



**German Hydrogen Association** 



# **Hydrogen Safety**

Ulrich Schmidtchen Federal Institute for Materials Research and Testing (BAM) Berlin

### **Facts and fiction**



"Experts see problems concerning transport and storage of the **highly elusive** and **explosive** hydrogen which after a while disappears even from steel vessels."

(Kölnische Rundschau, 11 January 2001)

"Every time I think about hydrogen I remember the **Zeppelin**." (Former VW chairman Ferdinand Piëch on 20 February 2001)

Parts of the public consider hydrogen as highly dangerous.

What are the facts?



# **Potential dangers**

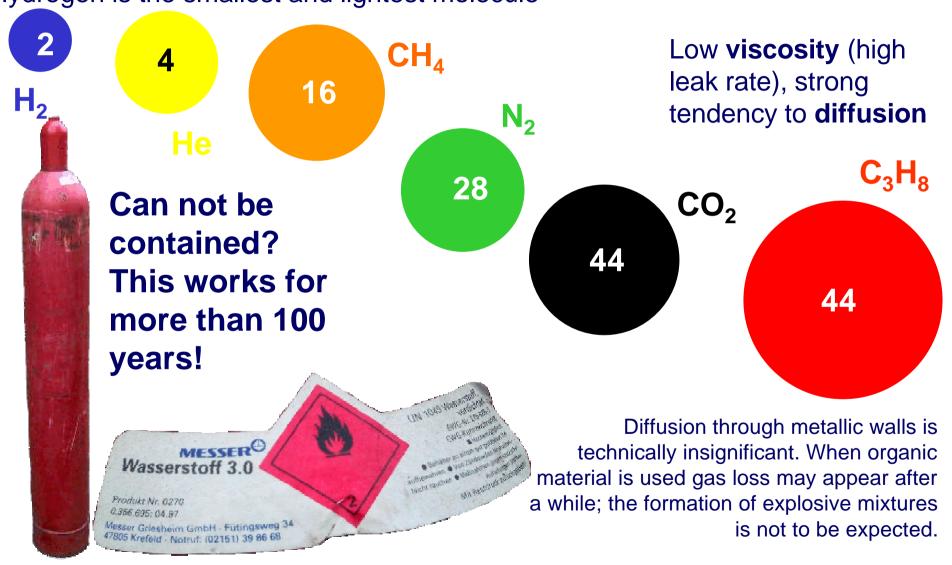


- Hydrogen is flammable
  - Mixtures with oxygen (air) can be explosive
  - low ignition energy
- Small molecule
  - low viscosity, high leak rate
  - diffuses rapidly (also downwards!)
    - embrittles certain materials
- Storage
  - compressed: under tension
  - liquefied: low temperature

# Hydrogen is "highly elusive"...?



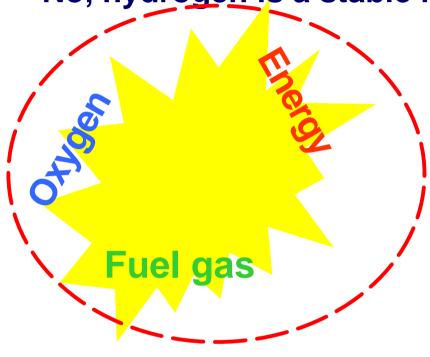
Hydrogen is the smallest and lightest molecule



# Hydrogen is explosive...?



### No, hydrogen is a stable molecule



A gas explosion requires:

Fuel gas

Mixed within certain concentration limits

**Ignition energy** (sufficient amount of it)

Unlike **explosives** (they need no external hydrogen)

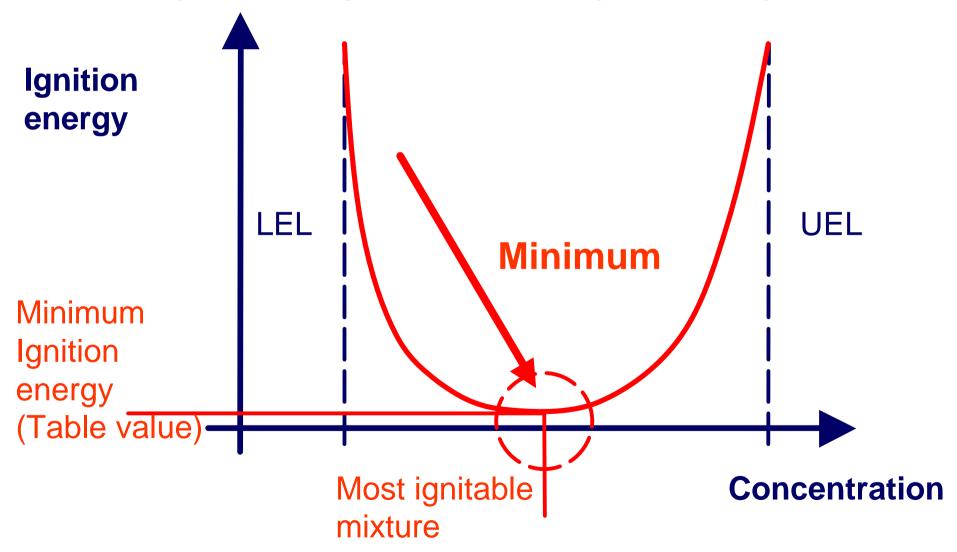
Unlike acetylene (molecule decays)

