what is hydrogen? why hydrogen?
hydrogen as a fuel - properties and bottlenecks
production, storage and use of hydrogen
case: solar hydrogen

Lectures: Univ. Lecturer Janne Halme (janne.halme@aalto.fi)
Slides: Peter Lund, Janne Halme
What is hydrogen (H) ?

- A hydrogen atom = 1 p$^+$ + 1 e$^-$
  (0 n=pototium, 1 n=deuterium, 2n=tritium)
  - $m_p = 1800 \, m_e$
  - $R_{\text{orbit}} \sim 10^5 \, R_{\text{nucleus}}$

- Quantum mechanics (Schrödinger) of H explains well its physics and chemistry

  \[ \frac{\hbar}{2\mu} \nabla^2 - \frac{e^2}{r} \] $\Psi(r) = E \, \Psi(r)$
  Wave function $\Psi(r,\theta,\phi)=R(r)P(\theta)F(\phi)$
  - $R,P,F$ quantum numbers
  - $r,\theta,\phi$ coordinates, $\mu$= effective mass
  Potential energy $U(r)=-\frac{e^2}{4\pi\varepsilon_0}$

- Hydrogen makes 75% of all visible mass of the universe, > 99% of all materia
What is a hydrogen molecule ($\text{H}_2$) ?

- A single nucleus-electron system is highly reactive $\rightarrow$ H forms a molecule with a hydrogen-hydrogen bond
  - Covalent bond, electron wave functions overlap (4.5 eV)

- $\text{H}_2$ can be either in ortho or para form (proton spin directions)
  - Ortho-para ratio = $1+1/I$, $\text{H}_2$:I=1/2
  - $\text{H}_2$ (gas): 75% ortho and 25% para
  - $\text{H}_2$ (liq, 20 K): 0.2% ortho and 99.8% para
  - Heat release in ortho-para conversion 0.146 kWh/kg (cf heat of liquefaction 0.123)
Energy release (with $H_2$) – reconfiguring bonds

- Atoms are connected through bonds that lower their total energy
- Bond is formed $\rightarrow$ energy is released
- Bond is broken $\rightarrow$ energy is absorbed
- Net release of energy if energy released $> \text{energy absorbed}$

**Figure 1.3.** Bonding energy versus internuclear separation for hydrogen–hydrogen bond. (1) No bond exists. (2) Most stable bonding configuration. (3) Further overlap unfavorable due to internuclear repulsion.
Simple hydrogen combustion reaction

- Basic combustion equation: $\text{H}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{H}_2\text{O} + 286 \text{ kJ/mol}$
  - Collision of molecules $\rightarrow$ $\text{O}_2$ and $\text{H}_2$ bonds break $\rightarrow$ New $\text{H}_2\text{O}$ bonds formed $\rightarrow$ Energy of new configuration lower $\rightarrow$ Heat released

- Reconfiguration of bonds in a chemical reaction involves electron transfer
  - thermal combustion: very fast electron transfer (picoseconds)
  - electrochemical combustion (fuel cells): separating reactants slows down $e^-$ transfer from fuel species to oxidant species

![Figure 1.2. Schematic of H$_2$–O$_2$ combustion reaction. (Arrows indicate the relative motion of the molecules participating in the reaction.) Starting with the reactant H$_2$–O$_2$ gases (1), hydrogen–hydrogen and oxygen–oxygen bonds must first be broken, requiring energy input (2) before hydrogen–oxygen bonds are formed, leading to energy output (3, 4).]
Hydrogen as a gas

- Hydrogen follows the ideal gas law at low pressure

\[ PV = n\bar{R}T \]

where:
- \( P \) = absolute pressure
- \( V \) = volume
- \( n \) = number of moles of gas molecules present
- \( T \) = absolute temperature
- \( \bar{R} \) = universal gas constant = 3.4067 ft-lb/mol (8.31434 Nm/mol K)

