees, (1991), Anon (1922), and Fenning and Cotton (1930). In these incidents, no specific cause for ignition was identified. Several mechanisms have been suggested, of which two are worthy of note for discussion. The first mechanism is that of the reverse Joule-Thomson effect exhibited by hydrogen, and the second, the so-called "diffusion ignition" mechanism.

References & sources

Reider, Roy, (1965) An Unconfined, Large-Volume Hydrogen-Air Explosion, *Pyrodynamics*, **2**, 249-261.

Lees, F.P., (1991), in *Loss Prevention in the Process Industries*, Vol 3, Butterworth Heinemann Ltd., Oxford - Case History A77, at Ilford, Essex, Appendix 1 page 48; Case History A126, at Richmond, California, Appendix 1 page 62; Case History B33, at an unreported location, Appendix 1 page 72.

Anon, (1922), Spontaneous Ignition of Escaping Hydrogen, Engineering, **113**, April 21, page 502.

Fenning, R.W., & Cotton, F.T., (1930), Two Unexpected Hydrogen-Air Explosions, Engineering, **130**, August 22, page 252.

Kuchta, Joseph M., (1985), *Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries A Manual*, U.S. Bureau of Mines Bulletin 680.

ISO (2004), Basic considerations for the safety of hydrogen systems, ISO/TR15916: 2004

Molnárné, M., Schendler, T. and Schröder, V., (2003) *Sicherheitstechnische Kenngrößen, Band 2: Explosionsbereiche von Gasgemischen*, Wirtschaftsverlag NW, Bremerhaven, ISBN 3-89701-746-6

Article III. Static Electricity

The ignition hazards posed by static electricity require specific precautions to be taken. A Technical Report by CENELEC (2003) does not specifically refer to hydrogen but does refer to the flammable gas Group IIC and the ignition hazards associated with static electricity. This report addresses the maximum areas of insulating materials that may become charged, and restricting the maximum area limits the maximum charge that can be transferred from the surface in the form of a brush discharge. Such a discharge does not have a specific energy, but the ignition properties can be compared to those of a spark discharge between two conductors. The comparison has been discussed by Gibson and Harper (1988), who proposed the term *incendivity* to compare the quantity of charge transferred with its capability to ignite a flammable mixture with a given minimum ignition energy. Further work by von Pidoll (2004) gives specific guidance on the maximum tolerable charge transfer to ensure freedom from ignition. However, he has correlated the charge transferred with minimum ignition energy and the gas groups defined by the IEC in their standard, but does not take account of the time and spatial characteristics of the discharge. The maximum tolerable charge transferred for hydrogen is given by the CENELEC (2003) as 10 nC. This is a very small quantity of charge, and hence hydrogen is extremely prone to ignition from electrostatic discharges from insulating or non-conductive materials.

When using non-conductive solid materials there are restrictions on the size of chargeable surfaces. The restriction on the size of chargeable surfaces depends on the ignitability of the gases and vapours and the classification of the hazardous area:

- a) For sheet materials the area is defined by the exposed (chargeable) area;
- b) For curved objects the area is the projection of the object giving the maximum area;
- c) For long narrow materials, such as cable sheaths or pipes, the maximum size is defined by the transverse dimension.

The restrictions on areas are given in the following tables:

Zone	Maximum area, cm ²		
	Group IIA	Group IIB	Group IIC
0	50	25	4
1	100	100	20
2	No limit	No limit	No limit

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-7: Restriction on chargeable surface depending on zones and gas categories

Zone	Maximum area, cm ²		
	Group IIA	Group IIB	Group IIC
0	0.3	0.3	0.1
1	3.0	3.0	2.0
2	No limit	No limit	No limit

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-8: Restrictions on widths of narrow materials depending on zones and gas categories

There have been several instances in the past where accidental hydrogen releases have ignited spontaneously. Whilst these have been investigated, no satisfactory explanation has been produced, but there have been suggestions that some form of electrostatic charging has been present, resulting in an ignition. In view of the very low ignition energy of hydrogen, such ignitions are a distinct possibility. Astbury and Hawksworth (2005) have undertaken a critical review of several incidents with their postulated mechanisms, and has concluded that there is a distinct possibility that releases which ignite spontaneously may be of an electrostatic origin.

Whilst electrostatics can be due to an obvious charging mechanism, such as the discharge from a sheet of insulating plastic as described above, ignition of hydrogen from electrostatics generated from or by the hydrogen itself is a far more difficult mechanism to define. Generally, there is no particular propensity for pure gases to become electrostatically charged, as described by CENELEC (2003). As reported by Astbury and Hawksworth (2005), work at the U.K. Health and Safety Laboratory on releasing high pressure (15 MN m⁻²) hydrogen through various nozzles from 0.5 to 12 mm in diameter did not result in any spontaneous ignition at all. This would suggest that straightforward *pure* hydrogen does not in itself ignite.

