

2nd Joint Summer School on Hydrogen and Fuel Cell Technologies

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Hazards related to hydrogen properties and comparison with other fuels

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Lecture topics

- ❖ Definitions of hazards, risk and safety
- ❖ Hazards related to hydrogen properties
 - ✓ Physical and chemical properties
 - ✓ Combustion properties
- ❖ Comparison with other fuels

Hazard (definition)

- ❖ Hazard can be defined as a chemical or physical condition that has the potential for causing damage to people, property and the environment.
- ❖ Hydrogen accident could have different hazards, e.g. asphyxiation due to release in closed space, frostbite by liquefied hydrogen, thermal hazards from jet fire, pressure effects from deflagrations and detonations, etc.
- ❖ Hazard could lead to no damage, if the proper safety measures are applied, or could lead to costly consequences up to fatalities if the system or infrastructure has been designed and used without professional knowledge in hydrogen safety.

Risk and safety (definitions)

- ❖ The modern definition of *risk* is provided by ISO/IEC Guide 73:2002 (2002) stating that it is the “***combination of the probability of an event and its consequence***”.
- ❖ ***Safety*** is defined there as the “***freedom from unacceptable risk***”.
- ❖ This means that *safety is a societal category* and cannot be numerically defined while *risk is a technical measure* that can be calculated (LaChance et al., 2009)..

Topic 1: **Hazards related to hydrogen properties**



Hydrogen

- ❖ As a unique gas hydrogen was discovered by Henry Cavendish in 1766.
- ❖ It was given the name “water forming” by Antoine Lavoisier 1773, who proved that water was composed of hydrogen and oxygen.
- ❖ The word “hydrogen” originates from the Greek words hydōr (water) and gignomai (forming).
- ❖ However, it has to be mentioned that hydrogen was observed and collected by Robert Boyle in 1671, who dissolved iron in diluted hydrochloric acid, i.e. long before it was recognized as a unique gas by Henry Cavendish.
- ❖ Hydrogen is one of the main compounds of water and of all organic matter. It is the most abundant element in the Universe representing 75% by mass or 90% by volume of all matter. Hydrogen forms 0.15% of The Earth crust.

Physical and chemical properties



Atomic hydrogen

- ❖ Atomic number of hydrogen (symbol H) in the periodic table is one, and atomic mass is 1.008 g/mol.
- ❖ H atom is formed by a nucleus with one unit of positive charge (proton) and one electron. Charges of the proton and electron cancel each other out (atom is electrically neutral).
- ❖ The proton is more than 1800 times more massive than the electron. Neutron can be present in the nucleus.
- ❖ Neutron has almost the same mass as proton and does not carry a charge. The radius of the electron's orbit, is 100,000 times as large as the radius of the nucleus. Size of hydrogen atom in its ground state is 10^{-10} m (1 angstrom).
- ❖ Three isotopes: protium (only a proton in the nucleus, 99,985% in nature), deuterium (P+N, 0.015%), tritium (P+2N) with atomic mass 1, 2 and 3. Tritium is unstable and radioactive (β rays – fast moving electrons as a result of neutron conversion into a proton, 12.3 years half-decay time).

Molecular hydrogen

- ❖ In normal conditions hydrogen is a gas formed by diatomic molecules, H_2 (molecular mass 2.016), in which two hydrogen atoms have formed a covalent bond.
- ❖ This is because the atomic arrangement of a single electron orbiting a nucleus is highly reactive. For this reason, hydrogen atoms naturally combine into pairs.
- ❖ Hydrogen is ***colourless, odourless and insipid***. That is why its leak is difficult to detect. Compounds such as mercaptans, which are used to scent natural gas, cannot be added to hydrogen for use in PEM (proton exchange membrane) fuel cells as they contain sulphur that would poison the fuel cells.

Ortho- and para-hydrogen

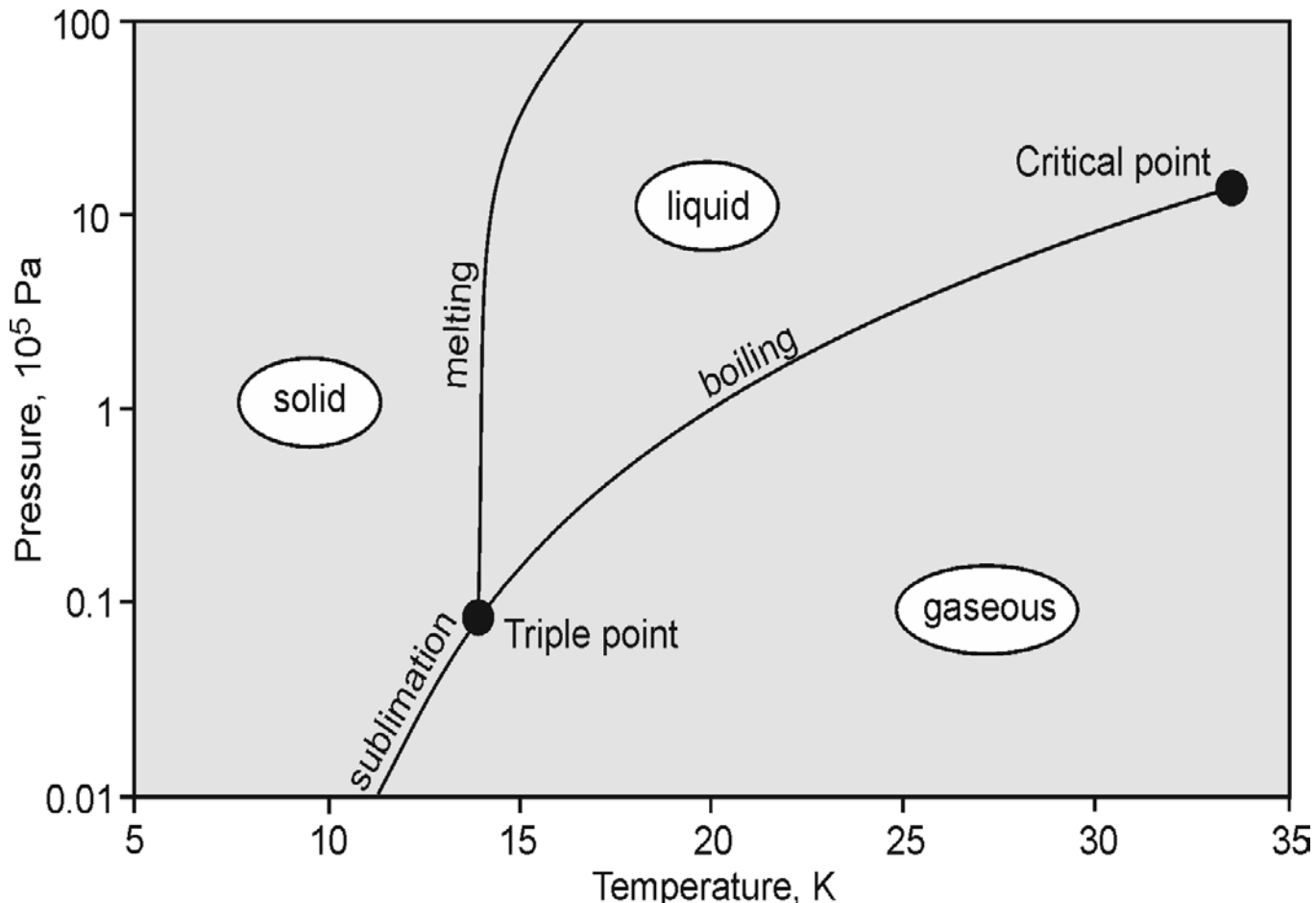
- ❖ Two forms of molecules: with nuclear spins in the same direction (parallel) are called ortho-hydrogen; with spins in the opposite direction (anti-parallel), para-hydrogen.
- ❖ These molecules have slightly different physical properties but are chemically equivalent. The chemistry of hydrogen, and in particular the combustion chemistry, is little altered by the different atomic and molecular forms.
- ❖ Normal hydrogen: mixture of 75% ortho- and 25% para- at room temperature. Liquid hydrogen at 20 K is composed of 99,8% of para-hydrogen (less energetic). The ortho-para conversion is accompanied by heat release (and vice versa), 703 kJ/kg at 20 K – ***cryo-compressed storage***.