- At higher pressures, gas occupies less space than IGL predicts
  - With compressibility or non-ideality factor \( Z = Z(p) \)
  \[ P = Z\rho RT, \; \rho = \text{gas density} \]
Basic macroscopic properties of hydrogen as a fuel

- Boiling point at 20 K
- Density 1 m$^3$ hydrogen gas 0.09 (20 °C) . . . liquid 71 kg (-252 °C)
- Heating value 120-142 kJ/kg or 33.3 – 39.4 kWh/kg (gas 3-3.6 kWh/m$^3$)
- High octane number (130)
Safety issues with hydrogen

- Hydrogen differs in most properties and characteristics from conventional fuels, e.g.
  - Highly flammable with air over a range of 4 to 75wt % of H₂
  - Low flash point (20 K)
  - High autoignition temperature (585 C), but low ignition energy (0.02 mJ)
  - Low electroconductivity (flow may create electrostatic charges)
  - High burning speed (2.65-3.25 m/s)
  - Pale flames, almost invisible, but safer fire
  - Hydrogen embrittlement

- Hydrogen explosion 24 g TNT/g H₂ (2 × methane)
  - Burning speed 2.65-3.25 m/s (≠ flame speed); turbulence hundred’s of m/s; explosion> km/s

- Safety rules and limitations for transport, storage and use of hydrogen
Figure 1-7 Flammability Ranges of Comparative Fuels at Atmospheric Temperature
Why H\textsubscript{2} – abundance?

- Hydrogen is abundantly available in compounds, but not in free form; e.g. water, hydrocarbons, alcohols, chemicals
  - Covalent bond: H\textsubscript{2}O, CH\textsubscript{4}
  - Hydrogen bond: H\textsubscript{2}O molecules, DNA, proteins
  - Hydrid compounds with electropositive elements (H\textsuperscript{−}): MeH\textsubscript{x}
  - 1 m\textsuperscript{3} of: water = 111 kg H\textsubscript{2}, methanol = 100 kg, LH\textsubscript{2} = 71 kg

- Fuels with H\textsubscript{2}:
  - Hydrocarbons: light HCs are gases and heavy 5-12 C-atoms liquids
  - Alcohols: OH connects to HCs
Why $H_2$ - relevance?

- The relative share of hydrogen in energy production increases (now in average $CH_2$)
- Hydrogen economy? "Will water be the coal of future"? Tradable fuel?
- Hydrogen is not an energy source
  - a clean energy carrier
  - produced from all primary energy sources
  - can be converted to all final energy forms
  - important industry raw material
How to produce H₂?
– several paths available

• Outgoing from hydrogen resources
  – Hydrocarbons (CₙHₘ...)
  – Water (H₂O)

• Outgoing from production process
  – Thermal processes
  – Electrical processes (electrolysis)
  – Photonic processes (photolysis, biology)

• Outgoing from primary energy used
  – Fossil fuels. Nuclear power, renewable sources
Thermal H$_2$ processes

- Hydrogen is extracted thermally (p,T, catalysts) from molecular structures
  - Reactants: hydrocarbon; Product: H$_2$, CO$_2$, heat

- Examples of processes
  - Steam reforming, partial oxidation, thermolysis, thermochemical processes

- Well applicable for large scale H$_2$ production
  - > 95% of all H$_2$ used is based on natural gas reforming

---

**Methane steam reformation**

1) CH$_4$ reforming: high T steam (700°C - 1000°C) [endothermic reaction]+ CH$_4$ [3–25 bar + catalysts] $\rightarrow$ H$_2$+CO+CO$_2$

2) Water gas shift reaction: CO+H$_2$O [steam+catalyst] $\rightarrow$ H$_2$+CO$_2$+heat

3) Adsorption: gas cleaning and removal of impurities
Examples of H\textsubscript{2} production through stem reforming and partial oxidation