However, there have been reports, particularly one by the periodical Engineering (Anon, 1930) reporting work undertaken by Nusselt in Germany, after a spontaneous ignition of hydrogen. Much of this work centred on the possibility of a catalytic effect from fine rust that was present. However, when hydrogen was released in the dark through a nozzle fitted with a funnel and a wire probe, corona discharges were seen, and on tapping the nozzle to disturb the rust, an ignition took place. Clearly under these circumstances the corona discharge was sufficient to ignite the released hydrogen. It is likely that the corona was started by the movement of the hydrogen generating an electrostatically charged dust cloud which was sufficient to produce an electrostatic field of a strength high enough to initiate a corona from the wire inserted into the funnel.

References & sources

CENELEC (2003), Electrostatics – Code of practice for the avoidance of hazards due to static electricity, PD CLC/TR 50404:2003.

Gibson, N. and Harper, D.J., (1988), Parameters for Assessing Electrostatic Risk from Non-Conductors - A Discussion, J. Electrostatics, **21**, 27-36.

von Pidoll, U. et al, (2004), Determining the Incendivity of Electrostatic Discharges without Explosive Gas Atmospheres, IEEE Trans. Ind. Applic., **40**, No.6, 1467-75.

IEC (1996), International Electrotechnical Commission Report IEC 60079-20:1996, *Electrical apparatus for explosive gas atmospheres – Part 20: Data for flammable gases and vapours, relating to the use of electrical apparatus.*

Astbury, G.R. and Hawksorth, S.J., (2005), Spontaneous Ignition of Hydrogen Leaks: A Review of Postulated Mechanisms, Proceedings of the International Conference on Hydrogen Safety, September 8th-10th, Congress Palace, Pisa, Italy.

Anon., (1922), Spontaneous Ignition of Hydrogen, *Engineering*, 113, April 21, p. 502.

Article IV.3.1.5.3 Electrical Spark

Electrical sparks are defined as discontinuous electrical discharges across a gap, in an otherwise complete electric circuit, between at least two electrodes occurring when the voltage exceeds the breakdown voltage. The characteristics of the discharge depend very much on the discharge circuit involving capacitors, resistors and inductors. In many technical applications, especially in spark ignition engines, optimized, standard ignition systems are used. Typically the systems are based on a capacitor to store the energy supplied by a high voltage generator, complemented by a circuit of low inductance and resistance containing an electronic device triggering the spark for control and synchronization purposes. In Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-9 a schematic diagram of the voltage and current of ignition spark as a function of time is presented after Maly and Vogel (1978)

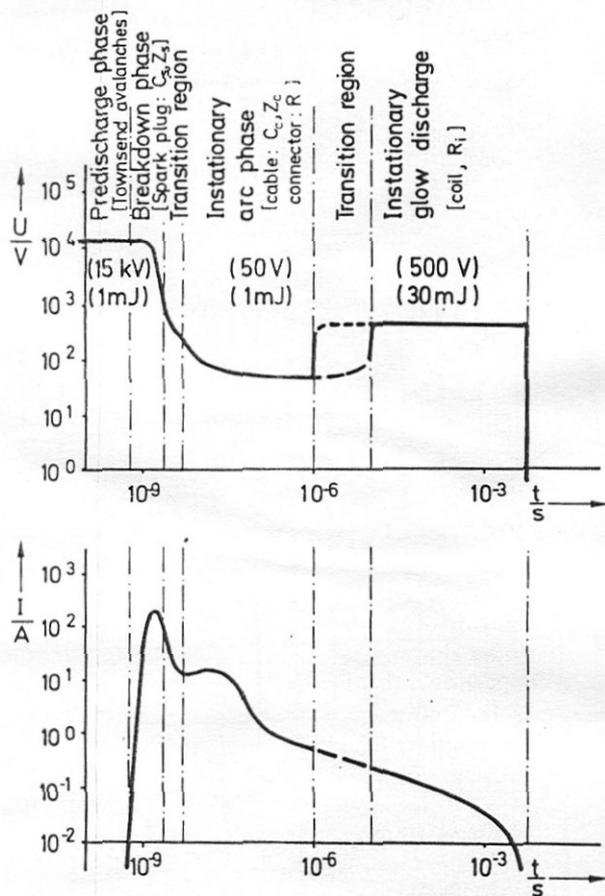


Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-9: Schematic diagrams of voltage and current of technical ignition systems as functions of discharge time. Typical values are given in parentheses, circuit parameters responsible for a discharge mode are indicated in brackets.

