1
Storage of Hydrogen in the Pure Form

Manfred Klell

1.1
Introduction

Due to its low density, the storage of hydrogen at reasonable energy densities poses a technical and economic challenge. This chapter is dedicated to the storage of hydrogen in the pure form, which is defined by the thermodynamic variables of state and thus can best be analyzed on the basis of a depiction of these variables like the T–s-diagram.

Conventionally hydrogen is stored as compressed gas or as a cryogenic liquid. Apart from gravimetric and volumetric energy densities, the energies required for compression and liquefaction are evaluated. A short thermodynamic analysis of the storage infrastructure, including storage vessels, distribution, dispensary and refueling is given.

Hybrid storage of hydrogen, where a combination of technologies is applied, such as the storage of hydrogen as slush or as a supercritical fluid, is briefly mentioned.

A comparison of the energy densities of storage technologies for hydrogen and other energy carriers and a conclusion round off this chapter.

1.2
Thermodynamic State and Properties

Hydrogen is the most abundant element in the universe; more than 90% of all atoms are hydrogen. Hydrogen is the simplest atom and element number 1, consisting of one proton and one electron only. Apart from this ordinary isotope called protium, a small fraction of hydrogen atoms exist as deuterium (1 proton, 1 neutron, 1 electron) and an even smaller fraction as unstable tritium (1 proton, 2 neutrons, 1 electron).

An atomic property with relevance for the liquefaction of hydrogen molecules is its spin, the quantum analogy to the rotation of an elementary particle about its axis. If the spins of two hydrogen protons are parallel, the molecule is called ortho-hydrogen,

Handbook of Hydrogen Storage. Edited by Michael Hirscher
Copyright © 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-32273-2

if the spins are opposed, the molecule is called para-hydrogen. Ortho- and para-hydrogen have slightly different properties [29]. At standard (normal) conditions, molecular hydrogen is a mixture of about 75 vol% ortho- and 25 vol% para-hydrogen, which is called normal hydrogen. With a reduction in temperature, the content of para-hydrogen increases and reaches 100 vol% below −200 °C. The mixture of ortho- and para-hydrogen at thermodynamic equilibrium at a certain temperature is called equilibrium hydrogen. Para-hydrogen has a lower energy level than ortho-hydrogen, so during the liquefaction of hydrogen, additional energy has to be dissipated to convert ortho- to para-hydrogen.

Due to its single valence electron, hydrogen is very reactive and usually combines to yield the molecule H_2. On Earth hydrogen is rarely found in the pure form, but usually in a wide variety of inorganic and organic chemical compounds, the most common being water H_2O. Hydrogen forms chemical compounds (hydrides) with nearly all other elements. Due to their ability to form long chains and complex molecules, combinations with carbon play a key role for organic life (hydrocarbons, carbohydrate). Hydrogen is of crucial importance as an energy carrier in the metabolism of plants, animals, and humans. It is found in sugar, fat, proteins, alcohols, oils, and so on.

For the storage of pure hydrogen, H_2 has first to be separated from its compounds. A number of technologies exist for the production of hydrogen from different sources [3].

1.2.1
Variables of State

As the pure substance, hydrogen H_2 may exist in various physical phases as vapor, liquid and solid. As with any pure substance, the thermodynamic state of hydrogen is completely defined by specifying two independent intensive state variables. All other variables of state can then be determined by using one of the three relationships of state.

The *equation of state* is the mathematical relationship between the following three intensive thermodynamic properties: pressure p, temperature T, and specific volume v (or density $\varrho = 1/v$)

$$f_1(p, T, v) = 0 \tag{1.1}$$

The *calorific equation of state* relates the internal energy u to T and v or enthalpy h to T and p

$$f_2(u, T, v) = 0 \quad \text{or} \quad f_3(h, T, p) = 0 \tag{1.2}$$

The third state relationship relates entropy s to T and v or T and p

$$f_4(s, T, v) = 0 \quad \text{or} \quad f_5(s, T, p) = 0 \tag{1.3}$$

These relationships of state have to be determined experimentally and are available in the form of equations, tables or diagrams [21].

At ambient conditions, hydrogen fulfils well the relationship f_1 in the following simple form

$$p\,v = R\,T \quad \text{or} \quad p\,V_\mathrm{m} = R_\mathrm{m}\,T \tag{1.4}$$

In extensive form with mass

$$p\,V = n\,R_\mathrm{m}\,T = m\,R\,T \tag{1.5}$$

With:

V [m^3]: volume, $V_\mathrm{m} = V/n$ [m^3 mol^{-1}]: molar volume,
$n = N/N_\mathrm{A}$ [mol]: number of mols, N: number of entities,
$N_\mathrm{A} = 6.22 \cdot 10^{23}$ 1 mol^{-1}: Avogadro constant,
$M = m/n$ [kg kmol^{-1}, g mol^{-1}]: molar mass, m [kg]: mass,
$R_\mathrm{m} = 8314.72$ J kmol^{-1} K^{-1}: universal gas constant,
$R = R_\mathrm{m}/M$ [J kg^{-1} K^{-1}]: particular gas constant

A gas fulfilling Eq. (1.4) is called an ideal gas. Kinetic gas theory shows, that a gas behaves like an ideal gas, first if the he gas molecules are infinitesimally small, round, hard spheres occupying negligible volume and, secondly, if no forces exist amongst these molecules except during collisions. This holds true for most gases at low pressure and temperatures well above the critical temperature. This is the highest possible temperature at which a substance can condense.