Even in the presence of ignition energy there is no explosion danger in a tank of pure hydrogen, because no oxygen is present (unlike gasoline etc.)

# Ignition energy, explosion limits etc.

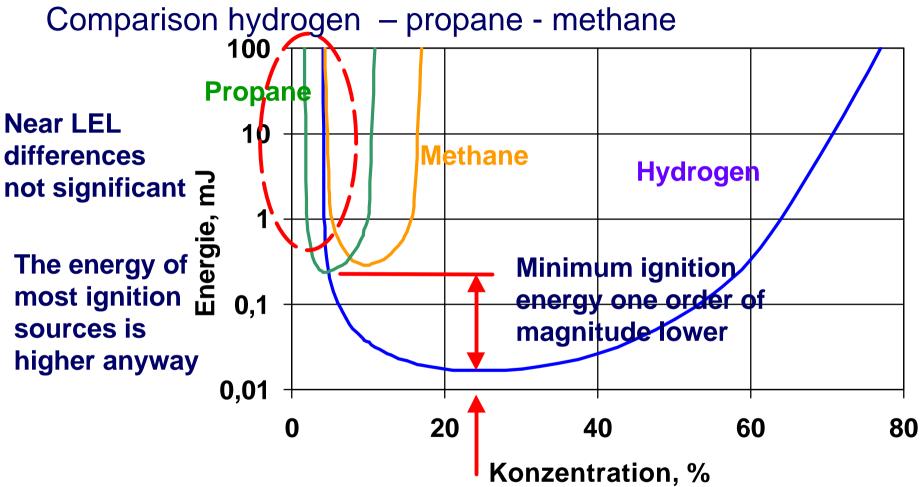


What are ignition energy and minimum ignition energy?



# Low ignition energy ...?

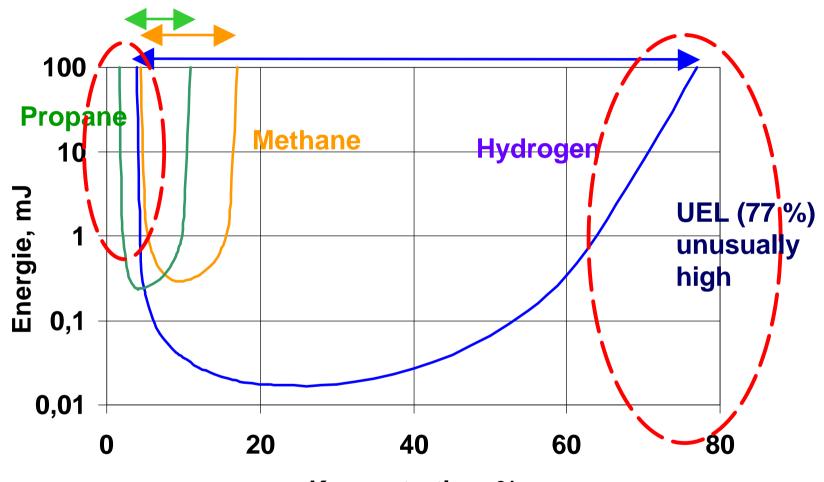




**Associated concentration** very high

# Wide explosive range ...?





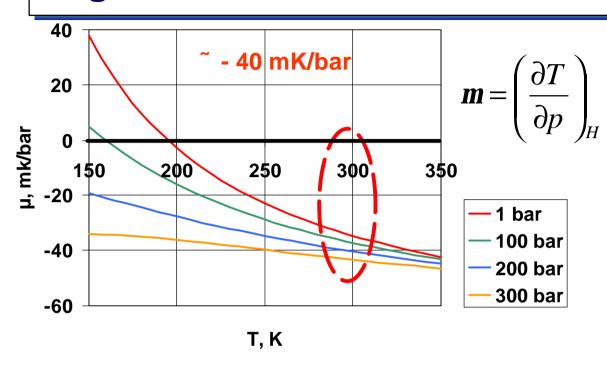
But it is usually the lower that matters