As it can be seen a typical electrical spark of a commercial ignition system can be divided in three phases. First a breakdown phase is initiated which creates in the gas a small diameter (~40 μm)

conducting plasma channel between the two electrodes. The phase is very short (1-10 ns) and characterized by high voltages (~10 kV) and currents (~200 A). Temperatures in the plasma channel reach up to 60 000 K, the molecules are fully dissociated and ionized causing the pressure to jump to 200 bar creating an intense shock wave and expansion of the discharge zone. The high conductivity of the plasma reduces the voltage provided by the circuit and the arc phase is initiated. The arc voltage is low (<100 V) although the current may be as high as the electrical circuit permits (up to several kA). The maximum temperature in the discharge zone drops to about 6000 K and ionization falls to a 1% level. The arc expands mainly due to conduction and diffusion producing bell shaped temperature and ionization profiles. Heat losses create appreciable cathode and anode voltage falls and the glow phase begins during which currents drop to a 200 mA level, the gas temperature is less than 3000 K and ionization less than 0,01%. The conversion efficiency of electrical to thermal energy of the gas decreases from the breakdown to the glow phase mostly due to the heat losses to the electrodes. To initiate a flame shortly after breakdown the chemical reaction must produce enough energy to overcome heat losses and the ignition kernel has to grow beyond a critical size for the flame to develop, typically must be two times larger than the laminar flame thickness. Obviously the electrodes, their separation, shapes and material play an important role in this process.

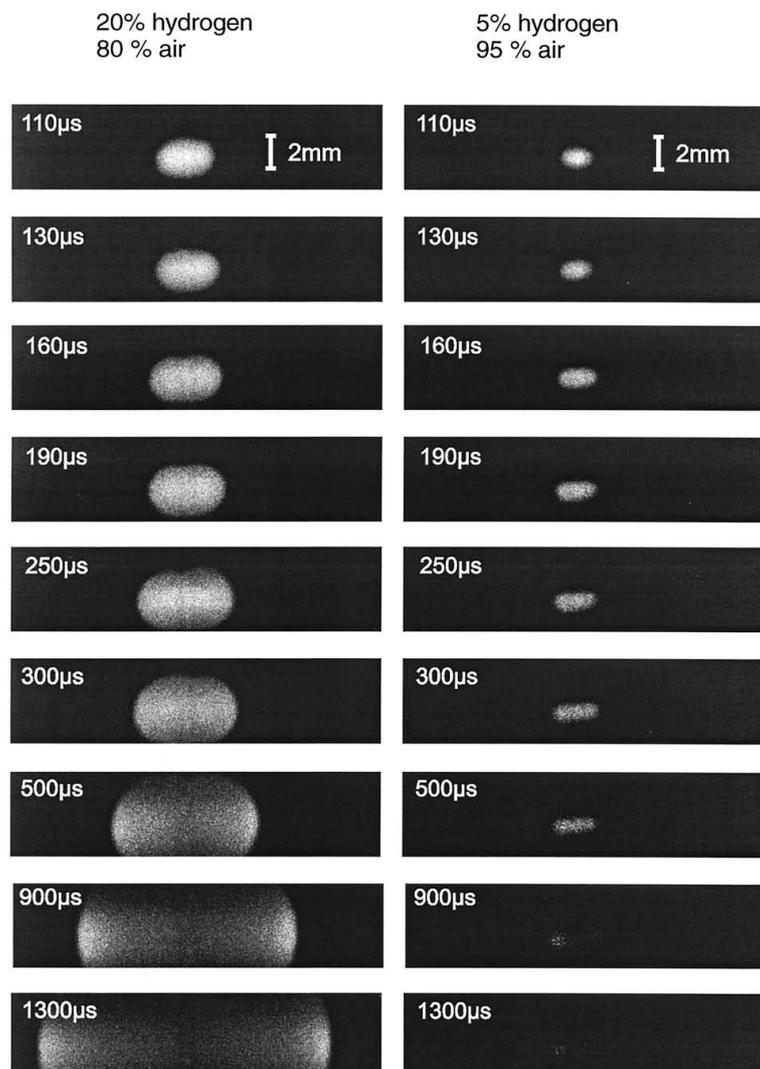


Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.- 10: Temporal evolution of a flame kernel visible as a relative OH concentration profiles recorded by PLIF for an ignitable and below the ignition limit mixture of hydrogen and air. Spark duration was 100 μ s.

