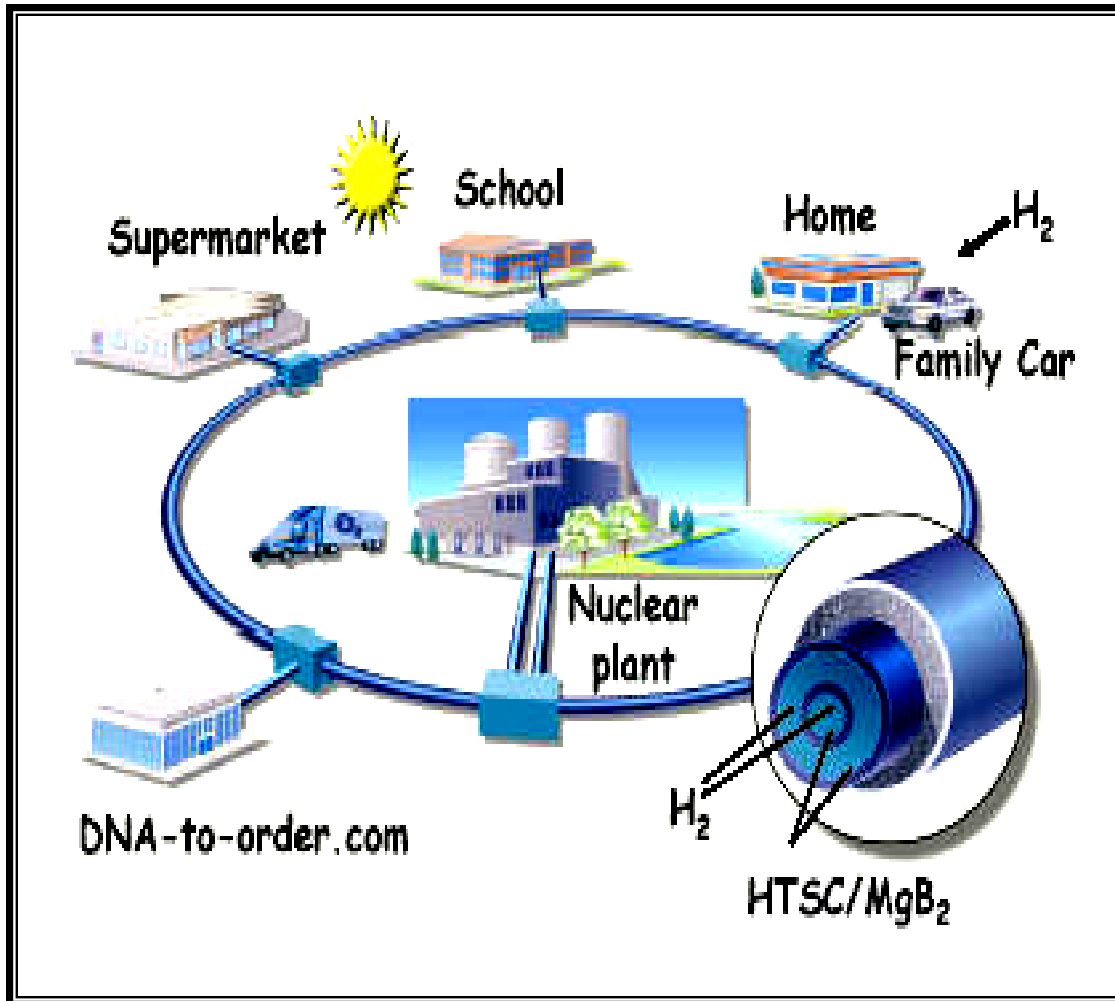


Hydrogen: Background Info & R&D Needed For Application To The SuperGrid



Presented to:

SuperGrid 2 Workshop
University of Illinois
Urbana, IL

Presented by:

Dr. Robert B. Schainker
Power Delivery & Markets
EPRI, Palo Alto, CA
rschaink@epri.com

October 25, 2004

Hydrogen: Properties

- Liquefies at 20.27 K (at 1 Atm.)
- Boils at 20.27 K (for para-hydrogen) and 20.38 for ortho-hydrogen)
- Nucleus spin of two atoms in H₂ molecule are in different directions
- Dielectric constant, $\epsilon = 1.228$ at 20.4 K
[Note: Liquid Nitrogen, $\epsilon = 1.454$ at 70 K, N₂ Liquefies at 77.4 K]
- Dielectric breakdown: below critical electric field gradient, hydrogen is an insulator. At present, the breakdown electric field values have a 25% level of scatter, and it depends on pressure changes from 1 to 5 Atm at 20 K. Hydrogen in the gaseous phase, like the liquid, is an insulator below the breakdown voltage, and it follows Paschen's dielectric law, which states the breakdown voltage does not change as long as the product of its density and the gap distance is held constant. The breakdown voltage is in the range of 250 to 300 volts at a Paschen's $\rho \cdot d$ of 10^{-7}g/cm^2 .

Hydrogen: Two States

Para-hydrogen

- Anti-parallel nuclear spin of two atoms in H₂ molecule
- Even quantum numbers
- Lower energy state than Ortho-hydrogen