Konzentration, %

Here hydrogen offers no particular features

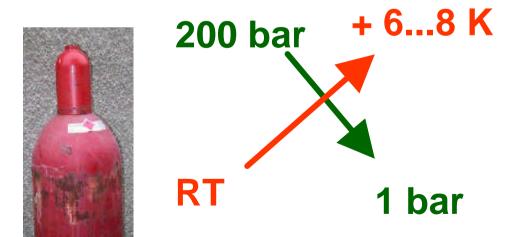
# **Negative Joule-Thomson coefficient ...?**





Under isenthalpic expansion (Joule-Thomson process) hydrogen at ambient temperature does not cool down, like many other gases, but becomes warmer.

# Is this dangerous?

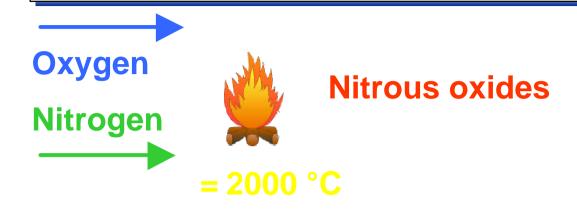


Theoretical warming of 6...8 K

No danger of ignition!

# Combustion generates nitrous oxides ...?





During combustion in air the oxygen and the nitrogen from the air react with each other.

Not a hydrogen specific problem

### With hydrogen the problem is even smaller:

The wider reactive concentration range of hydrogen/air mixtures permits the choice of operating conditions with emissions which are lower than what could be achieved with hydrocarbons, even theoretically.

"When the air leaves our motor it is sometimes cleaner than when it came in." (BMW developer)

# Hydrogen embrittles materials ...?



**Cold** embrittlement: by contact with cryogenic liquids or cooling of any kind. Reversible process. Can be controlled by choice of materials.



Hydrogen embrittlement: Interaction of hydrogen atoms (!) with crystal lattices, enhances the generation of stress corrosion cracks. Body-centered cubic lattices (ferrite steel) are susceptible under inappropriate conditions (high tension in the material). Face-centered cubic lattices (austenitic steel, Al, Ni, Ms) are less susceptible.



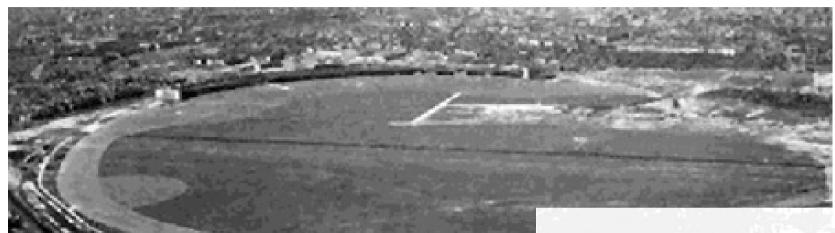
### **Case histories**



- There are not many cases of hydrogen accidents.
- Some "hydrogen accidents" were not hydrogen accidents.
- Lessons learnt from accidents contributed to a higher level of public safety.

# **Tempelhof airport**





Berlin central airport since 1923 Present buildings date from 1934-1941



around 1920

# **Tempelhof Field until 1914**





For 200 years training and parade ground of the Prussian army (picture: William I. during a victory parade in 1871)

Recreational area

Flight experiments: first motor flights in Germany (Wright brothers), balloons, air ships, including military ones



# Tempelhof Field, 25 May 1884 (1)



- The soldiers of the Royal Prussian Air Ship Division stored large amounts of hydrogen gas. They kept some 1000 cylinders in a shed. On 25 May 1894 about 400 of them burst without apparent reason. Damage was considerable.
- The famous professor Adolf Martens was appointed scientific head of the consequent investigation; Martens is seen as the father of materials research and testing in Germany. He founded metal and lattice microscopy and constructed many test machines.