Spark ignition constitutes a very complex interplay between plasma kinetics, chemical kinetics, molecular transport processes and fluid dynamics. Experimental investigations of spark kernels and their transition to flame kernels are rendered difficult because of very short process times, extremely high core temperatures and large gradients in the refractive index. In general, only flame propagation subsequent to spark ignition can be studied by laser diagnostic methods. Therefore, internal structures of the plasma core remain mostly unknown. A complete mathematical simulation of a spark ignition is also a difficult task because of the enormous numerical problems, due to the stiffness and high dimensionality of the problem (each chemical species introduces an additional conservation equation). Recently Thiele et al. (2002) have conducted detailed two dimensional numerical modeling of spark ignition of hydrogen-air mixtures. Their model considered heat conduction from the gas phase to the electrodes, detailed chemistry and molecular transport as well as the coupling of the gas dynamics to the properties of the electrical discharge through heating by the electrical current. They also performed spark ignition experiments using a highly reproducible ignition system. Shapes of early flame kernels were monitored by 2-D laser-induced fluorescence PLIF imaging of OH radicals produced during the ignition and the combustion process (Fig.2). In addition, for a central position within flame kernel, temperatures were measured using CARS. Results from experiments and simulations suggest the birth of a self sustaining flame propagation for process times between 50 to 70 μ s after arc breakdown.

References & Sources

R. Maly, M. Vogel. *Initiation and propagation of the flame fronts in lean CH-air mixtures by three modes of the ignition spark*. Published in the Proceedings of the Combustion Institute, Vol. 17, 1978 pp. 821-831.

M.Thiele, J.Warnatz, A.Dreizler, S.Lindenmaier, R.Schiesl, U.Mass, A. Grant, P.Ewart, (2002), Spark Ignited Hydrogen/Air Mixtures: Two Dimensional Detailed Modeling and Laser Based Diagnostics, Combustion & Flame 128:74-87

Article V. Auto-ignition

Generally auto-ignition results from either the exothermic of chain branching character of the oxidation reactions that at certain conditions self-accelerate to reach high conversion and heat release rates. Auto-ignition limits can be established testing experimentally or theoretically a homogeneous mixture of volume V filling a vessel whose walls have a temperature T_w . Once the heat release rate in the volume due to reactions exceeds the heat lost to the walls or if the reaction rates in the vessel exceed the reaction quenching (termination) rates by the walls or in the gas a thermal or branched-chain (isothermal) auto-ignition occurs. Typically, as almost all combustion reactions are exothermic, chain auto-ignitions cause also self heating and are accelerated by both factors. Obviously auto-ignition limits are not only a feature of the mixture composition and parameters (pressure, temperature) but also of the vessel size, wall properties and internal flow conditions.

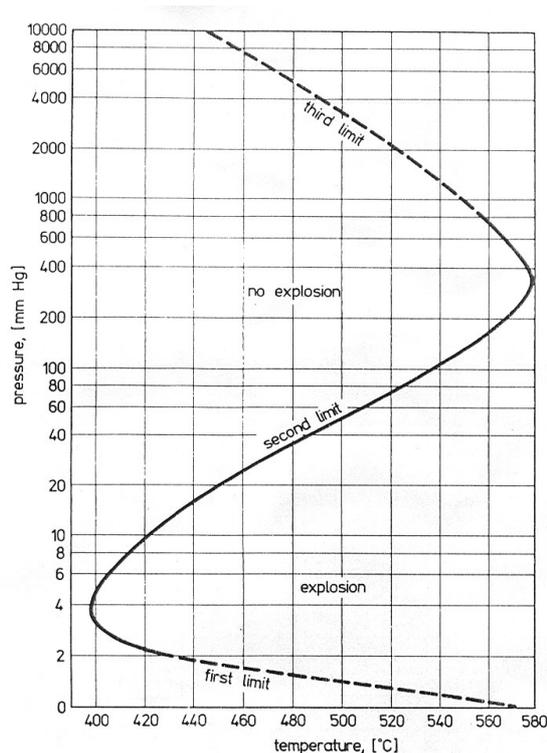


Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-11 - Explosion limits of a stoichiometric hydrogen-oxygen mixture in a spherical HCl coated vessel of 7.4 cm diameter.

This is illustrated in Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-11 showing the auto-ignition limits often called also explosion limits for a stoichiometric mixture of hydrogen and oxygen (B. Lewis, 1987) providing the important parameters of the test vessel. We may note the logarithmic scale of pressure and linear scale of temperature showing that pressure effects on reaction rates are weaker than temperature effects as one would expect by the consideration of Arrhenius chemistry.