- **Steam reforming:**
  - Methane: CH\textsubscript{4} + H\textsubscript{2}O (+heat) \rightarrow CO + 3H\textsubscript{2}
  - Propane: C\textsubscript{3}H\textsubscript{8} + 3H\textsubscript{2}O (+heat) \rightarrow 3CO + 7H\textsubscript{2}
  - Ethanol: C\textsubscript{2}H\textsubscript{5}OH + H\textsubscript{2}O (+heat) \rightarrow 2CO + 4H\textsubscript{2}
  - Gasoline (iso-octane or toluene): C\textsubscript{8}H\textsubscript{18} + 8H\textsubscript{2}O (+heat) \rightarrow 8CO + 17H\textsubscript{2}
    or C\textsubscript{7}H\textsubscript{8} + 7H\textsubscript{2}O (+heat) \rightarrow 7CO + 11H\textsubscript{2}

- **Partial oxidation:**
  - Methane: CH\textsubscript{4} + \frac{1}{2}O\textsubscript{2} \rightarrow CO + 2H\textsubscript{2} (+heat)
  - Propane: C\textsubscript{3}H\textsubscript{8} + 1\frac{1}{2}O\textsubscript{2} \rightarrow 3CO + 4H\textsubscript{2} (+heat)
  - Ethanol: C\textsubscript{2}H\textsubscript{5}OH + \frac{1}{2}O\textsubscript{2} \rightarrow 2CO + 3H\textsubscript{2} (+heat)
  - Gasoline (iso-octane and toluene): C\textsubscript{8}H\textsubscript{18} + 4O\textsubscript{2} \rightarrow 8CO + 9H\textsubscript{2} (+heat)
    or C\textsubscript{7}H\textsubscript{8} + 3\frac{1}{2}O\textsubscript{2} \rightarrow 7CO + 4H\textsubscript{2} (+heat)

- **Shift Reaction:** CO + H\textsubscript{2}O \rightarrow CO\textsubscript{2} + H\textsubscript{2} (+small amount of heat)
Hydrocrackering

• Through hydrocrackering poor quality hydrocarbons can be upgraded to good quality; tailormade fuels possible (cf biodiesel production)

• \((\text{CH}_x)_n + \frac{ny}{2} \text{H}_2 \rightarrow n(\text{CH}_{x+y}) + \Delta H\) (exothermic); H/C ratio is increased

• Hydrogen added may correspond to 10-100% energy increase of input material; hydrogen functions both as an energy carrier and reduction agent

How much hydrogen is needed (m\(^3\)H\(_2\) per ton)?

• Heavy oil type of raw material (H/C~1.4) to crude naphta (H/C~2.3) 670 m\(^3\) H\(_2\)

• Crude oil (~1.7) to middle destillate (~2) 400 m\(^3\) H\(_2\)

• Hard coal (~0.8) to to crude naphta (~2.3) 1270 m\(^3\)

• Hard coal (~0.8) to methane (=4) 2850 m\(^3\) H\(_2\)
Hydrogen through biomass gasification

- Solid biomass
  1. Biomass + O₂ + steam [high p,T] \(\rightarrow\)
     synthesis gas (CO, H₂): \(C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + ...\)
     cleaning \(\rightarrow\)
  2. shift-reaction: CO + H₂O [steam + catalyst] \(\rightarrow\) H₂ + CO₂ + little heat
  3. H₂ separation (e.g. membranes or adsorption)

- Pyrolysis
  - Pyrolysis \(\rightarrow\) CO + CO₂ + H₂ + other HCs \(\rightarrow\) catalytic reformation of HCs
    \(\rightarrow\) CO + CO₂ + H₂
  - Shift + cleaning as above
Chemical splitting of water

- Iron sponge reaction: $\text{H}_2\text{O} + \text{Fe} \rightarrow \text{H}_2 + \text{FeO}$; $\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$

- Steam reformation
  $\text{C}_m\text{H}_2n + m\text{H}_2\text{O} \rightarrow m\text{CO} + (n+m)\text{H}_2$ ($\eta \sim 80\%$)