An improvement of Eq. (1.4) was introduced by van der Waals. By replacing pressure p with $\left(p + a/V_\mathrm{m}^2\right)$, intermolecular forces are accounted for, and by replacing volume V_m with $V_\mathrm{m} - \mathrm{b}$, the molecular volume is accounted for.

$$\left(p + \frac{a}{V_\mathrm{m}^2}\right)(V_\mathrm{m} - b) = R_\mathrm{m} T \tag{1.6}$$

In the *van der Waals* Eq. (1.6) the substance specific parameters for hydrogen are $a = 0.025$ m^6 Pa mol^{-2}, $b = 2.66 \cdot 10^{-5}$ m^3 mol^{-1}.

A convenient approach to account for real gas behavior is to use the dimensionless *compressibility factor* Z in the equation of state.

$$\frac{pV_\mathrm{m}}{R_\mathrm{m} T} = \frac{pv}{RT} = Z \tag{1.7}$$

The deviation of Z from the value 1 is a measure of the deviation from ideal gas behavior, especially for the deviation of real mass from ideal mass.

$$\frac{pV}{n_\mathrm{real} R_\mathrm{m} T} = \frac{pV}{m_\mathrm{real} RT} = Z = \frac{n_\mathrm{ideal}}{n_\mathrm{real}} = \frac{m_\mathrm{ideal}}{m_\mathrm{real}} \tag{1.8}$$

The compressibility factor Z has to be determined experimentally and can be found in the literature as a function of pressure p and temperature T for a number of gases [21]. By reducing the pressure p to the critical pressure p_cr and the temperature T to the critical temperature T_cr, a generalized compressibility factor for all gases can be drawn as a function of $p_\mathrm{R} = p/p_\mathrm{cr}$ and $T_\mathrm{R} = T/T_\mathrm{cr}$ [28].

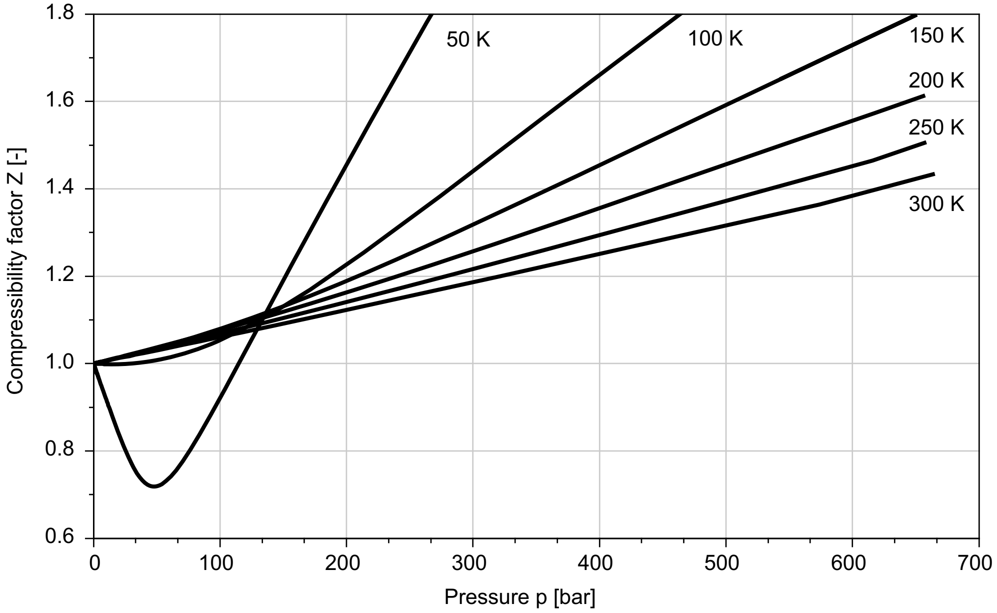


Figure 1.1 Compressibility factor Z of hydrogen.

The value of the compressibility factor Z for hydrogen at high pressures and low temperatures in Figure 1.1 shows that, at ambient temperature, a value of 1.2 is reached at 300 bar, and at low temperatures even earlier. This means that a calculation of the hydrogen mass in a container from a measurement of temperature and pressure using the ideal gas equation will result in a mass 20% greater than in reality.