The first and second limits, although interesting from the fundamental point of view, correspond to very low pressure (up to about 0.3 bar) and are thus of little practical interest. The third limit follows the trend that one would expect from simple density considerations. As the pressure increases, the initial densities of the reactants increase and a lower temperature is necessary for the reactions to reach a critical reaction rate for explosion. For safety considerations explosions in large volumes where wall effects can be neglected at atmospheric conditions and for most violently reacting, i.e. stoichiometric mixtures are considered. Thus, in typical safety manuals a temperature of 585°C is given as the auto-ignition temperature for hydrogen air systems.

The initial reaction rate in auto-ignition is very small thus a certain time must pass before the reaction has reached a defined rate. This time interval is called ignition delay. Ignition delays are particularly important for operation of engines as they provide the engine speed limits where operation is possible due to auto-ignition (compression ignition engines) or where auto-ignition can be avoided when detrimental (knock in spark ignition engines).

Most accurate ignition delay measurements can be performed in shock tubes in wall reflected shocks where the heating of the mixture is practically instantaneous. A research issue is then prediction of the ignition delays using available kinetic data. The state of the art in this field is far from satisfactory as

illustrated in Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-12 - after Wang et al. (B. L. Wang, 2003) where a comparison of measured and calculated ignition delay times using different chemical reaction mechanism, available in the literature is provided.

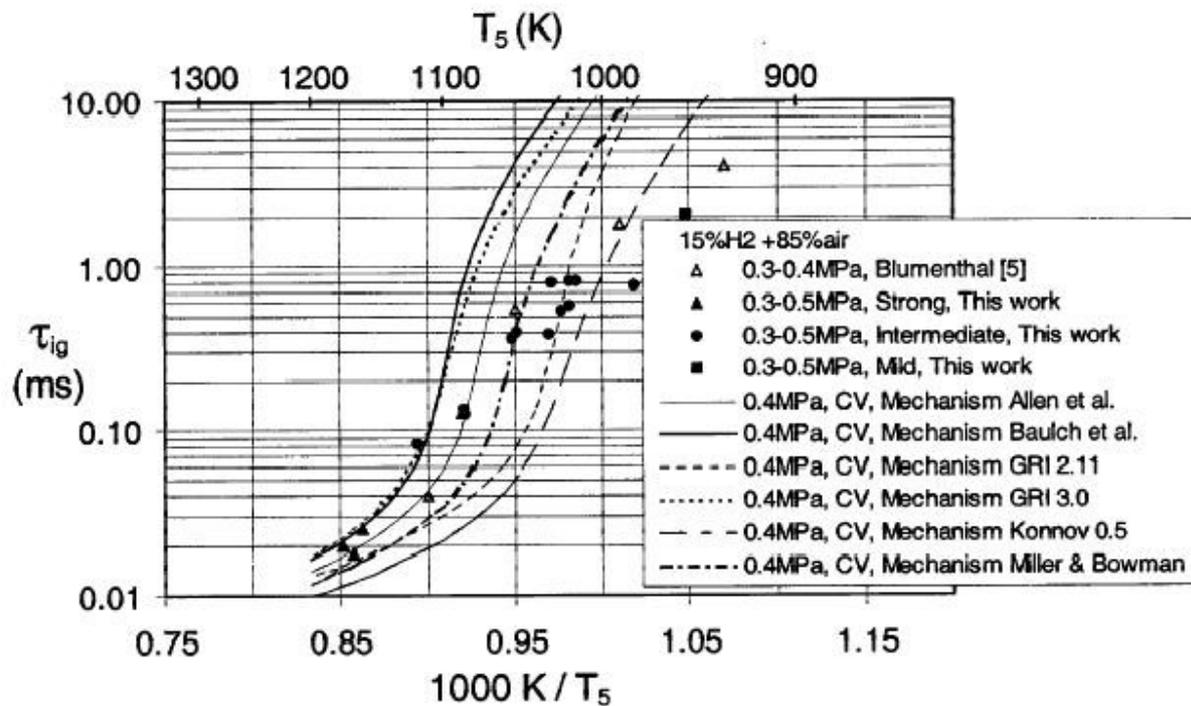


Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-12 - Measured and calculated ignition delay times in a H₂-air mixture.

In the low temperature range the measured ignition delay times are much shorter (even by orders of magnitude) than the theoretically predicted ones. Partially this is because in shock wave ignition mild and strong ignition regimes are possible. For the case of mild ignition multiple and random ignition kernels appear in the mixture. In the case of strong ignition typically reproducible direct transitions to detonation occur. Mild ignition is extremely sensitive to homogeneity of the mixture, impurities, wall properties of the shock tube and particularly to presence of even minute obstacles causing shock reflections, shock focusing and thus generating local hot spots. Thus, this form of ignition is very difficult to control particularly in natural conditions. If the volume of the mixture is large enough deflagration to detonation transition will eventually occur even after mild ignition causing convergence of effects of both types of ignition in accidental explosions.