Cryo-compressed storage

- ❖ Inherently safer storage of hydrogen as cryo-compressed rather than liquefied fluid (fluids with $T < -73^{\circ}\text{C}$ are cryogenic fluids) in automotive applications due to essential reduction if not exclusion at all of the hydrogen boil-off phenomenon at day-to-day normal driving.
- ❖ Due to conversion of para- to ortho-hydrogen during “consumption” of external heat the release of hydrogen as a result of boil-off is practically excluded with clear safety implications.
- ❖ The process of hydrogen liquefaction includes the removal of the energy released by the ortho-para state conversion. The heat of conversion is 715.8 kJ/kg. This is 1.5 times of the heat of vaporization (ISO/TR 15916:2004).

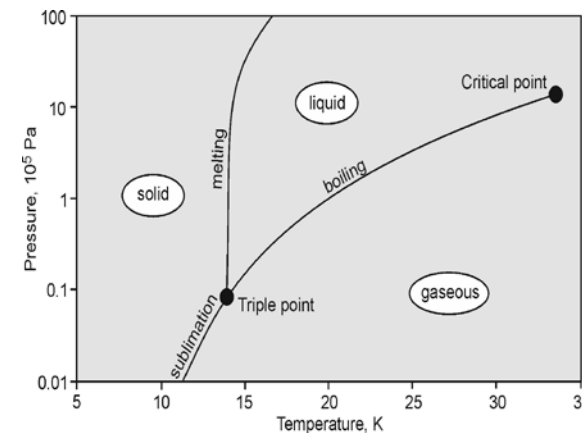
The phase diagram

Three curves: boiling (condensation=liquefaction for the opposite phase transition) temperature with pressure, melting (freezing) temperature with pressure, sublimation curve.



Gas, liquid, and solid phases

- ❖ H₂ is used in gaseous, liquid, or slush forms.
- ❖ Slush hydrogen is a mixture of solid and liquid hydrogen at the triple point temperature.
- ❖ The triple point: all three phases can coexist ($T=13.8$ K, $p=7.2$ kPa).
- ❖ The vapour pressure of SH₂ can be as low as 7.04 kPa.
- ❖ The highest temperature, at which a hydrogen vapour can be liquefied, is the critical $T=33.145$ K.
- ❖ Heat of vaporization (cond.) at NBP is 445.6 kJ/kg.
- ❖ Heat of melting (fusion) at melting (freezing) point is 58.8 kJ/kg.
- ❖ Heat of sublimation is 379.6 kJ/kg.



Liquid para-hydrogen

- ❖ Liquid para-hydrogen at normal boiling point (NBP) has a density 70.78 kg/m^3 . The specific gravity is 0.071 (water is 1). Thus, liquid hydrogen is approximately 14 times less dense than water.
- ❖ Ironically, every 1 m^3 of water (made up of H_2 and O_2) contains 111 kg of H_2 whereas 1 m^3 of liquid hydrogen contains only 70.78 kg of hydrogen. Thus, water packs more mass of hydrogen per unit volume, because of its tight molecular structure, than hydrogen itself.
- ❖ This is true of most other liquid hydrogen-containing compounds such as hydrocarbons. The cloud may flow horizontally or downward immediately upon LH₂ release. These facts have to be accounted for by first responders.

Low temperatures (1)

- ❖ The phase transition of hydrogen is dominated by the low temperatures at which transitions between gas, liquid, and solid phases occur.
- ❖ The normal boiling point (NBP, boiling temperature at absolute pressure of 101,325 kPa) is 20.3 K.
- ❖ The normal melting point is 14.1 K (101,325 kPa).
- ❖ Hydrogen has the second lowest boiling and melting points of all substances (helium has lowest value of boiling temperature of 4.2 K and melting temperature of 0.95 K).
- ❖ All these temperatures are extremely low and **below the freezing point of air.**

Low temperatures (2)

- ❖ An essential safety concern of LH2 low temperature is that, with the exception of helium, all gases will be condensed and solidified.
- ❖ Leaks of air or other gases into direct exposure with liquid hydrogen can lead to several hazards:
 - The solidified gases can plug pipes/orifices, jam valves.
 - In a process known as cryo-pumping the reduction in volume of the condensing gases may create a vacuum that can draw in yet more gas, e.g. oxidiser like air.
 - Large quantities of material can accumulate displacing the LH2 if the leak persists for long periods. At some point, should the system be warmed for maintenance, these frozen materials will re-gasify possibly resulting in high pressures or explosive mixtures. These other gases might also carry heat into the LH2 and cause enhanced evaporation losses or “unexpected” pressure rise.

Oxygen enrichment (1)

- ❖ LH2 is usually transferred in vacuum insulated lines. However, cold hydrogen flowing through tubes which are not sufficiently thermally insulated can easily cool the system below 90 K so that condensed air with an oxygen content of up to 52 % is present (NBP of N₂ is 77.36 K, NBP of O₂ is 90.15 K, NBP of CO₂ is 216.6 K).
- ❖ The liquid condensate flows and looks like liquid water. This oxygen-enriched condensate enhances the flammability of materials and makes materials combustible that normally are not, e.g. bituminous road covers (safety concern when transferring large quantities of H₂). If a piece of equipment cannot be insulated, the area underneath should be free of any organic material.

Oxygen enrichment (2)

- ❖ Oxygen enrichment can increase the flammability and even lead to the formation of shock-sensitive compounds.
- ❖ Oxygen particulate in cryogenic hydrogen gas may even detonate.
- ❖ Vessels with liquid hydrogen have to be periodically warmed and purged to keep the accumulated oxygen content in the vessel to less than 2% (ISO/TR 15916:2004).
- ❖ Caution should be exercised if carbon dioxide is used as a purge gas. It may be difficult to remove all carbon dioxide from the system low points where the gas can accumulate.

Hydrogen expansion ratio (1)

- ❖ The volume of LH2 expands with the addition of heat significantly more than can be expected based on our experience with water. The coefficient of thermal expansion at NBP is 23 times that of water at ambient conditions.
- ❖ The significance for safety arises when cryogenic storage vessels have insufficient ullage space to accommodate expansion of the liquid. This can lead to an over pressurisation of the vessel or penetration of the LH2 into transfer and vent lines.
- ❖ A considerable increase in volume is associated with the phase change of liquid to GH2, and yet another volume increase occurs for gaseous hydrogen that is allowed to warm from the NBP to NTP.