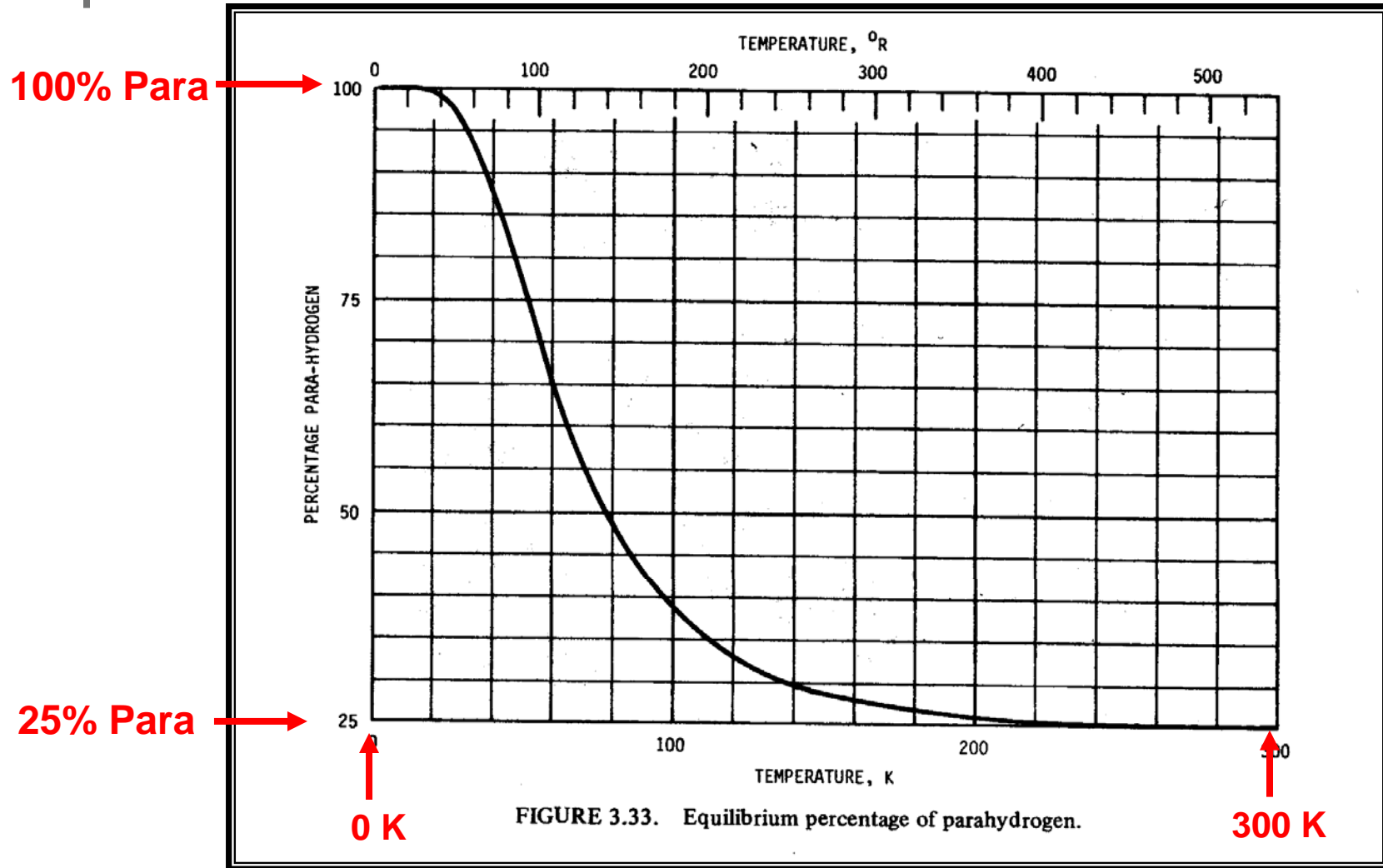
Ortho-hydrogen

- Parallel nuclear spin of two atoms in H₂ molecule
- Odd quantum numbers
- Higher energy state than Para-hydrogen

Comparisons

- At 20C temperature, “Normal” Hydrogen has an equilibrium concentration of 75% Ortho and 25% Para
- **Conversion of Ortho to Para is an exothermic** temperature dependant process. Engineering design for worst case failure conditions have to accommodate for this exothermic reaction.
- Enthalpy, Thermal Conductivity, and Specific Heat Capacity show large differences for Ortho-hydrogen and Para-hydrogen
- Density properties vary less than 0.7%, which is maximum for “Normal” hydrogen at very low cryogenic temperatures

Para-Hydrogen Equilibrium %



At 20 K, most of the hydrogen is in the “Para” opposite spin state

Slush Hydrogen

- **Slush Hydrogen is the name given to a homogenous mixture of coexisting solid and liquid phases of hydrogen.**
- **If the slush mixture is 60% solid by mass, the density will be 11.5% greater than the pure liquid at its normal boiling point, thus slush hydrogen is used by NASA as a preferred hydrogen fuel.**
- **Slush hydrogen can be produced in a number of ways. The method used quite often is the so-called freeze thaw method, where ullage over the liquid is pumped to lower pressures causing a solid layer to form at the surface. The pumping is then stopped, and a solid layer partially melts at the edge of the container and settles into the liquid. The cycle is repeated until the desired amount of solid is formed. Some issues remain in controlling the solid particle sizes, especially for pumping purposes. The disadvantage of this approach is that the vapor over the liquid must be pumped down to very low pressures, which increases the likelihood of leaks.**

Hydrogen: Safety

- There are many rules and standards used by NASA and the oil, gas, and air products industry, if used properly, allow hydrogen to be used safely, at cryogenic and non-cryogenic temperatures.
- Hydrogen is colorless, odorless, and at temperatures higher than 6 K, it is lighter than air (at STP)
- Mixtures of hydrogen with air or oxygen are highly flammable over a wide range of compositions. The flammability limit range, by weight, as a percentage of Hydrogen is 4 to 75%.
- * • Leakage In Pipeline and Valves Has To Be Designed Into Any Engineering Applications Using Hydrogen
- * • Monitoring, Detection, and Fixing Leaks Has To Be Part Of Any Operational and Maintenance Practices For Applications Using Hydrogen