An interesting case of shock wave induced ignition is the jet release auto-ignition that may happen when gas kept at high pressure is rapidly released from a volume into the atmosphere. The flow velocities in the jets reach supersonic levels due to further expansion after the release valve. Then shock waves will appear in the jets due to interaction with the surrounding gas, heating the nascent mixture to temperatures exceeding auto-ignition levels (Wolanski and Wojcicki, 1972). If obstacles are in the way of the jets the process is highly facilitated.

References & sources

Lewis, B. and von Elbe, G. (1987), *Combustion, Flames and Explosions of Gases*. (3rd Edition), Academic Press, New York.

Wang, B.L., Olivier, H. and Grönig, H. (2003), Ignition of shock-heated H₂-air-stream mixtures. *Combust. Flame*, **133**, 93-106.

Wolanski, P and Wojcicki, S., (1972), *Investigation into the mechanism of the diffusion ignition of a combustible gas flowing into an oxidizing atmosphere*. Proc. of the Combustion Institute, **14**, 1217-1223.

Article VI. Mechanical Friction and Impact

Mechanical Rubbing

Brearley and Tolson (1995) measured power levels and contact loads required to ignite flammable gas mixtures by a 25 mm cube of stainless steel frictionally heated through rubbing against a stainless steel wheel at circumferential velocities of 5 and 20 m/s. In these tests a contact load of 750 N was required to ignite hydrogen. This equates to a dissipated power of approximately 2 kW and a power density of approximately 0.5 W/mm². No temperature recordings were made in the tests. It was noted that in most cases the ignition was caused by the hot spot close to the point of contact.

In Powell's (1984) review he summarises data from various experiments breaking them into two categories with rubbing speeds above and below 10 m/s. The Table is presented below and shows results from Group IIC gases (hydrogen etc).

Work at HSL (MECHEX Project) has shown that at low rubbing speeds, hydrogen was ignited at a temperature close to the auto-ignition temperature. The conditions were: power 0.7 kW and rubbing speed 0.7 m/s which caused ignition at 530°C. Ignition occurred from the hot surface with few sparks produced from the low speed conditions.

Impact

In his paper, Powell (1986) states how little energy is needed to ignite flammable gases and vapours with impact of light metals and their alloys, producing burning particles with temperatures in excess of 2000°C from light impacts (<1J) with material such as Cerium, Titanium Zirconium, Hafnium and their alloys. Impacts on smears of aluminium or magnesium on rusty steel are also equally incendive. There is therefore a high probability of igniting hydrogen under these conditions.

Powell reports on ignitions caused by impacts between very hard steels (>550 VPN). Energies of 250 to 1000 J are required to ignite methane-air, with slightly lower energies igniting IIA vapours. For steel with VPN pf approximately 550, an energy of 180 J was sufficient to cause ignition. Ignition of hydrogen-air mixtures from impacts involving very hard steels are therefore very likely.

Mechanical sparks

There are a number of key properties of burning metal particles or sparks that are relevant to their ability to cause ignition of a flammable atmospheres. These include: size, material, velocity, temperature, number, combustion rate and time. There is a metal to metal contact pressure and relative velocity threshold for spark production during impact, rubbing or grinding. Above the threshold metal particles are lost from the weaker of the two materials. Generally, particles are only produced when the relative velocity between the two surfaces exceeds 1 m/s (Bernend and Ritter).

References & sources:

ISO (2004), Basic considerations for the safety of hydrogen systems, Technical report ISO/TR 15916:2004(E)

Brearily and Tolson, (1995), The frictional ignition properties of (18/8) stainless steel. HSL internal report IR/L/IC/95/02

Powell F., (1984), Ignition of gases and vapours by hot surfaces and particles – a review, 9th International Symposium on the Prevention of Occupational Accidents and Diseases in the Chemical industry, Luzer, pp. 267-292.

Powell F. (1986), Can non-sparking tools and materials prevent gas explosions?, *Gas-Wasser-Abwasser* **66**, Jahrgang Nr. 6

Bernend E. and Ritter K. Mechanically produced sparks. Section 2.4 of the Handbook of Explosion Protection, Edited by Henrikus Steen, Published by in Germany by Wiley VCH. HSE translation No 2000/20.

Snee T. J. and Griffiths J. F., (1989), Criteria for spontaneous ignition in exothermic, autocatalytic reactions: chain branching and self-heating in the oxidation of cyclohexane in closed vessels. *Combustion and Flame*, **75**, 381-95.