Hydrogen expansion ratio (2)

- ❖ The ratio of the final volume to the initial volume for the phase change from liquid to gaseous hydrogen and expansion of heated gas is **847** (ISO/TR 15916:2004).
- ❖ This total volume increase can result in a final pressure of **177 MPa** (starting with an initial pressure of 0.101 MPa) if the gaseous hydrogen is in a closed vessel.
- ❖ Pressure relief devices (PRD) should be installed as a safety measure in any volume in which liquid hydrogen or cold gaseous hydrogen could be trapped, to prevent overpressure from expansion of the liquid hydrogen or cold gaseous hydrogen.

Buoyancy as safety asset (1)

- ❖ The main hydrogen safety asset, i.e. its highest on The Earth buoyancy, confers the ability to rapidly flow out of an incident scene, and mix with the ambient air to a safe level below the lower flammability limit (LFL) of 4% by volume of hydrogen in air. Indeed, hydrogen has a density of 0.0838 kg/m^3 (NTP) which is far below than air density of 1.205 kg/m^3 at the same conditions.
- ❖ The unwanted consequences of hydrogen releases into the open atmosphere are drastically reduced by buoyancy. Contrary, heavier hydrocarbons are able to form a huge combustible cloud, e.g. Flixborough (1974) and Buncefield (2005) explosions. In many situations, hydrocarbons may pose stronger fire and explosion hazards than H₂.

Buoyancy as safety asset (2)

- ❖ Hydrogen high buoyancy affects its dispersion considerably more than its high diffusivity.
- ❖ Pure hydrogen is positively buoyant above a temperature of 22 K, i.e. over almost the whole temperature range of its gaseous state.
- ❖ In unconfined conditions only small fraction of released hydrogen would be able to deflagrate. Indeed, a hydrogen-air cloud evolving from the inadvertent release upon the equipment failure liberates only a small fraction of its thermal energy in case of a deflagration, which is in the range 0.1-10% and in most cases below 1% of the total energy of released hydrogen (Lind, 1975). This makes safety considerations of H₂ accident with large inventory at the open quite different from that of other gases.

Diffusivity

- ❖ Diffusivity is higher compared to other gases (smallest size). Diffusion coefficient: $D=6.1E-05$ m²/s (Alcock et al. 2001) to $6.8E-05$ m²/s (Baratov, 1990).
- ❖ Hydrogen effective diffusion coefficients through gypsum panels (Yang et al. 2011) is $D=1.4E-05$ m²/s at room temperature 22 C. This diffusion process should not be overlooked in the hazard assessment of accidental release of hydrogen in garages or enclosures lined with gypsum panels.
- ❖ The quasi-steady diffusive molar flux (mol/m²/s) through the unit area of a panel of thickness δ (m) can be approximated by $D(C-C_S)/\delta$, where C (mol/m³) is the molar concentration of hydrogen in enclosure and C_S (mol/m³) is the concentration in the surrounding.

Viscosity

- ❖ Viscosity of gaseous hydrogen (μPoise): 89.48 (NTP) and 11.28 (NBP). Viscosity of liquid hydrogen at NBP is 132.0 μPoise .
- ❖ The low viscosity of hydrogen and the small size of the molecule cause a comparatively high flow rate if the gas leaks through fittings, seals, porous materials, etc.
- ❖ This negative effect is to a certain extent offset by the low energy density (volumetric) of hydrogen in comparison with e.g. methane or other hydrocarbon gases.

Interaction with materials

- ❖ H₂ can cause a significant deterioration in the mechanical properties of metals. This effect is referred to as embrittlement (depends on T and p; purity, concentration, and exposure time; the stress state, physical and mechanical properties, microstructure, surface conditions, and nature of the crack front of the material. Many material problems involve welds or the use of an improper material.
- ❖ H₂ is non-corrosive. Many metals absorb H₂. Hydrogen absorption by steel can result in embrittlement. There is an atomic solution of hydrogen in metals. Permeated through a metal atomic hydrogen recombines to molecules on the external surface of storage to diffuse into surrounding gas afterwards. **The choice of material is an important part of hydrogen safety.**

Specific heat, thermal conductivity (1)

- ❖ The larger property differences between ortho- and para-hydrogen occur in those properties for which heat is important, that is enthalpy, specific heat capacity and thermal conductivity, whereas other properties, such as density, vary little.
- ❖ On a molar basis, the heat capacity of H₂ is similar to that of other diatomic gases despite its low molecular mass. Specific heat of gaseous hydrogen at constant pressure c_p (kJ/kg/K): 14.85 (NTP), 14.304 (STP), 12.15 (NBP). Specific heat of LH₂ at boiling point is 9.66 kJ/kg/K. The specific heat of liquid para-hydrogen is $c_p=9.688$ kJ/kg/K. This is more than double that of water and greater than 5 times that of liquid oxygen at its NBP.

Specific heat, thermal conductivity (2)

- ❖ Gas constant of hydrogen is 4.1243 kJ/kg/K (this is the universal gas constant divided by the molecular mass).
- ❖ The specific heats ratio of hydrogen at NTP is $\gamma=1.39$ and STP conditions is $\gamma=1.405$.
- ❖ Thermal conductivity of hydrogen is significantly higher than that of other gases:
 - ❖ Gaseous hydrogen (W/m/K): 0.187 (NTP), 0.01694 (NBP).
 - ❖ Liquid hydrogen (W/m/K): 0.09892 (NBP).

The Joule-Thomson effect (1/9)

- ❖ In 1843 Joule investigated the dependence of energy of gases on pressure using the simple apparatus that included a copper bulb N1 filled with air under pressure, isolated from an evacuated similar bulb N2 by a valve. The bulbs were immersed in a well-stirred water bath equipped with a sensitive thermometer. After thermal equilibrium had been established, the valve was opened to allow the gas to expand into bulb N2. No change in temperature was detected and Joule concluded that "no change of temperature occurs when air is allowed to expand in such a manner as not to develop mechanical power", i.e. do no external work, $\Delta W = 0$. Since "no change of temperature" was observed, $\Delta Q = 0$, and therefore " $\Delta U = 0$ "...

The Joule-Thomson effect (2/9)

- ❖ Unfortunately, the system used by Joule for this experiment had a very large heat capacity compared with the heat capacity of air, and the small change of temperature that took place was not observed.
- ❖ Later Joule and Thomson, who devised a different experimental procedure, performed another study of the dependence of the energy and enthalpy of real gases during expansion. The gas from a pressure P_1 to pressure P_2 by the throttling action of the porous plug. The system was thermally insulated, thus the expansion occurred adiabatically. When steady state conditions have been reached the temperatures of the gas before and after expansion, T_1 and T_2 , were measured by sensitive thermocouples.