Application of Hydrogen To The SuperGrid: Hydrogen Dielectric Coolant Topic

Cryogenics - Observations

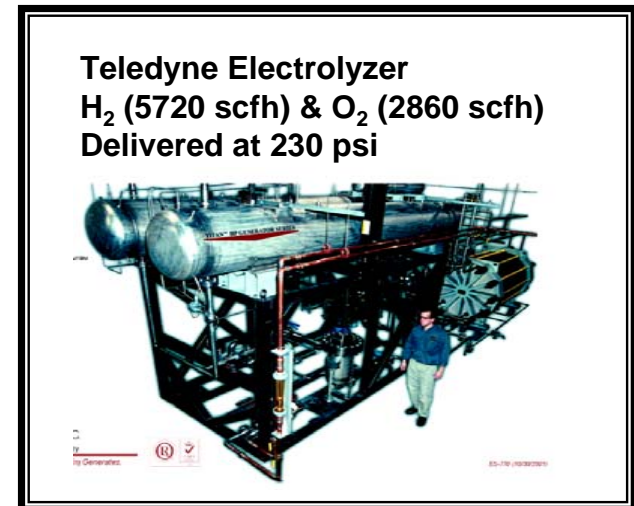
- Excellent Dielectric, But Choice of Pressure, Temperature and Engineering Margins Need To Be Determined.
* Note: MgBr_2 Is Superconducting Below 39 K.
- Cryogenic Container/Pipeline Issues Need To Be Identified and Resolved Via Engineering and Testing Programs
*
- Imbrittlement of Pipeline Material Is an Issue That Needs to Be Further Addressed, Especially at Cryogenic Temperatures.
*
- Pumping, Operational and Maintenance Issues Need To Be Identified and Resolved Via Engineering and Testing Programs
*
- Hydrogen Cryogenic Systems Are Available Today, but Not at the Scale Needed for the SuperGrid, But This Should Not Be a Major Problem. In Fact, for the SuperGrid, Economy of Scale Principles Will Lower Per Unit Costs to Bring Hydrogen to Cryogenic Temperatures.

* R &D Needed

Application of Hydrogen To The SuperGrid: Electrolysis Topic

Production of Hydrogen From Electrolysis - Observations

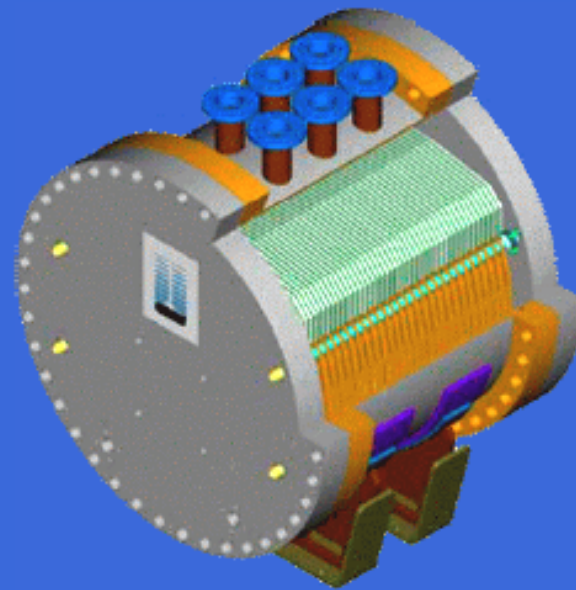
- Yes, electrolysis works and is commercially available today at low pressure (up to about 230 psia)
- Electrolysis at high pressure (1500 psi_a to 10,000 psi_a) is the most efficient way to produce hydrogen, but no such systems are commercially available today. A few pilot scale demos have been built (e.g., Mitsubishi, Proton). These units do not use the “concentrator” cell approach which should be “best” for SuperGrid application. (Mechanical compression to these pressures has been done, but too much energy is lost in the process and depends on the final pressure needed.)