BS EN 1127-1:1997 Explosive atmosphere – Explosion prevention and protection Part 1. Basic concepts and methodology, (1997).

Lees F. P., (1991), *Loss Prevention in the Process Industries*, Vol 3, Case History A77, pp A1/48, Butterworth Heinemann Ltd., Oxford.

NASA, (1997), Report NSS 1740.16. Safety Standard for Hydrogen and Hydrogen Systems.

Article VII. Ignition by Explosive

An explosive is a powerful ignition source and will readily ignite a flammable fuel/air mixture and even under the right conditions directly initiate a detonation in an unconfined mixture. No data has been found in the literature on the minimum amount of explosive required to ignite a fuel/air mixture, but there have been a number of experimental and theoretical studies to determine the minimum amount of explosive required to initiate an unconfined detonation by Bull et al (1978) and Bull (1979).

As might be predicted from the general behaviour with other ignition sources the mass of explosive required to initiate an unconfined detonation in a hydrogen/air mixture is very much less than that required for less reactive fuel/air mixtures such as propane or methane. Table 1 compares the minimum amount of tetryl required to initiate an unconfined detonation in the most detonable hydrogen/air mixture and other common fuel/air mixtures. For hydrogen and the other fuels listed in Table 1, apart from acetylene, the most detonable mixture lies within a stoichiometry range of between 1.1 and 1.3. For acetylene the value for the most detonable mixture is 2.05. For all fuels the minimum amount of explosive required increases rapidly as the mixture approaches the detonation limits. In the case of hydrogen it is predicted there is about a hundred-fold increase in the mass of tetryl required to initiate a detonation in near limit mixtures compared to the most detonable mixture (stoichiometry of about 1.1).

Fuel	Mass tetryl (g)
Hydrogen	0.8
Methane	16,000

Propane	37
Ethylene	5.2
Acetylene	0.4

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.-13: Minimum mass of tetryl required to initiate unconfined detonation

Article VIII. References & sources

D.C.Bull, J.E.Elsworth and G.Hooper, (1978), Acta Astronautica **5**, 997.

D.C.Bull, (1979), Concentration limits to the initiation of unconfined detonation in fuel/air mixtures, Trans IChemE **57**, 219-227.

Article IX. Ignition by Open Flame and Hot Surface

Open flames will in any circumstances ignite an explosive hydrogen / air mixture

Article X. Ignition by Hot Surfaces

Ignition by a hot surface occurs as a result of local heating of the hydrogen-oxidant mixture to the point where a sufficiently large volume reaches the autoignition temperature and the combustion reaction is initiated. For this to occur generally requires the surface to be at a temperature well above the autoignition temperature (see Powell, 1984), although the actual temperature depends on a number of factors in addition to the usual mixture concentration, ambient temperature etc. These additional factors determine the hot surface ignition behaviour of flammable gases and not just hydrogen, and include the size and shape of the hot surface, the degree of confinement around the surface, the strength of the convection currents across the surface (See Laurendau, 1982) and the material of the surface (Lewis von Elbe, 1987, page 380).

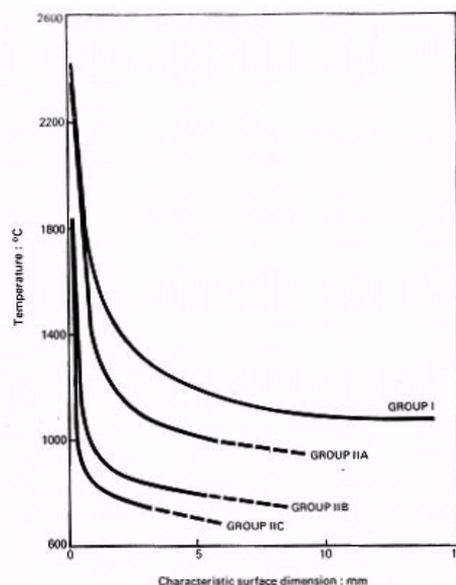


Figure * Summarises size dependence of hot surface ignition temperatures as a function of size (Hydrogen is represented by curve IIC).

For a particular hot surface, ignition is characterised by an ignition delay, which under ideal circumstances multiplied by the power for ignition gives a linear relationship between the product

(energy) and ignition delay (Lewis von Elbe, 1987, page 365 & Carleton et al (2000)). The offset on the y-axis in this plot is the minimum power for ignition for that arrangement.