The equation of state (1.3) can be depicted in a three-dimensional diagram with the three thermodynamic properties pressure p, temperature T, and specific volume v as axes. Two-dimensional projections with the third variable as a parameter are widely used to explain thermodynamic processes.

1.2.2
T–s-Diagram

For thermodynamic analysis, the T–s-diagram with temperature T versus entropy s as axes and lines of constant pressure, density, and enthalpy has proven very helpful. Changes of states and heat or work released or absorbed can be illustrated clearly using the T–s-diagram.

From the definition of entropy

$$ds = dq_{\mathrm{rev}}/T \tag{1.9}$$

it follows that the reversible heat corresponds to the area below the curve of the process in the T–s-diagram:

$$q_{\mathrm{rev}} = \int T\mathrm{d}s \tag{1.10}$$

With the definition of the reversible heat

$$\mathrm{d}q_{\mathrm{rev}} = \mathrm{d}u + p\mathrm{d}v = \mathrm{d}h - v\mathrm{d}p \tag{1.11}$$

it follows that the heat, and thus the area below the curve of the process in the *T*–*s*-diagram corresponds to the change in internal energy *u* or enthalpy *h* given an isochoric or isobaric process. Moreover, the specific heat capacity corresponds to the subtangent of the curve of the process in the *T*–*s*-diagram:

$$c = \mathrm{d}q_{\mathrm{rev}}/\mathrm{d}T = T\,\mathrm{d}s/\mathrm{d}T \tag{1.12}$$

The *T*–*s*-diagram for equality hydrogen for temperatures from 15 to 85 K is shown in Figure 1.2, and for temperatures from 85 to 330 K in Figure 1.3.

1.2.2.1 Joule–Thomson Coefficient

The Joule–Thomson coefficient μ_{JT} describes the extent and direction of the temperature change for an isenthalpic change of state (constant enthalpy *h*):

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial p}\right)_h \tag{1.13}$$

A positive Joule–Thomson coefficient means that a decrease in temperature takes place along an isenthalpic pressure decrease. In the *T*–*s*-diagram, this is reflected as a falling isenthalpic line with a pressure decrease (cooling during expansion in a restriction). This effect is used in the liquefaction of hydrogen when cooling the fluid using a nozzle.

A negative Joule–Thomson coefficient means that an increase in temperature takes place along an isenthalpic pressure decrease. In the *T*–*s*-diagram, this is reflected as a rising isenthalpic line with pressure decrease (heating during relaxation in a restriction). This effect has to be accounted for when filling a high-pressure vessel with hydrogen.

The Joule–Thomson effect occurs when a gas or gas mixture experiences a change in temperature during an isenthalpic pressure change. An ideal gas does not show any Joule–Thomson effect. With ideal gases, the internal energy *u* and thus also the enthalpy *h* are only a function of temperature *T*. Thus ideal gases do not experience a change in temperature while the enthalpy remains constant, for example, in a flow through a restriction. This means that the Joule–Thomson coefficient is zero. Thus it can easily be judged from the *T*–*s*-diagram that a gas can be regarded as an ideal gas in an area where the isenthalpic lines are horizontal.

1.2.3
Properties

At normal temperature and pressure, hydrogen is a colorless, odorless gas with no toxic effects. It is the lowest density element, whilst also having a high diffusion