“High” Pressure Electrolyzers From Norsk Hydro

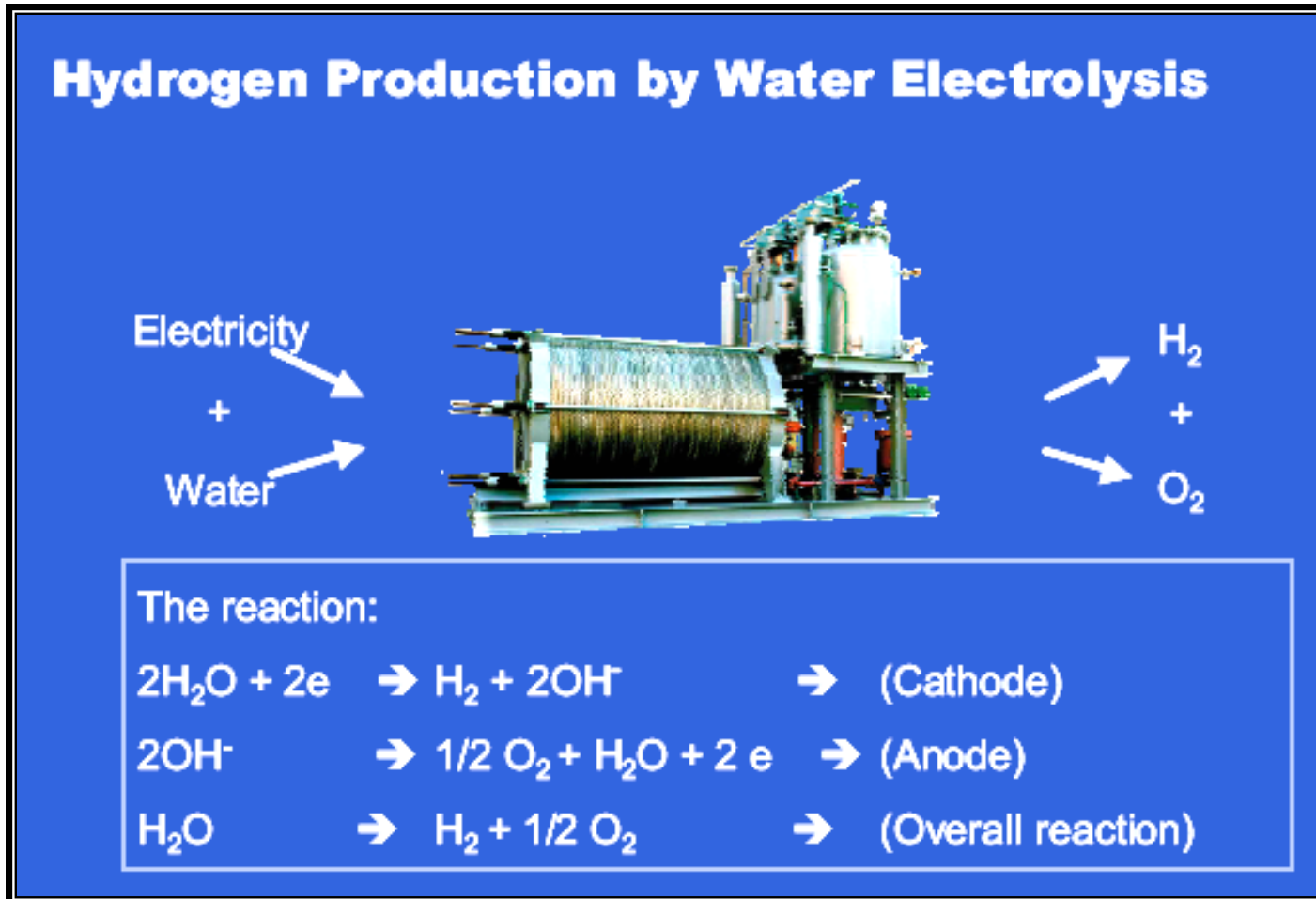
High pressure electrolysis development

- GHW: High pressure alkaline electrolyser
 - compact, simplified design
 - 30 bar operating pressure
 - very high energy efficiency
 - lower cost
- PEM Electrolysis
 - high operating pressure
 - no alkaline solution required
 - very high energy efficiency



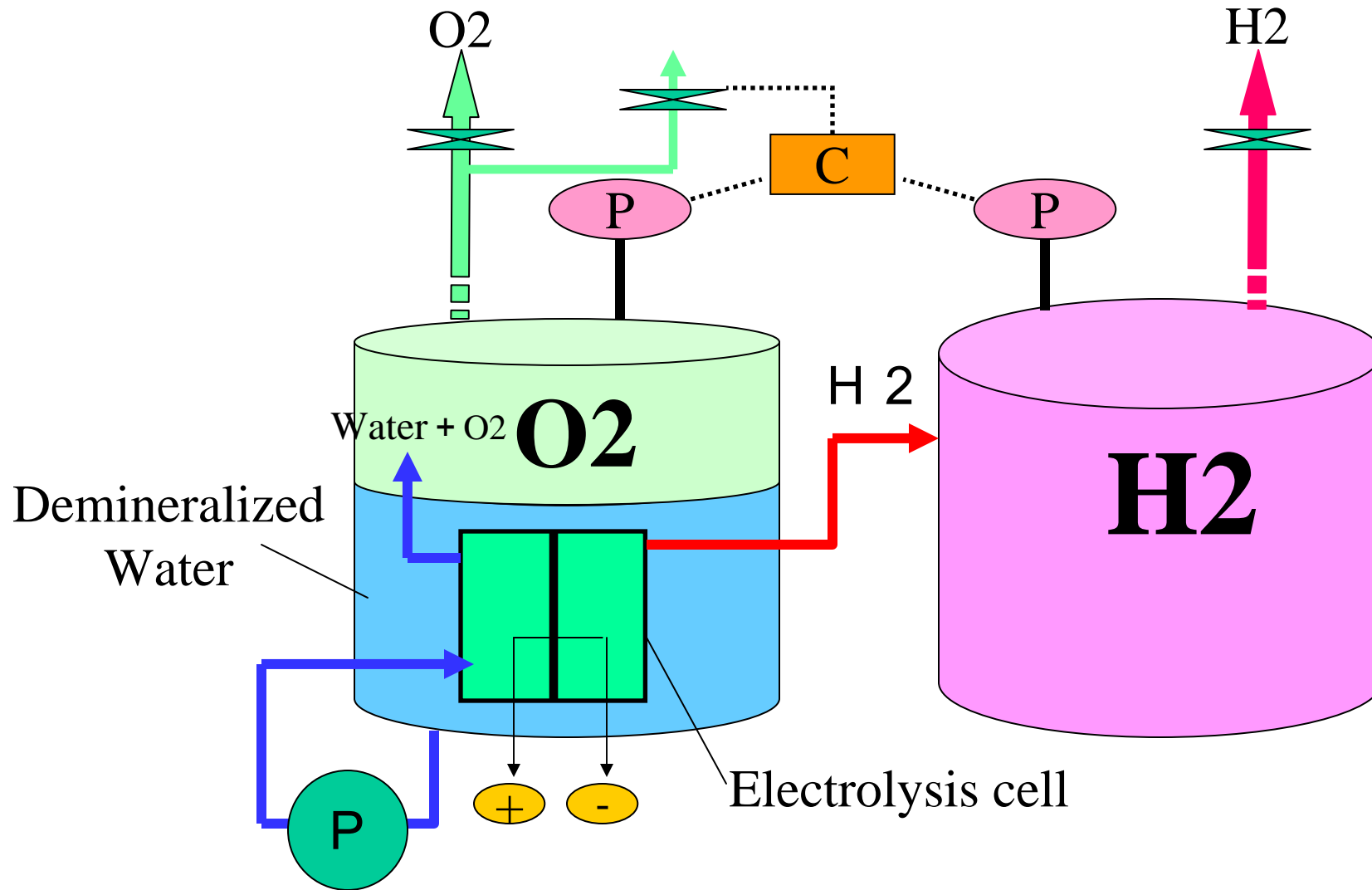
Note: 30 bar = 435 psi (and we may need 1500 psi)