The temperatures required to cause ignition of mixtures of hydrogen with air and oxygen (see review in J W Buckle and S Chandra (1996) & Carleton et al 2000, Hawksworth et al 2005) range from 640oC to 930oC, the spread of temperatures being explained the size, geometry effects etc described in the first paragraph. While the temperatures quoted are above the auto ignition temperature, the increase is much less than seen for hydrocarbon-fuel air mixtures, as illustrated by the IIA curve in Figure *. In terms of simple modelling of hot surface ignition, Laurendau (1982) presents a simple model in terms of a one step reaction chemical kinetics model.

Interestingly, the most easily ignited mixture of hydrogen wit air lies lean of stoichiometric (See Calcote and Gregory (1952)) while work using very small hotsurfaces (Carleton et al (2000) and Hawksworth et al (20004)) suggests that mixtures as low as 10 to 15% are the most easily ignited. For hydrogen-oxygen mixtures, the work of Buckle and Chandra indicates a fairly flat H₂ concentration dependence (slight positive slope with increasing hydrogen concentration) between roughly 20 and 90% hydrogen in oxygen.

Catalytic surfaces (e.g platinumium) have a dramatic effect on the ignition temperature required (Cho and Law 1986), ignitions reported at temperatures as low 70oC.

1. Powell F (1984), "Ignition of Gases and Vapours by Hot Surfaces and Particles - A Review", 9th International Symposium on the Prevention of Occupational Accidents and Diseases in the Chemical Industry, Luzer pg 267-292.
2. Laurendau N M (1982), "Thermal Ignition of methane-air mixtures by hot surfaces: A critical examination" Comb. and Flame, 46, pg 29-49.
3. Lewis B & von Elbe G (1987), "Combustion, Flames and Explosions of Gases (Third Edition)", Academic Press, 1987, ISBN 0-12-446751-2,
4. Carleton F, Bothe H, Proust C & Hawksworth S (2000), "Prenormative research on the use of optics in potentially explosive atmospheres" European Commission BCR Information Project Report EUR 19617 EN.
5. J W Buckle and S Chandra (1996) "Hot Wire Ignition of Hydrogen-Oxygen Mixtures", Int. Journal of Hydrogen Energy Vol. 21, No. 1, pp 39-44
6. Calcote, H F and Gregory C A Jr, Barnett C M and Gilmer R B (1952) Spark ignition - effect of molecular structure. Industrial and Engineering Chemistry, 44 (11), 2656-2662.
7. Cho P O and Law C K (1986) "Catalytic Ignition of Fuel/Oxygen Nitrogen Mixtures Over Plantinium", Combustion and Flame 66, 159, 70.

Article XI. Miscellaneous

Microwaves

Lightning

Chemical incompatibility/exothermic reaction

Lasers

Acoustics

These subjects will be covered in the next edition.

Article XII. Ignition of Liquid hydrogen and solid oxygen mixtures

Liquid hydrogen has properties which set it apart from the other cryogenic fuel of liquefied natural gas, in that its atmospheric boiling point is much lower than that of air. Pipe-work and vessels at liquid hydrogen temperatures of about 20 K will condense air from the atmosphere. It will also be cold enough to condense and freeze water and carbon dioxide from the air.

Material	Melting Point K	Boiling Point, K
Hydrogen	14	20
Helium	1	4
Oxygen	54	90
Nitrogen	63	77
Carbon Dioxide	sublimes	195 [#]

Fig Erreur! Il n'y a pas de texte répondant à ce style dans ce document.- 14 Data from Yarwood, T.M., and Castle, F., Physical and Mathematical Tables, 2nd Edition, Macmillan & Co. Ltd., (1961) except #International Critical Tables, McGraw Hill, (1933).

Work undertaken by Perlee et al (1964) indicated that liquid hydrogen can condense and freeze oxygen. The resultant solid oxygen in an excess of liquid hydrogen can be detonated by impact. They used a rifle and with a muzzle velocity of 600 m s^{-1} , detonation always occurred when the bullet impacted the mixture. Detonation was indicated by the use of thin metal strip gauges which deflected permanently when a detonation occurred. The results indicated that the explosive yield of liquid hydrogen-solid oxygen mixtures was greater than those for equal weights of trinitrotoluene (TNT).

Various experiments were carried out in which there was a large excess of liquid hydrogen. The specific gravity of liquid hydrogen is typically about 0.07, and that for the solid oxygen in the α state is about 1.426. The sonic velocities in the hydrogen and solid oxygen phases

Article XIII. References & sources

Perlee, H.E., Litchfield, E.L. and Zabetakis, M.G., (1964), Review of Fire and Explosion Hazards of Flight Vehicle Combustibles, Technical Report No. ASD TR 61-278 Supplement 3, AF Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio.