The Joule-Thomson effect (3/9)

- ❖ It can be shown that throttling (the expansion of fixed mass flow rate of gas) occurs at constant enthalpy.
- ❖ Indeed, if two imaginary pistons introduced into the system with parameters V_1 , P_1 , T_1 upstream of the plug and V_2 , P_2 , T_2 downstream of the plug then the work done by the surroundings on the system downstream and upstream of the plug is respectively $+P_1V_1$ and $-P_2V_2$. Thus, the overall change in internal energy of the gas during the adiabatic expansion ($\Delta Q=0$) following the second law of thermodynamics is $\Delta U= P_1V_1 - P_2V_2$. By definition $\Delta H=\Delta U+\Delta PV$ and thus this expansion is isenthalpic ($\Delta H=0$), i.e. $H_1=H_2$

The Joule-Thomson effect (4/9)

- ❖ It is worth noting that this is done in **an assumption that the difference in the specific kinetic energy of gas before and after the plug can be neglected** (Moran and Shapiro, 2006). However, this is not the case when there is a release from the storage with practically zero flow velocity through the small orifice where velocity can reach supersonic values.
- ❖ The throttling experiment by Joule and Thomson measures directly the change in temperature of a gas with pressure at constant enthalpy which is called the Joule-Thomson coefficient

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

The Joule-Thomson effect (5/9)

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H$$

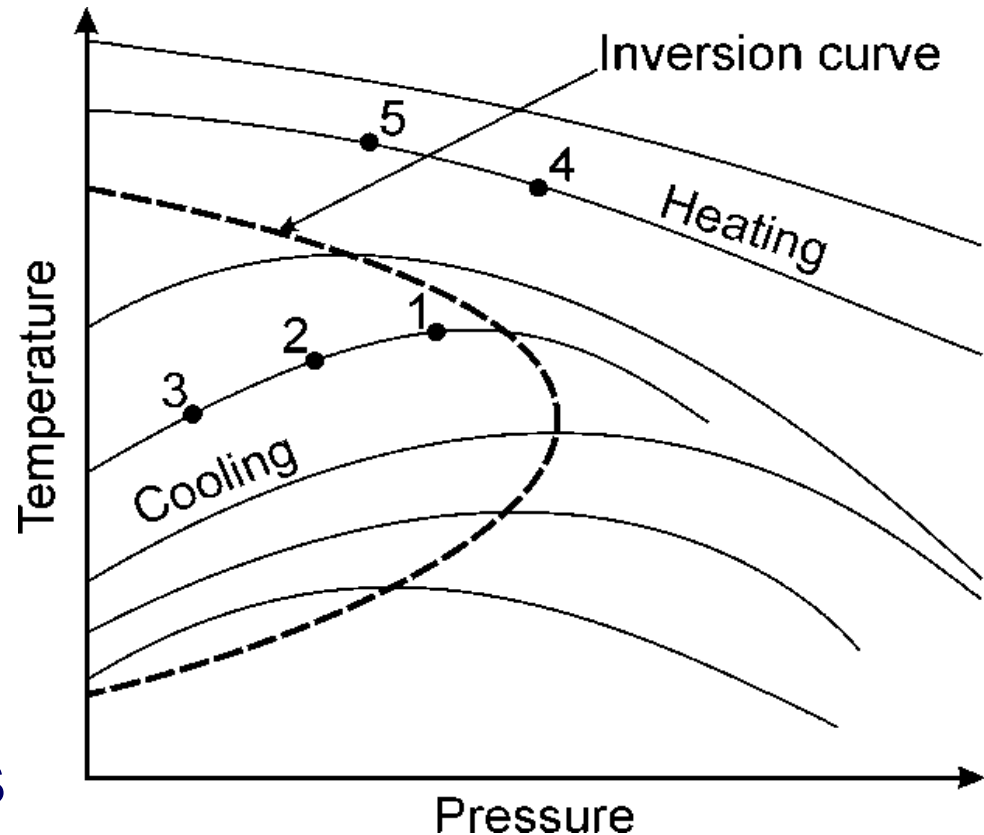
- ❖ For expansion, the change of pressure is negative and therefore a positive value for Joule-Thomson coefficient corresponds to gas cooling on expansion and negative coefficient corresponds to gas heating.
- ❖ For an ideal gas and isenthalpic process

$$\left(\frac{\partial H}{\partial P} \right)_T = \left(\frac{\partial H}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_H = -c_P \cdot \mu_{JT} = 0$$

Because the heat capacity at constant pressure c_P is not zero, Joule-Thomson coefficient **must be zero for an ideal gas.**

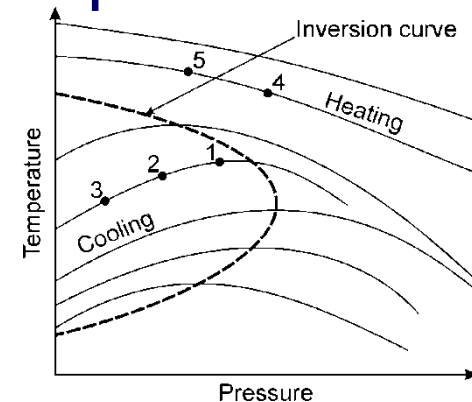
The Joule-Thomson effect (6/9)

- ❖ For real gases, if Joule-Thomson experiments are performed with different conditions downstream of the porous plug, a curve with constant enthalpy can be drawn in coordinates T-P.
- ❖ A series of curves could be generated by performing experiments at different conditions upstream of the plug.



The Joule-Thomson effect (7/9)

- ❖ If the temperature is quite low the curves pass through a maximum called the inversion point. The locus of these points is called the inversion curve.
- ❖ The slope of an isenthalpic curve at any point is equal to Joule-Thomson coefficient.
- ❖ It is evident that when the Joule-Thomson effect is to be used in the liquefaction of gases by expansion, the conditions must be chosen so that the temperature will decrease. For example, a drop in temperature would be produced by an expansion from point 1 to point 2 and then to point 3. However, a temperature rise would result in an expansion from point 4 to point 5.



The Joule-Thomson effect (8/9)

- ❖ At higher temperatures or lower temperatures **coupled with high pressures** expansion will heat the gas.
- ❖ **In a Joule-Thomson** process, starting at ambient temperature, the temperature of hydrogen will not drop but rise.
- ❖ Most gases at ambient temperatures cool when expanded across a porous plug. However, **the temperature of hydrogen increases when the gas is expanded at a temperature above its inverse Joule-Thomson temperature 193 K.**

The Joule-Thomson effect (9/9)

- ❖ Yet, the inverse Joule-Thomson effect cannot be the primary cause of any ignition that occurs when hydrogen is vented from a high-pressure storage. **The temperature increase from the Joule-Thomson effect is only a few degrees Kelvin at the most.**
- ❖ It would not raise the gas temperature to its ignition value unless the gas was already near the ignition temperature after mixing with surrounding gas.

Ideal and real gas equations

- ❖ The ideal gas equation is not applicable to hydrogen storage pressures above 10-20 MPa when effects of non-ideal gas are essential. The Abel-Noble equation of state for real hydrogen gas is applied (difference to the ideal gas equation is Z - the compressibility factor)

$$p = Z \cdot \rho \cdot R_{H_2} \cdot T \qquad Z = \frac{1}{1 - b\rho} = 1 + \frac{b \cdot p}{R_{H_2} \cdot T}$$

$b=7.69E-03$ m³/kg is the co-volume constant.

- ❖ Use of the real gas equation has an important safety implications. The ideal gas law if applied would overestimate the mass flow rate of the leak and the total mass discharged: $Z=1.01$ at 1.57 MPa, $Z=1.1$ at 15.7 MPa, and $Z=1.5$ at 78.6 MPa ($T=293.15$ K)

Speed of sound

- ❖ In ideal gases

$$C = \sqrt{\gamma \frac{p}{\rho}} = \sqrt{\gamma \frac{R \cdot T}{M}}$$

- ❖ Speed of sound in gaseous hydrogen is 1294 m/s at NTP, and 355 m/s at NBP.
- ❖ Speed of sound in liquid hydrogen is 1093 m/s (boiling point).
- ❖ Speed of sound in stoichiometric hydrogen-air mixture is 404 m/s (BRHS, 2009).