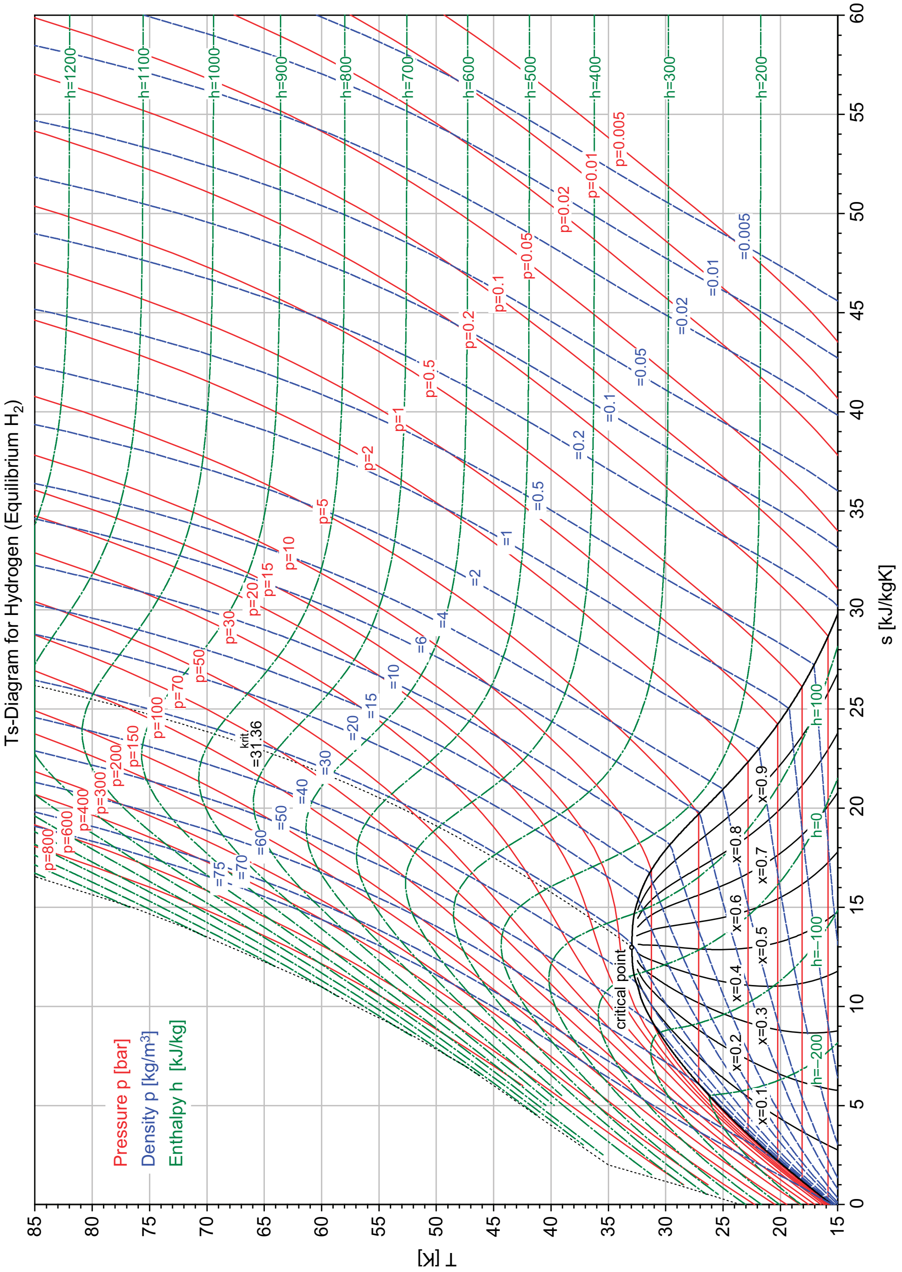


Figure 1.2 T–s-diagram for equilibrium hydrogen for temperatures from 15 to 85 K [8].