- Thermochemical cycles ($\eta \sim 40-50\%$): 1) $\text{Me}_2\text{O} \rightarrow 2\text{Me}_2 + \frac{1}{2} \text{O}_2$ (high T, $>1000$ K), 2) $2\text{Me} + \text{H}_2\text{O} \rightarrow \text{Me}_2\text{O} + \text{H}_2$ (low T)

- Electrolysis ($\eta \sim 70-80\%$): $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$
  - Cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
  - Anode: $2\text{OH}^- \rightarrow \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$

- Thermolysis: splitting water with heat only $T > 2000-4000$ K
Photobiological processes

- Hydrogen is produced from water using sunlight and specialized microorganisms (e.g. green algae and cyanobacteria).
- Microorganisms consume water and produce hydrogen as a byproduct of their natural metabolic processes.
- Fermenting bacteria (dark) may also produce hydrogen.
Photoelectrochemical water splitting

- Water is split through electrons produced in a photoexitonic process
- E.g. TiO$_2$
Hydrogen storage - general

- Storage properties of hydrogen
  - Density 0.08 kg/m$^3$, heating value 120 MJ/kg (33.3 kWh/kg)
  - Volumetric energy density
    - STP 2.7 kWh/m$^3$
    - If 200 bar $\rightarrow$ 500 kWh/m$^3$; 1000 bar $\rightarrow$ 2700 kWh/m$^3$
    - For comparison: gasoline 8,000 kWh/m$^3$, 42 MJ/kg

- Ways to store hydrogen
  - Compressed gas (high p $<$ 1000 bar)
  - LH$_2$ (cryogenic temperature -252.8°C)
  - Material based storage (on material surfaces or inside materials)
H₂ storage technologies

- **Compressed gas storage**
  - P = 200-750...1000 bar
  - Compression work \( (W = T \Delta s - \Delta h) \) 1.9 kWh/kg (20 Mpa)
  - Composite structures, diffusion barriers
    Komposiittirakenteita; carbon fibres

- **Cryo-compressed H₂ storage**
  - Liquid nitrogen (77 K) used to cool down H₂
  - Volumetric capacity 4 x

- **Liquid hydrogen storage**
  - Liquification uses 30% of the energy contents of H₂
  - Capacity 0.07 kg/L
  - Special cryogenic tanks
Hydrogen storage (sorption)

- Solid-state nanomaterials for hydrogen storage include carbon nanomaterials, metal–organic frameworks, nanocrystalline metal and complex hydrides.

![Diagram showing physical and chemical sorption](image)

Figure 6. Schematic illustration of basic mechanisms of solid-state hydrogen storage. By physisorption, hydrogen is attached to the surface of a material either as hydrogen molecules or as hydrogen atoms. By chemisorption, a hydrogen molecule is dissociated into hydrogen atoms, and then the hydrogen atoms are incorporated/distributed into the solid lattice. The potential energy for hydrogen sorption is also illustrated.
Formation of hydride phase

Hydrogen can be Stored in Different Forms

In tanks...

Compressed Gas

Cryogenic Liquid

and in materials...

Hydrogen can be stored on the surfaces of solids by adsorption or within solids by absorption. In adsorption (a) hydrogen attaches to the surface of a material either as hydrogen molecules (H2) or hydrogen atoms (H). In absorption (b), hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework—this method may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and temperatures close to room temperature. Finally, hydrogen can be strongly bound within molecular structures, as chemical compounds containing hydrogen atoms (c).