# **Tempelhof Field, 25. May 1894 (2)**

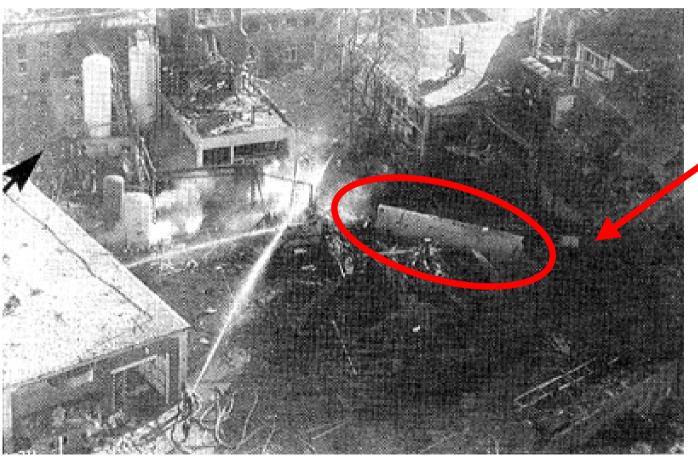


- Result: The cylinders were made from unsuitable material.
- Martens made numerous proposals for the prevention of such accidents. The quality assurance program he devised became the basis of the German pressure vessel code.

# Tank accident at Hanau 1991 (1)



A tank for 100 m³ hydrogen gas under a pressure of up to 45 bar was situated on an industrial ground at Hanau (Frankfurt area). One morning it burst without apparent reason. There was great damage.

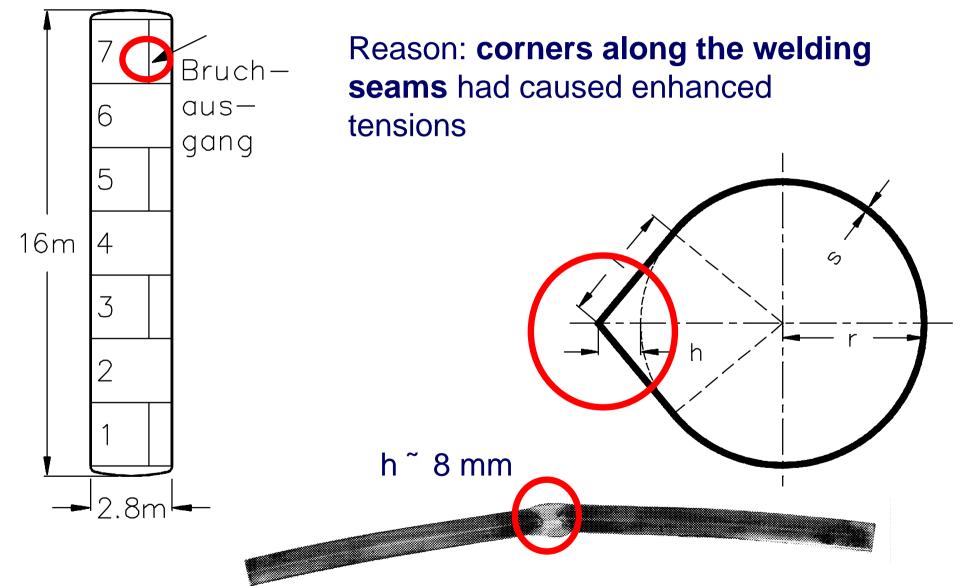


**Tank** 

Factory ground after explosion

# Tank accident at Hanau 1991 (2)

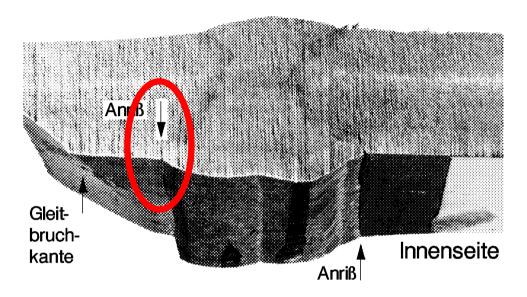




# Tank accident at Hanau 1991 (3)



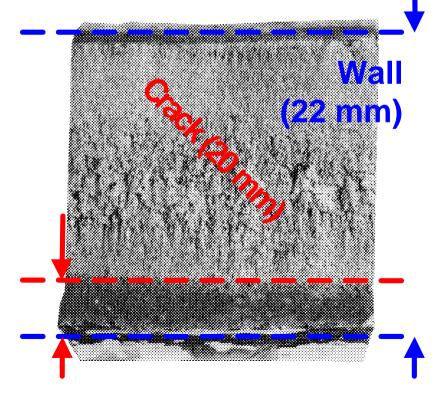
#### **Außenseite**



Soon the first cracks appeared. Under the influence of hydrogen they grew much faster than normally, ...

... until the tank could no longer resist even its normal operating pressure.

Rest wall (2 mm)



# Tank accident at Hanau 1991 (4)



### **Consequences:**

- All comparable tanks in Germany were checked.
- Manufacturing rules have been revised (upper limits for corners).
- The calculation method for the residual life time under cyclic stress was modernized.
- New test methods are able to detect cracks in earlier stages

The Hanau accident caused a progress in safety engineering.