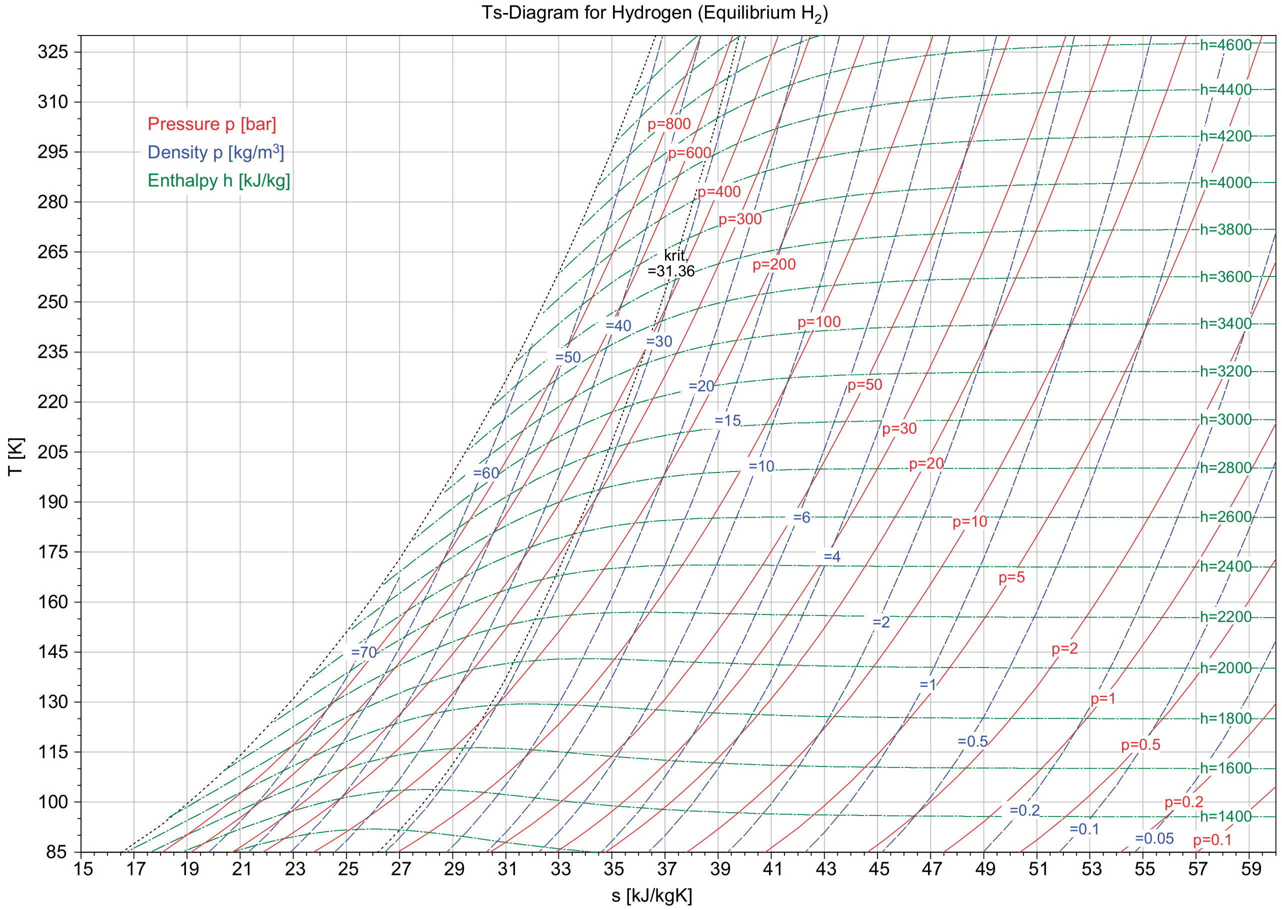


Figure 1.3 *T–s*-diagram for equilibrium hydrogen for temperatures from 85 to 330 K [8].

coefficient and a high specific heat capacity. After helium, hydrogen has the lowest melting and boiling points. Hydrogen is highly inflammable (EU rating F + and R12) with broadly spaced ignition limits in air (lower explosion limit 4% by volume, upper explosion limit 75.6% by volume) and low ignition energy (0.017 mJ for a stoichiometric air mixture).

As with all fuels, the use of hydrogen requires compliance with safety regulations, with EU safety sheets specifying:

- S9: keep containers in a well-aired location
- S16: keep away from ignition sources – do not smoke (explosion areas)
- S33: take precautions against electrostatic charge.

Because hydrogen is a very light and diffusive gas, explosive concentrations can normally be prevented easily through adequate ventilation. In the case of compressed gas CGH_2 storage, compliance with pressure vessel regulations is required. Direct contact with cryogenic liquids and gases can cause serious frostbite or freeze-burns. Furthermore, exposure to hydrogen can cause embrittlement and diffusion with a variety of materials, including most plastics and mild steel, which can in turn lead to fracture and leakage.

The properties of equilibrium hydrogen are summarized in Table 1.1. More extensive explanations about hydrogen and its properties can be found in [19, 21, 25, 29].

An important application of hydrogen is its combustion. Hydrogen can be burnt in internal combustion engines [3] producing low levels of pollutants, and in fuel cells free of pollutants [15]. Ideal combustion of hydrocarbon fuels takes place according to Eq. (1.14) [23].

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O \tag{1.14}$$

With hydrogen containing no carbon, Eq. (1.14) becomes

$$H_2 + {}^1\!/_2 O_2 \rightarrow H_2O \tag{1.15}$$

Thus hydrogen can be burnt without releasing CO_2, producing water only. A reaction enthalpy $\Delta_R H = -242\ \mathrm{MJ\ kmol^{-1}}$ is released if the water remains in gaseous form. Hydrogen has the highest gravimetric calorific value of all fuels with $H_u = 120\ \mathrm{MJ\ kg^{-1}} = 33.33\ \mathrm{kWh\ kg^{-1}}$. If the water condenses, the enthalpy of condensation adds to a total reaction enthalpy of $\Delta_R H = -285\ \mathrm{MJ\ kmol^{-1}}$ giving the gross calorific value (upper heating value) of hydrogen of $H_o = 142\ \mathrm{MJ\ kg^{-1}} = 39.44\ \mathrm{kWh\ kg^{-1}}$.

1.3
Gaseous Storage

The storage of gases in pressure vessels is a proven and tested technology. Most gases are available in containers at pressures up to 300 bar (30 MPa).

Table 1.1 Properties of hydrogen [3].