Combustion properties



General characteristics (1)

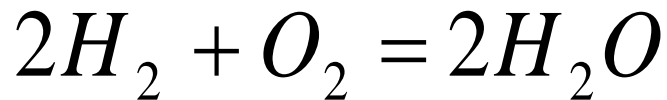
- ❖ At normal temperature hydrogen is a not very reactive substance, unless it has been activated somehow, e.g. by a catalyser.
- ❖ Hydrogen reacts with oxygen to form water at ambient temperature extraordinarily slow. However, if the reaction is accelerated by a catalyser or a spark, it proceeds with high rate and “explosive” violence.
- ❖ H₂ dissociates into free H atoms at high T. H is a powerful reductive agent, even at ambient temperature e.g. when it diffuses from a high temperature zone of a flame front into its pre-heating low temperature zone.

General characteristics (2)

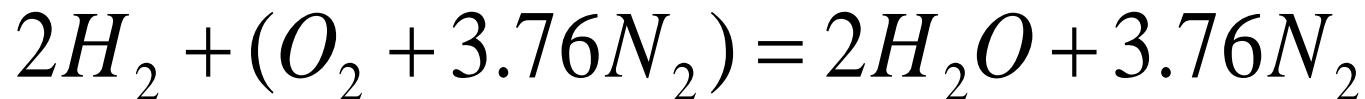
- ❖ The heat released when the hydrogen atoms recombine to the hydrogen molecule is used for example to obtain high temperatures in the atomic hydrogen welding.
- ❖ Hydrogen burns in a clean atmosphere with an invisible flame. This can be a reason for serious injury at an accident scene. However, hydrogen combustion and hot turbulent currents will cause changes in the surroundings that can be used to detect the flame. These changes are called the signature of the fire.

Stoichiometric mixture

- ❖ Stoichiometric mixture is a mixture in which both fuel and oxidiser are fully consumed (complete combustion) to form product(s).
- ❖ Stoichiometric H₂-O₂ mixture (66.66% by volume of H₂ and 33.33% of O₂)



- ❖ Stoichiometric concentration of H₂ in air (assuming 21% of O₂ and 79% of N₂) is 29.59% by volume ($2/(2+1+3.76)=0.2959$) with air content of 70.41%



The equivalence ratio

- ❖ The equivalence ratio is the ratio of the actual fuel-to-oxidizer (FOR) ratio to the fuel-to-oxidiser ratio in the stoichiometric mixture (m is mass and n is number of moles)

$$\phi = \frac{m_f / m_{ox}}{(m_f / m_{ox})_{st}} = \frac{n_f / n_{ox}}{(n_f / n_{ox})_{st}}$$

- ❖ It is 1.0 at stoichiometry, the ratios are less than 1.0 for lean by fuel mixtures, and are greater than 1.0 for rich mixtures.
- ❖ It does not depend on the units, i.e. it is the same value either mass or number of moles are used (contrary to the fuel–oxidiser ratio).

The mixture fraction (1)

- ❖ Dealing with FOR is not always convenient especially for CFD simulations as they have a value of infinity at either the pure air (oxidiser) or pure fuel side (computers get extremely upset when they try to tackle calculations with infinity). Thus, for simulations in many cases a property is needed which is bounded.
- ❖ The mixture fraction, ξ , is usually taken as unity in the fuel stream and is nil in the oxidizer stream. It varies linearly between these two bounds such that at any point the fuel mass fraction is $Y_F = \xi Y_{F_0}$ and the oxidizer $Y_O = (1 - \xi) Y_{O_0}$.

The mixture fraction (2)

- ❖ All of the atoms present at the unburned mixture are present in the combustion products although they may be reorganized into different molecules. The mixture fraction that is independent of element i is

$$\xi = \frac{Z_i - Z_{i,00}}{Z_{i,F0} - Z_{i,00}}$$

where Z_i is the element mass fraction, i.e. the ratio of the mass of element i to the total mass.

- ❖ It can be shown that for the stoichiometric mixture fraction, i.e. where diffusion flame front is located,

$$\xi_{st} = \frac{1}{1 + \phi}$$

Heat of combustion

- ❖ The lower heating value (heat of combustion) of hydrogen is 241.7 kJ/mol (BRHS, 2009). Per gram of hydrogen it is $(241.7 \text{ kJ/mol} / 2.016 \text{ g/mol}) = 119.89 \text{ kJ/g}$.
- ❖ The higher heating value is 286.1 kJ/mol, i.e. $(286.1/2.016)=141.91 \text{ kJ/g}$.
- ❖ The difference of about 16% is due to the heat of condensation of water vapour, and this value is larger compared to other gases.

TNT “equivalent”

- ❖ Release of energy during explosive reaction of 1 g TNT is arbitrarily standardized as 4.184 kJ (a gram of TNT releases 4.1–4.602 kJ upon explosion).
- ❖ The lower heat of combustion of 1 g of hydrogen is equal to $(241.7 \text{ kJ/mol} / 2.016 \text{ g/mol}) = 119.89 \text{ kJ}$.
- ❖ Thus, the TNT equivalent of hydrogen is high: 28.65, i.e. **28.65 g of TNT is energetic equivalent of 1 g of hydrogen.**

Direct initiation of detonation

- ❖ The ability of a hydrogen-air mixture to direct initiation of detonation is greater than that of hydrocarbons.
- ❖ The direct initiation of hydrogen-air mixture detonation is possible by 1.1 g of tetryl (high explosive).
- ❖ Only 1.86 g of TNT is needed to initiate detonation in 34.7% hydrogen-air mixture in the open atmosphere.
- ❖ However, for 20% hydrogen-air mixture the critical TNT charge **increases significantly to 190 g**.
- ❖ Ignition sources capable of forming shocks, for example high-energy spark discharges and high explosives, can directly initiate detonation

Flammability limits: direction

- ❖ The flammability range of hydrogen is wider compared to most hydrocarbons, i.e. 4% to 75% by volume in air at NTP.
- ❖ The flammability limits of hydrogen depend on a direction of flame propagation (Coward and Jones, 1952)

Upward propagation		Horizontal propagation		Downward propagation	
LFL	UFL	LFL	UFL	LFL	UFL
3.9-5.1%	67.9-75%	6.0-7.15%	65.7-71.4%	8.5-9.45%	68-74.5%

- ❖ In an initially quiescent mixture a conservative value of LFL changes from 3.9% v/v for upward propagation, through 6% for horizontal, to 8.5% for downward propagating flames.

Complete combustion?

- ❖ Upward flame propagation at concentrations close to LFL of 4% is in a form of a collection of small balls of flame, which travel steadily to the top of the vessel.
- ❖ There is unburnt mixture in between of these small ball flames. An increasing fraction of the hydrogen present was burned as the amount of it was increased. The mixture with 5.6% of hydrogen showed about 50% combustion. This observation explains why burning of a quiescent hydrogen-air mixture near LFL of 4% by volume in a closed vessel can generate negligible in a practical sense overpressure.