- Van’t Hoff law \( \Delta p = c \frac{RT}{V} \); 
  \( c = \text{concentration} \)
  \( R \ln \left( \frac{p}{p_0} \right) = \Delta S - \frac{\Delta H}{T} \)

- Different phases and hydrids depending on the M-H bonds

  - \( \alpha \)-phase: H2 dissolves into metal; Sievert’s law \( C_H = k \sqrt{p} \)

  - Two phase regime: \( \beta \) phase increases with H2 concentration; \( P = \text{constant} \)

  - \( \beta \) phase or hydrid: rapid increase in pressure vs. H2 concentration

Figure 2: Idealized PCT curves and van’t Hoff plots.
Case: Concentrating solar power (CSP) for hydrogen production

- Parabolic surfaces, heliostat (flat mirror) concentrate solar radiation to a focal point
  - Temperatures up to 600-1000 °C possible, instantaneous solar power close to 1 MW/m²
  - Solar hydrogen production through thermochemical reactions
- Large CSP: 350 MW (USA); Spain 50-100 MW; Under construction 1000 MW → potential in EU 2025 around 37,000 MW
Examples of CSP
Thermochemical water splitting at high temperature (solar-hydrogen)

- H₂ can be produced at 500-2000 °C through different thermochemical reactions and cycles
- Chemicals involved are recycled, only water is consumed
- Some 350 different cycles are known, e.g.
  - cerium(IV) oxide-cerium(III) oxide cycle (CeO₂/Ce₂O₃)
  - iron oxide cycle (Fe₃O₄/FeO)
  - sulfur-iodine cycle (S-I)
  - cerium-chlorine cycle (Ce-Cl)
  - iron-chlorine cycle (Fe-Cl)
  - magnesium-iodine cycle (Mg-Cl)
  - vanadium-chlorine (V-Cl)
  - copper-sulfate (Cu-SO₄)
  - zinc zinc-oxide cycle (Zn/ZnO)
- Here zinc/zinc oxide (1900°C) and sulfur-iodine (800-1000°C) are presented
## Examples of thermochemical cycles

<table>
<thead>
<tr>
<th>Thermochemical cycle</th>
<th>LHV Efficiency</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cerium(IV) oxide-cerium(III) oxide cycle (CeO2/Ce2O3)</td>
<td>? %</td>
<td>2,000 °C (3,632 °F)</td>
</tr>
<tr>
<td>Hybrid sulfur cycle (HyS)</td>
<td>43 %</td>
<td>900 °C (1,652 °F)</td>
</tr>
<tr>
<td>Sulfur iodine cycle (S-I cycle)</td>
<td>38 %</td>
<td>900 °C (1,652 °F)</td>
</tr>
<tr>
<td>Cadmium sulfate cycle</td>
<td>46 %</td>
<td>1,000 °C (1,832 °F)</td>
</tr>
<tr>
<td>Barium sulfate cycle</td>
<td>39 %</td>
<td>1,000 °C (1,832 °F)</td>
</tr>
<tr>
<td>Manganese sulfate cycle</td>
<td>35 %</td>
<td>1,100 °C (2,012 °F)</td>
</tr>
<tr>
<td>Zinc zinc-oxide cycle (Zn/ZnO)</td>
<td>44 %</td>
<td>1,900 °C (3,452 °F)</td>
</tr>
<tr>
<td>Hybrid cadmium cycle</td>
<td>42 %</td>
<td>1,600 °C (2,912 °F)</td>
</tr>
<tr>
<td>Cadmium carbonate cycle</td>
<td>43 %</td>
<td>1,600 °C (2,912 °F)</td>
</tr>
<tr>
<td>Iron oxide cycle (Fe3O4/FeO)</td>
<td>42 %</td>
<td>2,200 °C (3,992 °F)</td>
</tr>
<tr>
<td>Sodium manganese cycle</td>
<td>49 %</td>
<td>1,560 °C (2,840 °F)</td>
</tr>
<tr>
<td>Nickel manganese ferrite cycle</td>
<td>43 %</td>
<td>1,800 °C (3,272 °F)</td>
</tr>
<tr>
<td>Zinc manganese ferrite cycle</td>
<td>43%</td>
<td>1,800 °C (3,272 °F)</td>
</tr>
<tr>
<td>Copper-chlorine cycle (Cu-Cl)</td>
<td>41 %</td>
<td>550 °C (1,022 °F)</td>
</tr>
</tbody>
</table>

Source: Development of solar-powered thermochemical production of hydrogen from water [5]