# "Hindenburg", Lakehurst, 6 May 1937 (1)



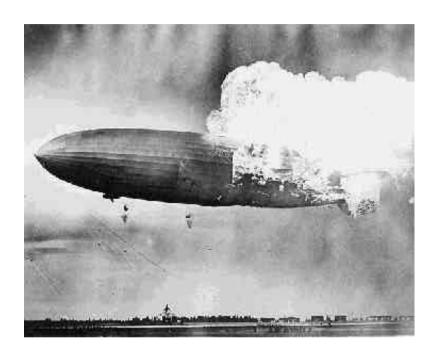
### **Accident reason:**

Paint of outer shell

- low conductivity
   (potential differences remained)
- extremely flammable (and not extinguishable)

### Lakehurst:

- Thunderstorm situation
- Potential difference ship-ground
- Potential difference ship-ship
- discharge (spark)



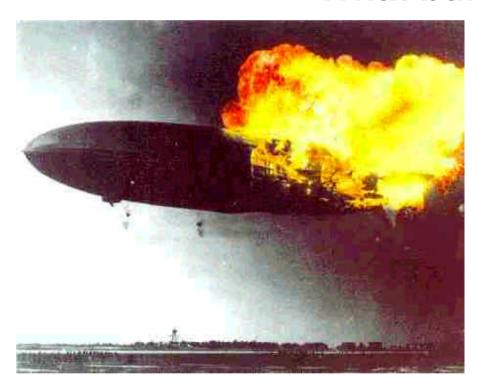
No explosion!

Comparatively few victims

# "Hindenburg", Lakehurst, 6 May 1937 (2)



### What burns here?



"Hindenburg": burnt with a very intensive flame (b/w photo, colored on the basis of witness reports) Picture: Bain



Hydrogen (right): almost invisible flame. The big flame tail on the left comes from the auxiliary boosters (solid fuel) Picture: NASA

# "Challenger", 28 January 1986





This explosion, which caused the death of seven astronauts, was caused by a **defective seal** in of of the auxiliary boosters (solid fuel).

A flame (arrow) escaped from the booster flank and damaged some main tank supply lines (liquid hydrogen, liquid oxygen). This caused a leak and ignition.



This would have happened in exactly the same way with any other fuel in the tank.

No hydrogen accident!

# Large scale accident simulation



# What happens if cryogenic hydrogen escaped into the open air?

# What is the influence of buildings?

Experiments were made in summer 1994 in an abandoned barrack ground in Brandenburg (Germany).

About 1 m<sup>3</sup> cryogenic hydrogen each was released, and the dispersion observed; analogous amounts of liquid propane were also released.

There was no ignition.

# Dispersion of hydrogen and propane







### **Propane**

- is heavier than air
- remains near the ground
- fills
   basements,
   trenches etc.
- ignition risk!

### Hydrogen

- is lighter than air
  - rises up
  - goes away from ignition sources
  - disappears rapidly





These photos were made during experimental simulations of an accident with gas escape between buildings. The experiments were performed in the framework of the EQHHPP project by the Federal Institute for Materials Research and Testing (BAM), Berlin.

# Hydrogen is not a toy!



- Hydrogen rises rapidly
  - Correct, but: diffusion makes it disperse in all directions.
     Including downwards, especially if it is trapped upwards (roof).
- Hydrogen is light and disappears rapidly
  - Correct, but: when cryogenic hydrogen escapes there is a mixture cloud consisting of hydrogen, air, and water; this is much heavier than hydrogen.
- Underestimation of the risks is the start of an accident!

# Hydrogen safety advantages



- Storage in pressure vessels
- Does not pollute ground or water
- Disappears rapidly if released
- Unconfined gas clouds unlikely to detonate
- Burns rapidly if ignited
- Does not leave harmful reaction products behind

# Hydrogen is not ...



- explosive
- unstable (acetylene!)
- autoignitive
- oxidizing
- poisonous
- corrosive
- radioactive

- ugly smelling
- contagious
- water polluting
- embryopathic
- cancerogenous
- expensive
- etc. etc. etc.

## Popular nonsense ...



"The wind power plants operating in Brandenburg reduce the emission of **poisonous carbon dioxide gas** by 677.000 tons per year, according to Wolfgang Fuerniss (CDU), state minister for economy."

Der Tagesspiegel, 17 December 2000





Thank you very much for your attention!

And see us occasionally under www.dwv-info.de!