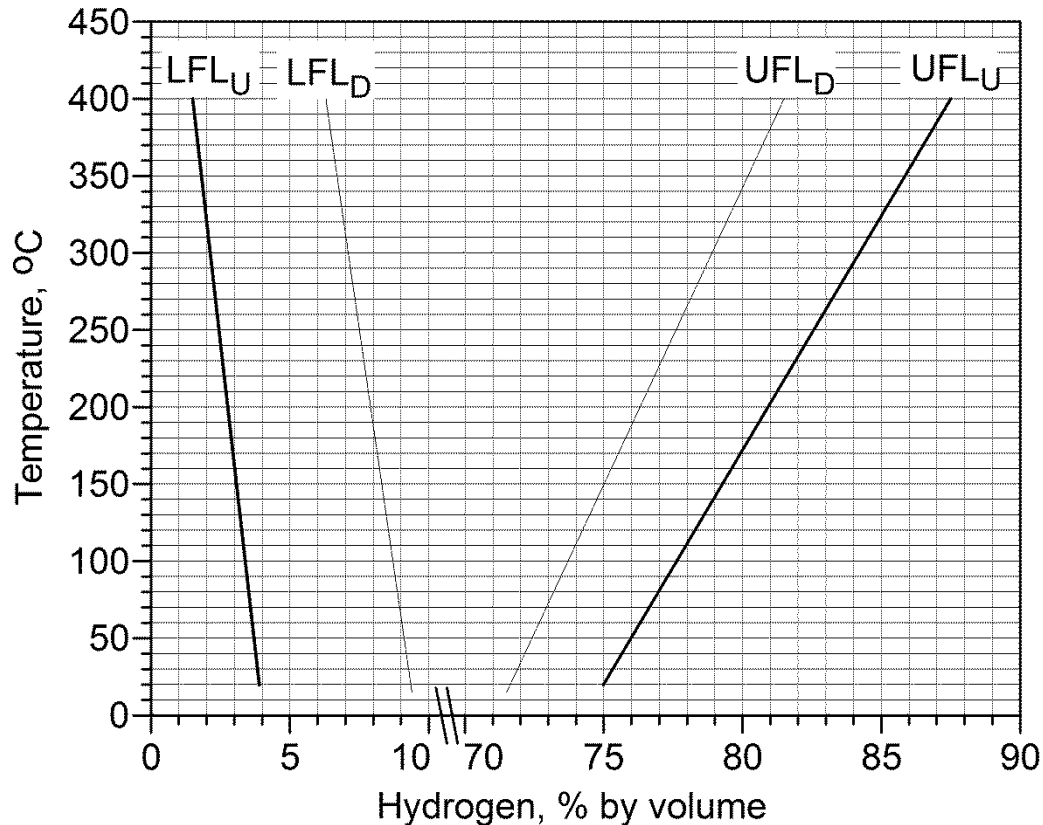
Flammability limits: standards

- ❖ The flammability limits (measured in % by volume) determined by different standard apparatuses and procedures applied at NTP (Schröder and Holtappels, 2005).

Limit	DIN 51649	EN 1839 (T)	EN 1839 (B)	ASTM E 681
LFL	3.8%	3.6%	4.2%	3.75%
UFL	75.8%	76.6%	77.0%	75.1%

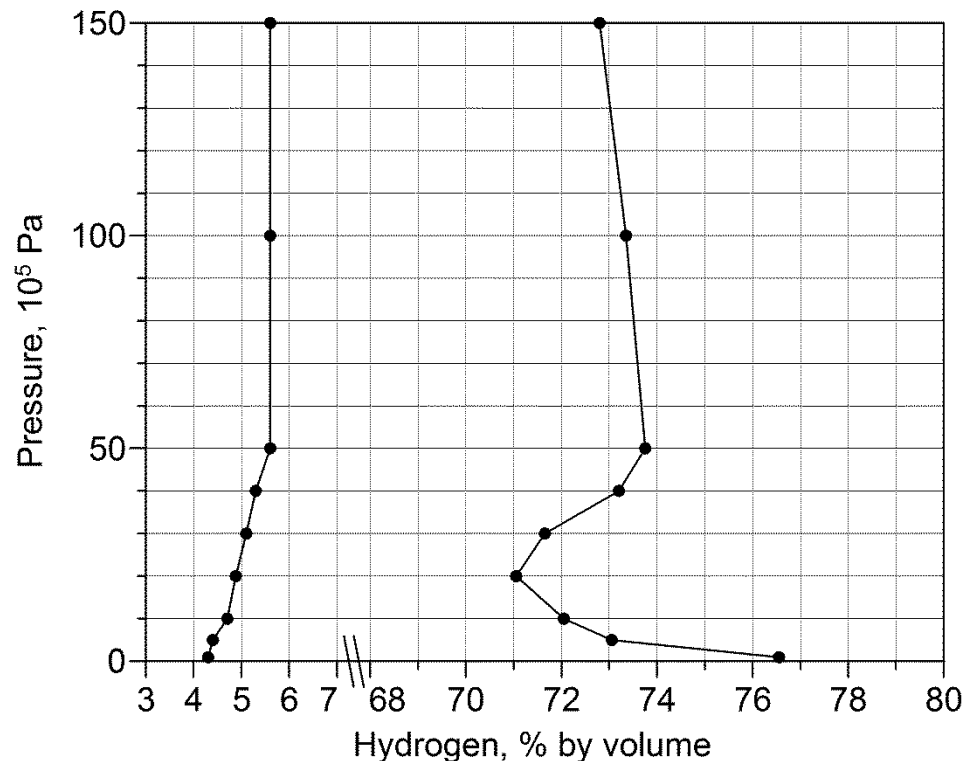
Flammability limits: temperature

The flammability range expands practically linearly with temperature. While LFL decreases by about 2.5% by volume (from 4% to 1.5% by volume) with increase of temperature from 20°C to 400°C, UFL increases more significantly - by about 12.5% by volume (U – upward; D – downward propagation).



Flammability limits: pressure

LFL monotonically decreases in the range 0.1-5.0 MPa to 5.6% v/v and then is constant up to pressure of 15 MPa. UFL changes not monotonically: decreases from 76.6% to 71% with pressure growth from 0.1 to 2.0 MPa, then increases from 71% to 73.8% with pressure increase from 2 to 5 MPa, and again decreases insignificantly from 73.8% to 72.8% with pressure raise from 5 to 15 MPa.



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.
- ❖ No mixture of hydrogen, air, and nitrogen at NTP conditions will propagate flame if the mixture contains less than **5% by volume oxygen** (NASA, 1997).

Ignition properties

- ❖ Experience shows that escaped hydrogen is very easily ignited (NASA, 1997).
- ❖ Ignition sources include mechanical sparks from rapidly closing valves, electrostatic discharges in ungrounded particulate filters, sparks from electrical equipment, catalyst particles, heating equipment, lightning strikes near the vent stack, etc.
- ❖ Ignition sources must be eliminated or isolated in appropriate way and **operations should be conducted as if unforeseen ignition sources could occur.**

Ignition energy

- ❖ The ignition energy of hydrogen-air mixture varies with its composition (infinite at the flammability limits). Less energy is needed to ignite a stoichiometric mixture.
- ❖ Over the flammable range the ignition energy varies by almost three orders of magnitude. The minimum ignition energy (MIE) is 0.017 mJ for the most ignitable mixture.
- ❖ Since most ignition sources generate more than 10 mJ, practically all common fuels would be ignited in mixture with air if their concentration exceeds the LFL.

Ignition by static electricity (1)

- ❖ Hydrogen is essentially an electrical insulator. The flow or agitation of hydrogen gas or liquid may generate charges of static electricity (for this reason, all hydrogen conveying equipment must be thoroughly grounded).
- ❖ Only above some critical “breakdown” voltage, where ionization occurs, does it become an electrical conductor. This property can potentially be responsible for the generation of static electrical charge of present in piping particulates by triboelectricity. The probability of hydrogen ignition by this mechanism increases with increase of the blowdown time (time to empty a storage tank) with the same other conditions.