	Property	**Value and Unit**
	molar mass	2.016 kg kmol^{-1}
	particular gas constant	4124 J kg^{-1} K^{-1}
	(gravimetric) calorific value H_u	120 MJ kg^{-1} = 33.33 kWh kg^{-1}
at triple point:	temperature	−259.35 °C (13.80 K)
	pressure	0.07 bar
	density gaseous	0.125 kg m^{-3}
	density liquid	77 kg m^{-3}
	heat of fusion	58.5 kJ kg^{-1} = 16.25 kWh kg^{-1}
at boiling point at 1.01325 bar:	boiling temperature	−252.85 °C (20.30 K)
	heat of vaporization	445.4 kJ kg^{-1} = 123.7 kWh kg^{-1}
liquid phase:	density	70.8 kg m^{-3}
	(volumetric) calorific value	8.5 MJ dm^{-3} = 2.36 kWh kg^{-1}
	specific heat capacity c_p	9.8 kJ kg^{-1} K^{-1}
	specific heat capacity c_v	5.8 kJ kg^{-1} K^{-1}
	thermal conductivity	0.099 W m^{-1} K^{-1}
	dynamic viscosity	11.9×10^{-6} N s m^{-2}
	speed of sound	1089 m s^{-1}
gaseous phase:	density	1.34 kg m^{-3}
	(volumetric) calorific value	0.16 MJ dm^{-3} = 0.044 kWh dm^{-3}
	specific heat capacity c_p	12.2 kJ kg^{-1} K^{-1}
	specific heat capacity c_v	6.6 kJ kg^{-1} K^{-1}
	thermal conductivity	0.017 W m^{-1} K^{-1}
	dynamic viscosity	1.11×10^{-6} Ns m^{-2}
	speed of sound	355 m s^{-1}
at critical point:	temperature	−239.95 °C (33.20 K)
	pressure	13.1 bar
	density	31.4 kg m^{-3}
at standard conditions: (0 °C and 1.01325 bar)	density	0.09 kg m^{-3}
	(volumetric) calorific value	0.01 MJ dm^{-3} = 2.8 Wh dm^{-3}
	specific heat capacity c_p	14.32 kJ kg^{-1} K^{-1}
	specific heat capacity c_v	10.17 kJ kg^{-1} K^{-1}
	thermal conductivity	0.184 W m^{-1} K^{-1}
	coefficient of diffusion	0.61 cm^{2} s^{-1}
	dynamic viscosity	8.91×10^{-6} N s m^{-2}
	speed of sound	1246 m s^{-1}
mixtures with air:	lower explosion limit	4 Vol% H_2 ($\lambda = 10.1$)
	lower detonation limit	18 Vol% H_2 ($\lambda = 1.9$)
	stoichiometric mixture	29.6 Vol% H_2 ($\lambda = 1$)
	upper detonation limit	58.9 Vol% H_2 ($\lambda = 0.29$)
	upper explosion limit	75.6 Vol% H_2 ($\lambda = 0.13$)
	ignition temperature	585 °C (858 K)
	minimal ignition energy	0.017 mJ
	max. laminar flame speed	about 3 m s^{-1}
	adiabatic combustion temperature	about 2100 °C

Of thermodynamic interest are, on the one hand, the compression and the work necessary for it, and, on the other hand, the expansion during the filling process of a pressure vessel from a reservoir.

High demands are placed on pressure vessels for hydrogen from the materials side, from safety and component dimensioning. The infrastructure used includes pipelines for distribution and dispensers for refueling.

1.3.1
Compression and Expansion

From the first law of thermodynamics, the internal work w_i needed for the compression of a gas can be calculated from the enthalpies h_1 and h_2 before and after the compression and the cooling energy q_K:

$$w_\mathrm{i} = h_2 - h_1 + q_\mathrm{K} \tag{1.16}$$

The minimum required ideal compression work is the work for isothermal compression w_is, where the temperature stays constant during compression through cooling. The ideal isothermal compression work w_is can be found using the *T–s*-diagram. In the absence of internal friction, the cooling energy q_K equals the reversible heat and can be visualized in the *T–s*-diagram as the area below the change of states, see Figure 1.4a. The value can be calculated from

$$q_\mathrm{K} = T \cdot \Delta s \tag{1.17}$$

For a compression from 1 bar to 900 bar at ambient temperature one finds the following value for equilibrium hydrogen: $w_\mathrm{is} = 4383 - 3787 + 8181 = 8777\,\mathrm{kJ\,kg^{-1}}$. This means that the compression needs an energy input of about 7.5% of the calorific value of hydrogen. Taking into account the efficiency of compressors at around 50%, one finds that the energy needed for the compression of hydrogen to 900 bar increases to about 15% of its calorific value. An overview of densities and energy densities at pressures relevant for containers is given in Tables 1.2 and 1.3, a comparison of densities and compressor work with liquid storage is given in Figure 1.22 (see later).