Electrolyzers From Norsk Hydro

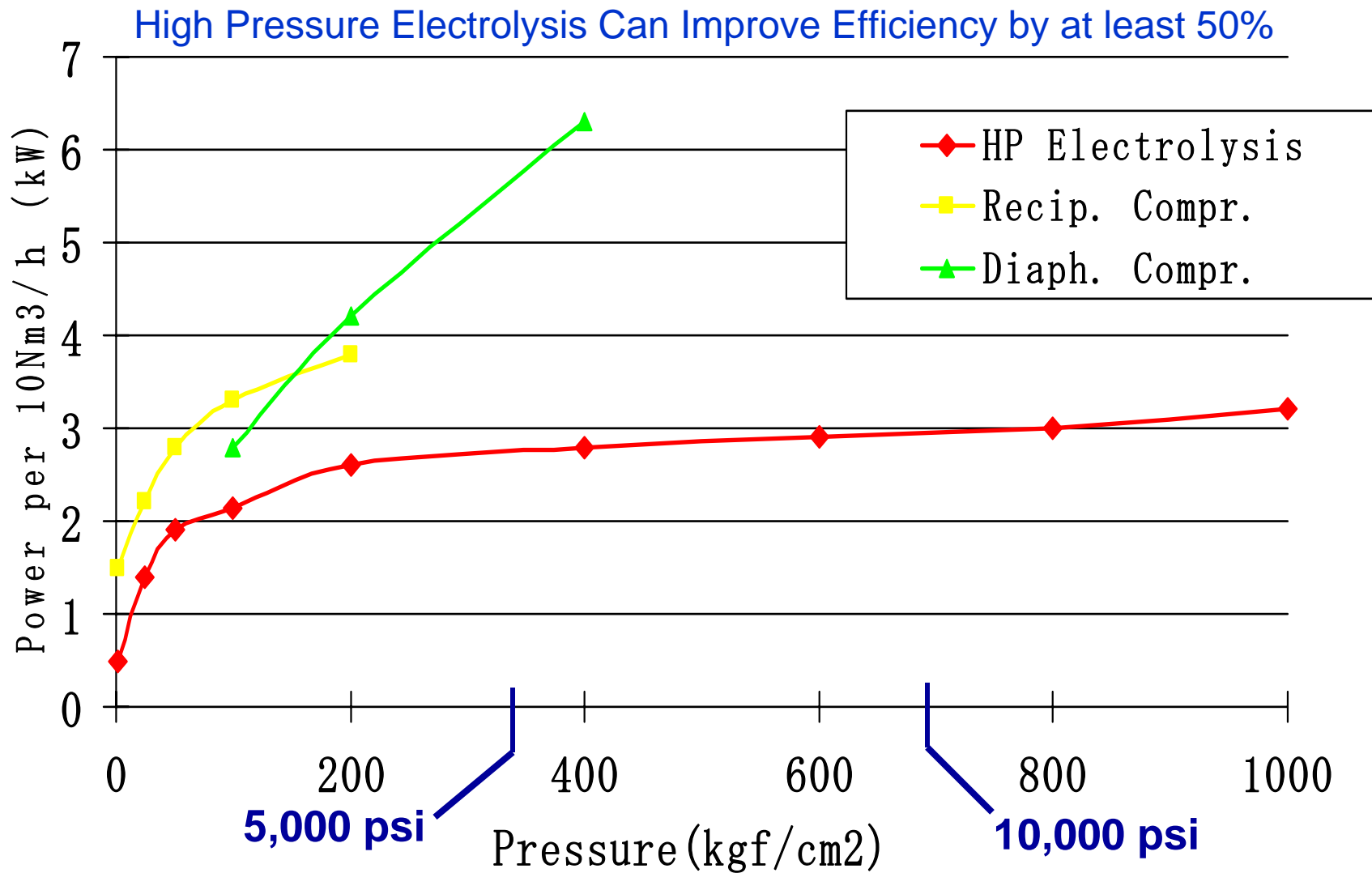


Note: Output pressure of H₂ and O₂ is about 200 psi

HP Electrolyzer Concept (by Mitsubishi)