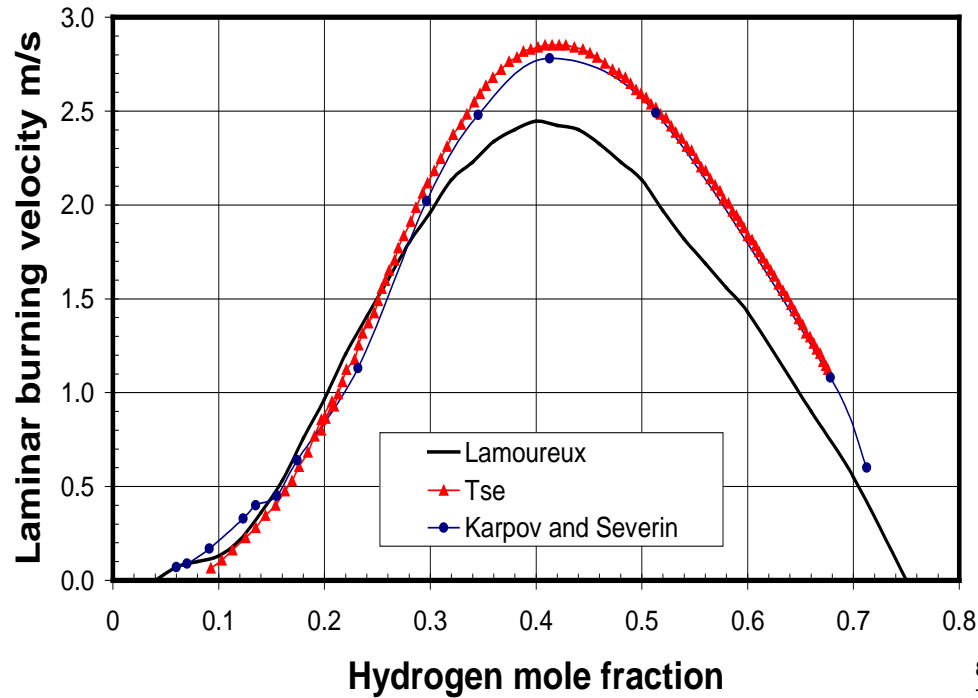
Ignition by static electricity (2)

- ❖ For modelling the effect of static discharge, a human being can be represented as a capacitor of 100 picofarads, charged to a voltage of 4,000 to 35,000 volts. The total energy is of the order of millijoules. This energy is typically discharged in less than a microsecond and **sufficient to ignite not only near stoichiometric mixtures yet mixtures close to the flammability limits.**
- ❖ Insulation materials such as wood, paper, and some fabrics will typically form a conductive layer that can prevent static build-up by **absorbing water from the air** when the relative humidity is greater than 50% (ISO/TR 15916:2004).

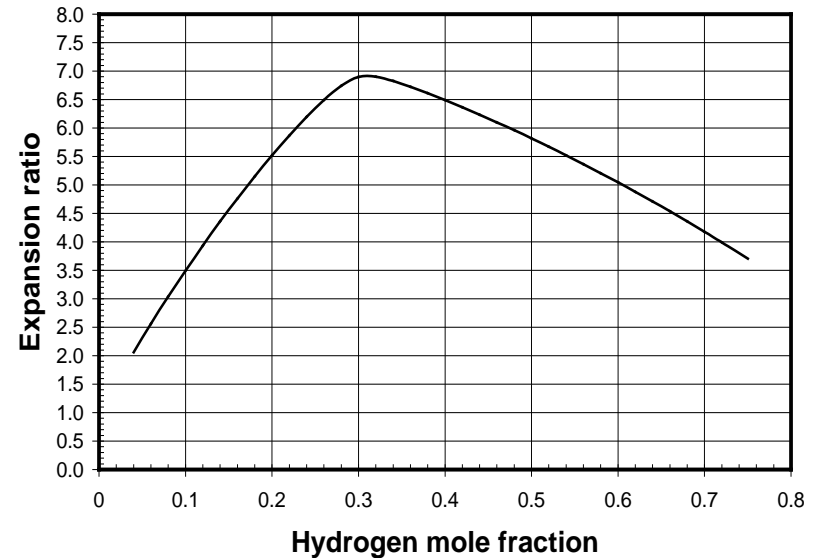
Auto-ignition temperature

- ❖ The standard auto-ignition temperature of hydrogen in air is above 510°C (Baratov et al. 1990). It is relatively high compared to hydrocarbons having long molecules.
- ❖ However, it can be lowered by catalytic surfaces.
- ❖ Objects at temperatures from 500 to 580°C can ignite hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure.
- ❖ Substantially cooler objects of about 320°C can cause ignition under prolonged contact at less than atmospheric pressure (NASA, 1997).
- ❖ Hot air jet ignition temperature is 670°C (BRHS, 2009).

Laminar burning velocity



$$S_u = S_v / E_i$$



Quenching

- ❖ Quenching of any flame occurs when heat losses from flame are comparable with heat generation due to combustion, and then the chemical reactions cannot be sustained.
- ❖ Usually quenching distance is reported as the minimum pipe diameter through which a premixed flame can pass. Kanury (1975) measured the quenching distance as **0.51 mm**. ISO/TR 15916:2004 states that the quenching gap in air (NTP) for hydrogen is 0.64 mm.
- ❖ Hydrogen has the narrowest maximum experimental safe gap (MESG) of **0.08 mm**. The MESG is always smaller than the quenching gap.

Detonability limits

- ❖ The detonability range mentioned in ISO/TR 15916:2004 is **18-59%** by volume of hydrogen in air. The detonation range of **13-70%** is reported for hydrogen-air in a 43 cm diameter tube (Tieszen et al. 1986). A lower detonability limit of **12.5%** was observed in the Russian test facility RUT, the largest of its kind. The widest detonability range of hydrogen in air **11-59%** by volume is recommended by Alcock et al. (2001).
- ❖ The detonability limits are not fundamental characteristics as they **strongly depend on the size of the experimental set up**. Indeed, a tube diameter, where detonation can propagate, should be of the order of a detonation cell size.

Run-up distance for DDT

- ❖ The experimentally observed run-up distance for transition from deflagration to detonation (DDT) in stoichiometric hydrogen-air mixture in a tube has typical length to diameter ratio of approximately 100.
- ❖ Safety measures to exclude the potential DDT are very important. Indeed, while the deflagration of quiescent stoichiometric hydrogen-air cloud in the open atmosphere generates pressure wave of only 0.01 MPa (below a level of eardrum injury), the detonation of the same mixture would be accompanied by a blast of more than two orders of magnitude higher pressure of 1.5 MPa (far above the fatal pressure of 0.08-0.10 MPa).

Health hazards (1)

- ❖ Hydrogen is not expected to cause mutagenicity, teratogenicity, embryotoxicity or reproductive toxicity. It is not a carcinogen. There is no evidence of adverse effects if skin or eyes are exposed to hydrogen, it cannot be ingested (unlikely route). However, inhaled hydrogen can result in a flammable mixture within the body.
- ❖ Hydrogen is classified as a simple asphyxiant (oxygen-deficient environment). Individuals breathing such an atmosphere may experience symptoms which include headaches, dizziness, etc. A victim may have a blue colour skin, and under some circumstances, death may occur.