Substituting the definition of the reversible heat

$$q_\mathrm{rev} = q_\mathrm{A} + q_\mathrm{R} = \mathrm{d}h - v\,\mathrm{d}p \tag{1.18}$$

in Eq. (1.16), we get, for compression without considering friction

$$w_\mathrm{i} = \int_1^2 v\,\mathrm{d}p \tag{1.19}$$

With the simplification of hydrogen as an ideal gas, we can substitute v from the ideal gas Eq. (1.4) and get:

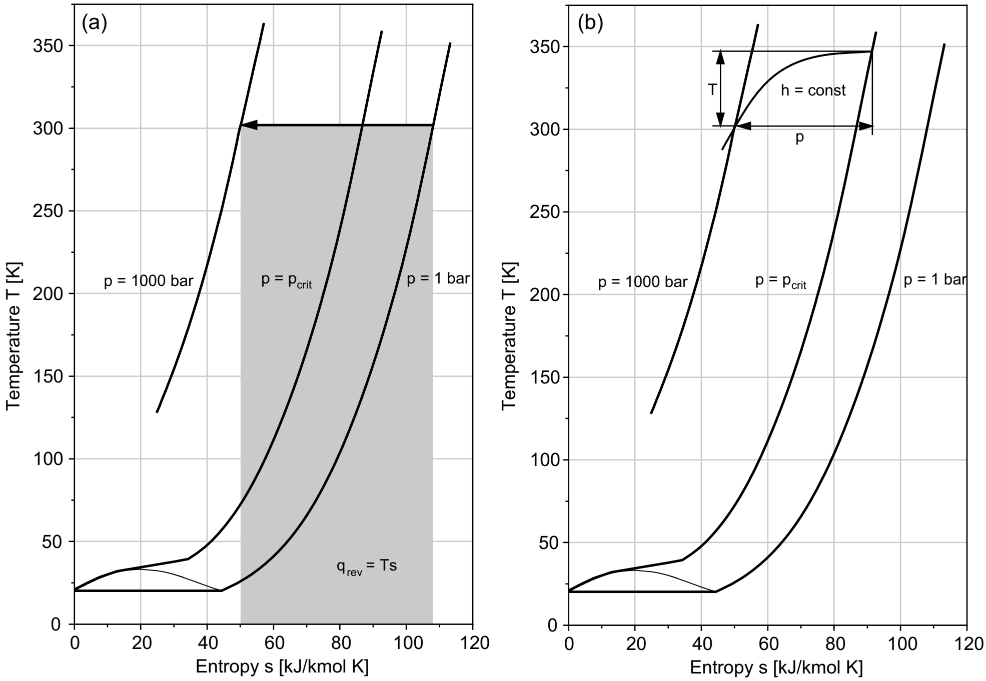


Figure 1.4 *T*–*s*-diagram: (a) isothermal compression from 1 to 1000 bar; (b) isenthalpic expansion from 1000 to 13 bar.

$$w_\mathrm{i} = RT\int_1^2 \frac{\mathrm{d}p}{p} = RT\ln\frac{p_2}{p_1} \tag{1.20}$$

In our case, the calculation gives $w_\mathrm{i} = 8220\,\mathrm{kJ\,kg^{-1}}$. In comparison with the work calculated above this is 6.2% less, which is because hydrogen deviates from ideal gas behavior in the pressure range under consideration.

With flowing gases, compression is generally linked with a temperature increase, while expansion leads to a decrease in temperature. During the filling of a pressure vessel, gas flows from a reservoir of even higher pressure into the tank. Thermodynamically the process can be approximated by an adiabatic flow through a restriction where the total enthalpy remains constant. The associated change in temperature is described by the Joule–Thomson coefficient. In the relevant range of pressures, hydrogen has a negative Joule–Thomson coefficient, which means the temperature increases with a pressure decrease. The expansion of hydrogen from 1000 bar to 13 bar produces a rise in temperature of about 50 K, see Figure 1.4b.

The compression of the gas in the tank to be filled also causes its temperature to rise. This effect even outweighs the Joule–Thomson effect. A simulation can be done based on the first law of thermodynamics. Regarding the reservoir and the tank as a closed adiabatic system, the internal energies of the two containers before and after the filling process are equal. Regarding the tank to be filled alone as an open adiabatic system, the enthalpy flow into the tank equals its increase in internal energy.

The temperature of the gas in the tank will increase considerably during the filling process causing the container to warm up. As the filled container cools to ambient temperature, the pressure of the gas will decrease accordingly, thus leaving the container at ambient temperature below nominal filling pressure. This loss of filling mass can be avoided by a so-called cold-fill device, where the hydrogen is cooled during the filling process in a heat exchanger, for example, with liquid nitrogen.

1.3.2
Tank Systems

For compressed storage of hydrogen, the gas is usually compressed to pressures between 200 and 350 bar though, more recently, storage pressures of 700 bar and even higher have been under trial. Such enormous pressures require consideration of questions regarding material choice, component dimensioning and safety.

Hydrogen has a tendency to adsorb and dissociate at material surfaces, the atomic hydrogen then diffuses into the material and causes embrittlement and diffusion. Materials suitable for hydrogen applications are mainly austenitic stainless steel and aluminum alloys [12, 29].