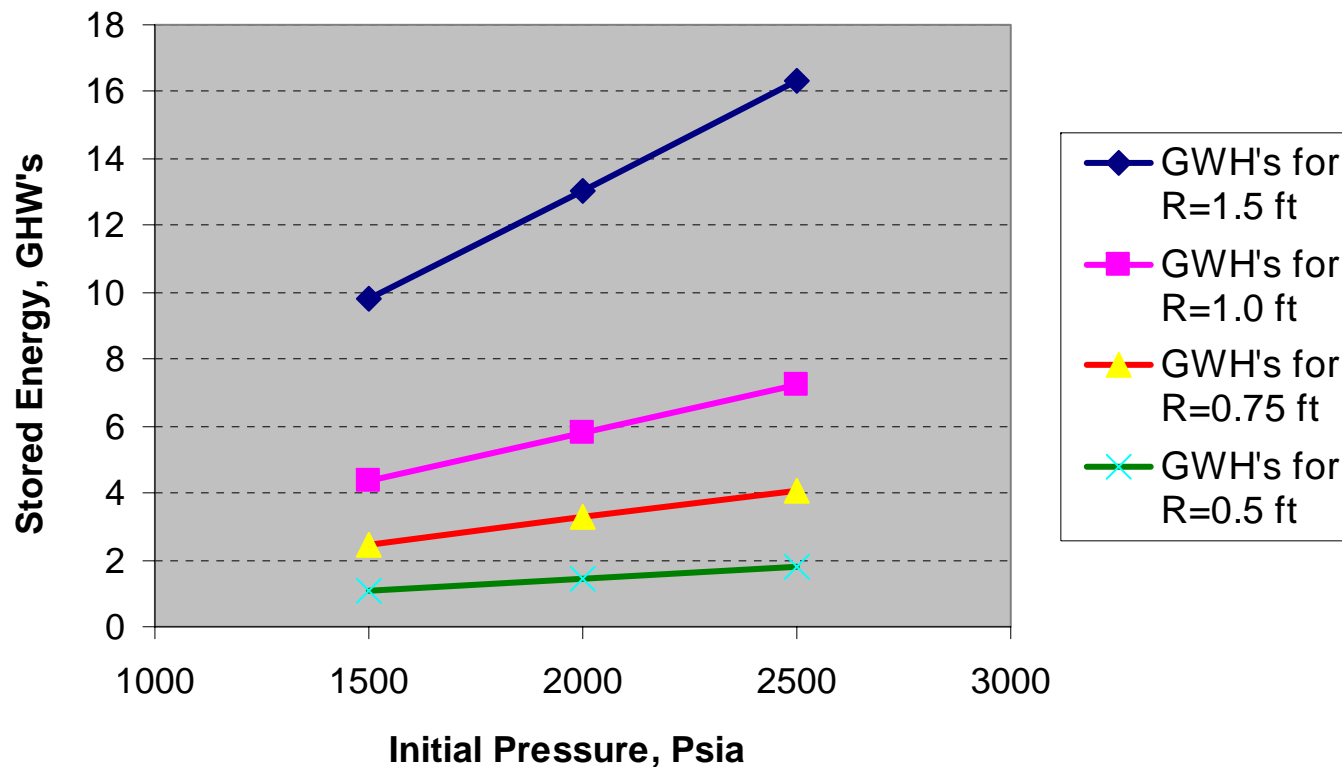


Comparison of Power Consumed To Produce HP Hydrogen



Application of Hydrogen To The SuperGrid: Hydrogen Energy Storage Topic

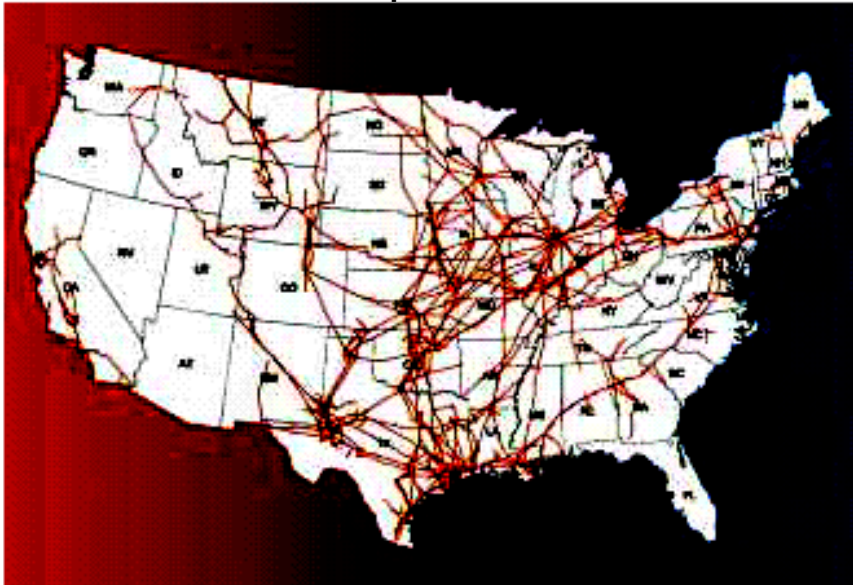
GWH's Stored In 300 Mile Hydrogen Pipeline, From 10% Increase In Pressure Level (Electrolyzer Eff.= 0.9, and Pipeline Radius = R)



The pipeline can store a tremendous amount of energy by operating between two different pressure levels.

U.S. Pipeline Technology That Hydrogen and the SuperGrid Can Build On

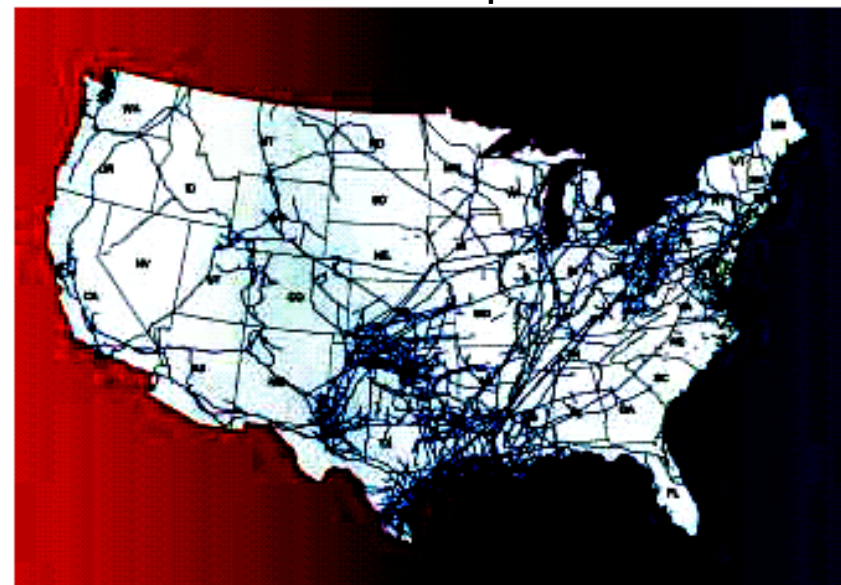
Oil Pipelines



The two million miles of oil pipelines in the United States are the principal mode for transporting crude oil and refined products. They account for about 88 percent of domestic product movements.

Source: U.S. Department of Transportation, Office of Pipeline Safety.

Natural Gas Pipelines



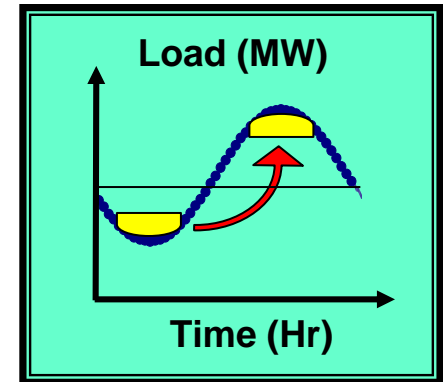
Virtually all natural gas in the United States is moved via pipeline. The forecast of a doubling in the number of new natural gas wells drilled annually and an 80 percent increase in the number of active drilling rigs will require new pipelines.

Source: U.S. Department of Transportation, Office of Pipeline Safety.

Note: About 1/3 of existing natural gas pipelines can be used to transport hydrogen without costly retrofits (welds need upgrading in another 1/3 of the pipelines).

Methods To Store Hydrogen

- **Compressed Gas Storage Tanks**
 - New tank materials (carbon fiber based) allow hydrogen to be stored at high pressure (5k to 10k psi); Cost is high, today.
- **Liquid Hydrogen**
 - Mass stored is high; Liquefaction cost is high.
- **Chemical Hydrides**
 - Pure and alloyed metals can combine with H₂; Cool to absorb H₂, heat to release H₂; Per cent stored is about 5-10%, by weight.
- **Gas-On Solid Adsorption**
 - Adsorb H₂ on Activated Carbon; Cost is very high; Percent adsorbed in high; Percent stored is about 70%, by weight.
- **Microspheres/Nano-Tubes**
 - Glass spheres store H₂ at high temperature & pressure; Cool to store and heat to release H₂. Basic R&D is progressing.
 - Carbon Nano-tubes store H₂. Basic R&D is progressing. Today, percent stored is about 5-10%, by weight.