Health hazards (2)

- ❖ Oxygen concentration levels below 19.5% by volume no effects of oxygen deficiency are usually observed. Below 12%, immediate unconsciousness may occur with no prior warning symptoms.
- ❖ Stages of asphyxiation (NASA, 1997):
 - 15-19% - decreased ability to perform tasks;
 - 12-15% - deeper respiration, faster pulse, poor coordination;
 - 10-12% - giddiness, poor judgment, slightly blue lips;
 - 8-10% - nausea, vomiting, unconsciousness, mental failure;
 - 6-8% - death in 8 min (50% death and 50% recovery with treatment in 6 min, 100% recovery with treatment in 4 to 5 min);
 - 4% - coma in 40 s, convulsions, respiration ceases, death.

Topic 2:

Comparison with other fuels



Hydrogen vs other fuels (1/6)

- ❖ Hydrogen is **not more dangerous or safer** compared to other fuels.
- ❖ Hydrogen safety fully depends on **how professionally it is handled** at the design stage and afterwards.
- ❖ **High pressures** (humans, equipment, structures): hydrogen systems are used at higher pressures up to 100 MPa.
- ❖ **Low temperatures** (cold burns): down to -253°C (liquefied hydrogen).
- ❖ Burns in clean atmosphere with **invisible** flame.
- ❖ More **prone to deflagration-to-detonation transition** compared to most of flammable gases.

Hydrogen vs other fuels (2/6)

- ❖ The main safety asset of hydrogen is **buoyancy** as underlined above. Indeed, hydrogen has a density of 0.0838 kg/m^3 (NTP). This is far lower than air which has a density of 1.205 kg/m^3 .
- ❖ The unwanted consequences of hydrogen releases into the open atmosphere, and in partially confined geometries, where no conditions of hydrogen accumulating, are drastically reduced by buoyancy.
- ❖ Contrary, heavier hydrocarbons are able to form a huge combustible cloud, as in disastrous Flixborough (1974) and Buncefield (2005) explosions.
- ❖ In many practical situations hydrocarbons may pose stronger fire and explosion hazards than hydrogen.

Hydrogen vs other fuels (3/6)

- ❖ Compared to other fuels hydrogen is the most prone to **spontaneous ignition** during sudden releases to air by so-called diffusion mechanism, when heated by a shock air mixes with cold hydrogen at the contact surface between these two gases and chemical reactions can be initiated when critical conditions are reached. Indeed, hydrogen sudden releases into piping with air can be spontaneously ignited at pressures as low as about 2 MPa.
- ❖ On the other hand, the standard **auto-ignition temperature** of hydrogen in air is above 520°C that is higher than for hydrocarbons.

Hydrogen vs other fuels (4/6)

- ❖ The **energy density** of hydrogen is 132.5 MJ/kg. This is approximately 2.5 times larger than of natural gas (and other fossil fuels). On the other hand, for the same volumetric leak rate the energy content of a hydrogen leak is smaller than that of hydrocarbons (lowest density).
- ❖ This laminar burning velocity about 2 m/s is far greater compared to most of hydrocarbons when velocities are in the range 0.30-0.45 m/s.
- ❖ Hydrogen has a somewhat higher **adiabatic flame temperature** of stoichiometric mixture in air of 2403 K.

Hydrogen vs other fuels (5/6)

- ❖ The lower flammability limit of hydrogen is high compared to most hydrocarbons.
- ❖ Near-stoichiometric hydrogen concentration of hydrogen 29.5% by volume in air is greatly higher compared to only a few percent for hydrocarbons.
- ❖ At the lower flammability limit the ignition energy requirement of hydrogen is similar to that of methane, and weak ignition sources such as electrical equipment sparks, electrostatic sparks or sparks from striking objects typically involve more energy than is required to ignite these flammable mixtures.

Hydrogen vs other fuels (6/6)

- ❖ Hydrogen has a very high research octane number and is therefore **resistant to knock** (combustion under lean conditions), i.e. 130+ (lean combustion) compared to other fuels: methane (125), propane (105), gasoline (87), diesel (30). The octane number has no relevance for use of hydrogen with fuel cells.
- ❖ The **quenching distance** (the minimum pipe diameter through which a premixed flame can propagate) for hydrogen, methane, and propane are 0.51 mm, 2.3 mm, and 1.78 mm respectively.

Hydrogen and other fuels

Substance	MM, g/mol	Density, kg/m ³	Viscosity, μ Poise	Diffusivity in air*, cm ² /s	Thermal conductivity, mW/(m·K)
Hydrogen (H ₂)	2.016	70.78 (L, NBP) 1.312 (G, NBP) 0.0838 (G, NTP)	132.0 (L, NBP) 89.48 (G, NTP) 11.28 (G, NBP)	0.68	168.35 (G)
Methane (CH ₄)	16.043	422.62 (L, NBP) 1.819 (G, NBP) 0.668 (G, NTP)	200 (G, NTP) 102.7 (G, STP)	0.196	32.81 (STP)
Propane (C ₃ H ₈)	44.096	582 (L, NBP) 2.423 (G, NBP) 1.882 (G, NTP)	1,100 (300 K)	0.0977	15.198 (STP)
Gasoline (C ₄ -C ₁₂)	100-105	677-798*	~6,000** (L, NTP)	-	~130**
Diesel (C ₈ -C ₂₅)	~200	788-920*	~25,000** (L, NTP)	-	-
Methanol (CH ₃ OH)	32.04	786.9 (L, 25° C)*	5,900 (L, NTP)	0.162	250
Water (H ₂ O)	18.016	1000 (NTP)	10,000 (L, NTP) 130 (G, NTP)	-	670
Air	28.9**	1.205 (NTP)	180 (G, NTP)		26

Hydrogen and other fuels

Substance	NBP, °C	Critical point	Critical density, kg/m ³	Heat of Vaporisation (SBP), kJ/kg	γ	Solubility in Water, v/v
Hydrogen (H ₂)	-252.8	-240 C 1.3 MPa	31.263	451.9	1.384 (25° C)	0.0214 (Poor)
Methane (CH ₄)	-161.58	-82.7 C 4.596 MPa	162	760	1.305 (25° C)	0.054 (2° C)
Propane (C ₃ H ₈)	-42.06	96.6 C 4.25 MPa	217	356	1.134 (25° C)	0.039 (NTP)
Gasoline (C ₄ -C ₁₂ *)	37-204	-	-	~349 (15.6° C)	-	Poor
Diesel (C ₁₂ H ₂₃ *)	180-340	-	-	~233 (15.6° C)	-	Poor
Methanol (CH ₃ OH)	64.9	239.45 C 8.09 MPa	272	1004	1.2	Infinitely
Water (H ₂ O)	100	373.946 C 22.064 MPa	322	2257 (NBP)	1.33 (steam)	-
Air	-(183-196)	-140.8 C 3.77 MPa	-	-	1.4	-

Fire and explosion indices

Fuel	Flashpoint, °C	AIT, °C	Flammability range, % vol.	P_{\max}^* , kPa	MIE*, mJ	MESG, mm
Hydrogen	< -253	510*	4-75	730	0.017	0.08
Methane	-188	537*	5.28*-15	706	0.28	-
Propane	-96*	470*	2.2-9.6	843	0.25	0.92*
Gasoline	-(11-45)*	230-480	0.79-8.1*	-	0.23-0.46	0.96-1.02
Diesel	37-110*	210-370*	0.6-6.5	-	-	-
Methanol	6*	385	6-36.5	620	0.14	-



MSc in Hydrogen Safety Engineering (distance learning course):
<http://www.ulster.ac.uk/elearning/programmes/view/course/10139>