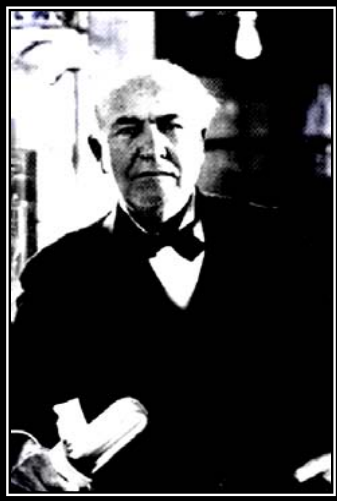


Hydrogen Applied To SuperGrid: Summary of Key Issues Needing Resolution

- **Integrated Hydrogen-Superconductor System Design Trade-off Studies Need To Define Temperature, Pressure, and Operating Voltage For SuperGrid System**
- **Fundamental Properties Of Hydrogen Need Further Identification and Verification Under Real World Conditions Where Impurities Will Be Present**
- **Proper Coating, Splices, Joints, Electrical Grounding, and Materials For The SuperGrid Hydrogen Pipeline Need Further Definition and Solution(s)**
- **Leak Detection, Leak Location, and Field Repair/Maintenance Of SuperGrid Hydrogen Pipeline Need Development and Testing Appropriate**
- **For The Integrated SuperGrid Design A Pilot-Scale Testing Program(s) Is Needed To Provide Data For Engineering Designers**
- **Development of High Pressure Electrolyzer (with High Efficiency) is a Key Enabling Technology. Electrolysis at High Pressure is Not the issue; Rather the Container and “Plumbing” is the Technical/Engineering Challenge. High Pressure Fuel Cells Are Also Needed To Directly Use The High Pressure Hydrogen In The Hydrogen Pipeline.**

Opportunity:

We Can Implement Wise Decisions To Continue To Stand On The Shoulder's Of "Giants" To Provide Immense Public Benefits



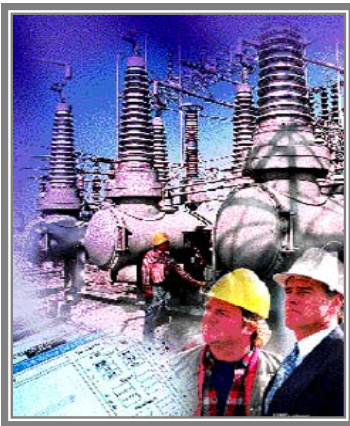
***We Can Create The
21st Century
Greatest Achievement***

***The Vast Networks Of Electrification Are The Greatest
Engineering Achievement Of The 20th Century.
-- U.S. National Academy of Engineering***

Thermal Energy Content Of Various Fuels

Heating Value

Fuel Type BTU's/Pound*



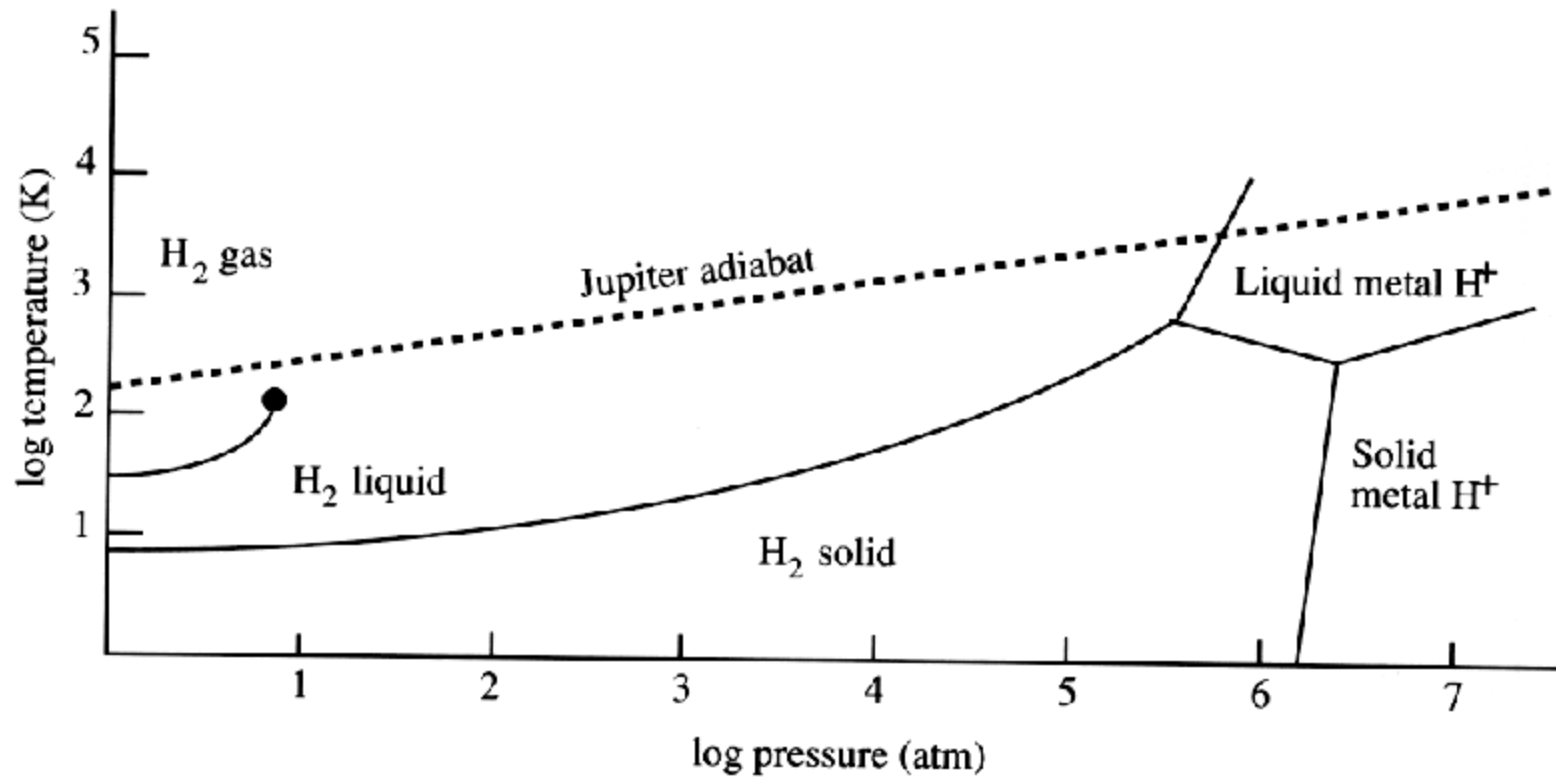
Hydrogen	61,100
Methane	23,900
Propane	21,700
Diesel Oil	19,500
Fuel Oil	18,700
Gasoline	20,750
Alcohol	11,620
Crude Oil (Tx)	19,460
Kerosene	19,810

***At 1 Atm. Of Pressure, 14.7 psi)**

1 BTU (British Thermal Unit) is the amount of heat needed to raise one pound of water one degree F.

Bottom-Line: On a Per Pound basis, Hydrogen contains about a factor of 3 times more energy than any fossil fuel. However, with its low mass density at one atmosphere, it has high storage costs, based on present day technology.

Hydrogen: Phase Diagram



Para-Hydrogen Density Vs Press. & Temp.

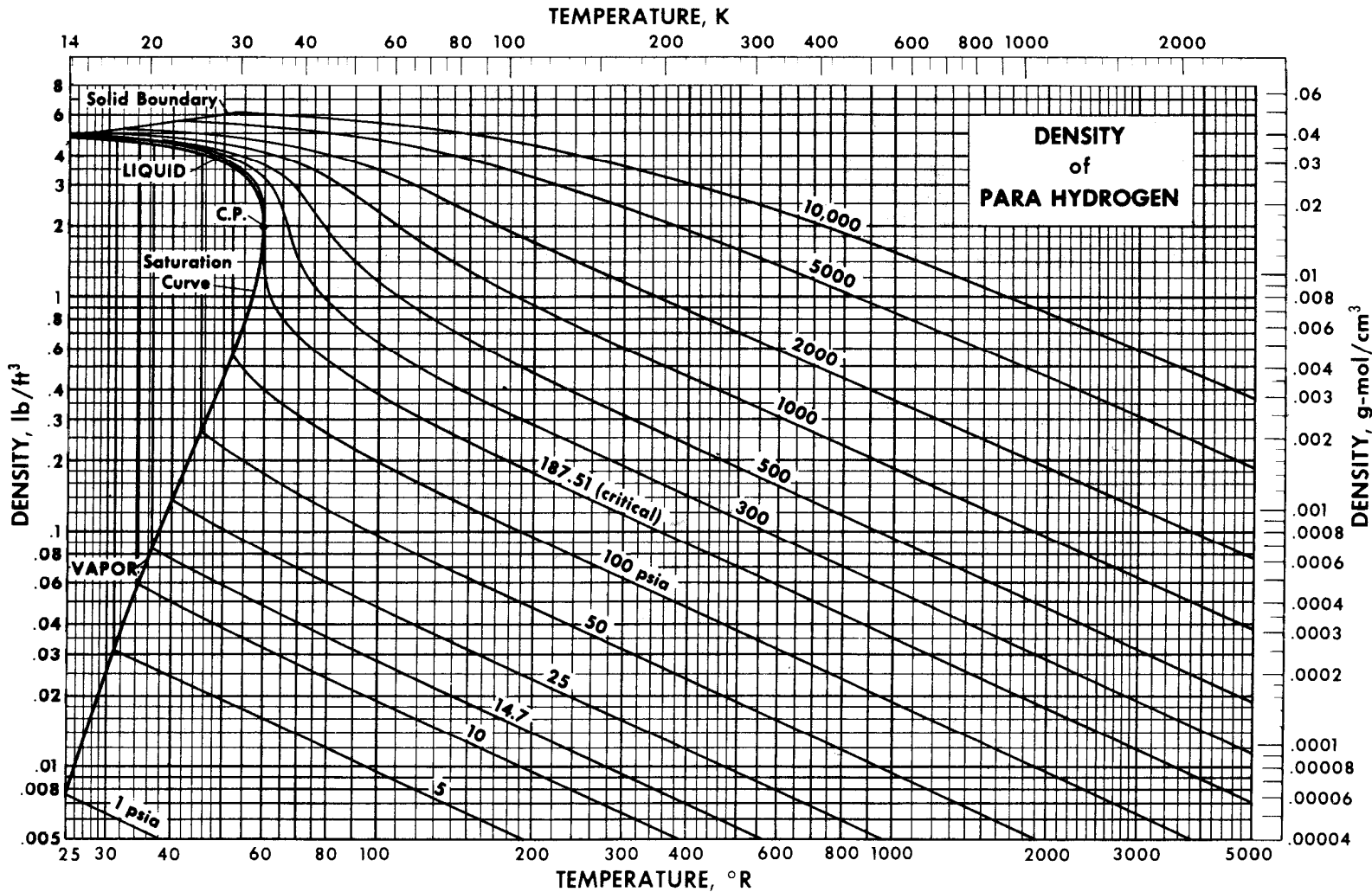


FIGURE 3.15. Density (P-ρ-T).

Hydrogen: Myths

- **Hydrogen Is a Difficult and Unsafe Fuel to Use**

➤ **No:** Hydrogen has been and can be used safely IF appropriate codes, standards, and guidelines are followed. Hydrogen has been and can be used safely by NASA and the oil/gas industry for many years. “Town gas,” a near 50-50 mixture of hydrogen and carbon monoxide, was widely used earlier in this century before it was replaced by natural gas. A recent study suggests the Hindenburg accident was not caused by a hydrogen explosion. It was likely caused by paint used on the skin of the airship, which contained the same component as rocket fuel.