Apart from the container itself, valves for reducing the pressure, pipelines, and sensors to control pressure, temperature and tightness are applied. For certification, tank systems have to undergo extensive tests, there are a number of regulations for pressure vessels and tank systems [16]. Electronic safety systems for monitoring pressure, temperature and tank filling level with leak monitoring and emergency stop measures have been developed especially for automotive applications [2].

Commercially available pressure containers are conventionally made of steel. These so called type I containers offer good properties concerning safety and strength, but at a high weight. They are available with net volumes from 2.5 to 50 l. Characteristics in Table 1.2 show that the pressures vary from 200 to 300 bar, the systems are quite heavy, the energy densities reach around 0.4 kWh kg^{-1}. To reduce the weight, steel containers have been replaced by composite containers. A thin inner liner of metal (steel or aluminum) ensures the gas tightness. Stability is given by a mesh partially (type II) or completely (type III) provided by carbon fibers. With type IV containers, the liners are also made of synthetic material. Composite containers are lighter but also expensive, especially with a growing demand for carbon fibers. For automotive applications, a number of type III and type IV tank systems are available. Their characteristics in Table 1.3 show that energy densities are considerably higher and reach gravimetrically 0.055 kg H_2 kg^{-1} or 1.833 kW h kg^{-1} and volumetrically 0.026 kg H_2 dm^{-3} or 0.867 kW h dm^{-3}. The costs of available tank systems vary from about 40 € per kWh of stored hydrogen energy for type III tanks for 350 bar up to about 150 € per kW h for type IV tanks for 700 bar. An example of a compressed hydrogen tank for automotive application is shown in Figure 1.5.

Table 1.2 Characteristics of commercially obtainable type I pressure containers.

Net volume [dm^3]	**2.5**	**10**	**20**	**33**	**40**	**50**
Nominal pressure [bar]	200	300	200	200	200	200/300
Testing pressure [bar]	300	450	300	300	300	300/450
Tank weight [kg]	3.5	21	31.6	41	58.5	58/94
Tank volume [dm^3]	3.6	14.3	27	41.8	49.8	60.1/64.7
H_2 density [kg m^{-3}] at 25 °C	14.5	20.6	14.5	14.5	14.5	14.5/20.6
H_2 content [Nm^3]	0.4	2.29	3.22	5.32	6.44	8.05/11.43
H_2 content [kg]	0.04	0.21	0.29	0.48	0.58	0.72/1.03
Grav. H_2 content [kgH_2 kg^{-1}]	0.01	0.009	0.009	0.012	0.011	0.012/0.011
Vol. H_2 content [kgH_2 dm^{-3}]	0.009	0.014	0.011	0.011	0.012	0.012/0.016
Grav. energy density [kWh kg^{-1}]	0.333	0.300	0.305	0.400	0.367	0.400/0.367
Vol. energy density [kWh dm^{-3}]	0.300	0.477	0.367	0.367	0.400	0.400/0.533

With adequate material and dimensioning, gaseous hydrogen storage takes place in a closed system and thus hydrogen can be stored without loss for extended periods of time.

Apart from storage in vessels, underground storage of large quantities of hydrogen in natural caverns has also been investigated [16].

1.3.3
High Pressure Infrastructure

The distribution of gaseous hydrogen from centralized production facilities is usually effected by transportation in large pressure containers by road or rail. To supply large amounts of hydrogen, distribution via pipelines is the most economical way [16].

Table 1.3 Characteristics of commercially obtainable automotive pressure containers.

Net volume [dm^3]	**34**	**100**	**50**	**100**	**36**	**65**	**30**	**120**
Type	III	III	III	III	IV	IV	IV	IV
Nominal pressure [bar]	350	350	700	700	350	350	700	700
Test pressure [bar]	525	525	1050	1050	525	525	1050	1050
Tank system weight [kg]	18	48	55	95	18	33	26	84
Tank system volume [dm^3]	50	150	80	150	60	100	60	200
H_2 density [kg m^{-3}] at 25 °C	23.3	23.3	39.3	39.3	23.3	23.3	39.3	39.3
H_2 content [Nm^3]	8.83	26	21.84	43.69	9.35	16.96	13.5	51.7
H_2 content [kg]	0.79	2.33	1.96	3.83	0.84	1.52	1.21	4.65
Grav. H_2 content [kgH_2 kg^{-1}]	0.044	0.049	0.036	0.041	0.047	0.047	0.047	0.055
Vol. H_2 content [kgH_2 dm^{-3}]	0.016	0.016	0.025	0.026	0.014	0.015	0.021	0.023
Grav. energy density [kWh kg^{-1}]	1.467	1.633	1.200	1.367	1.567	1.567	1.567	1.833
Vol. energy density [kWh dm^{-3}]	0.533	0.533	0.833	0.867	0.467	0.500	0.700	0.767

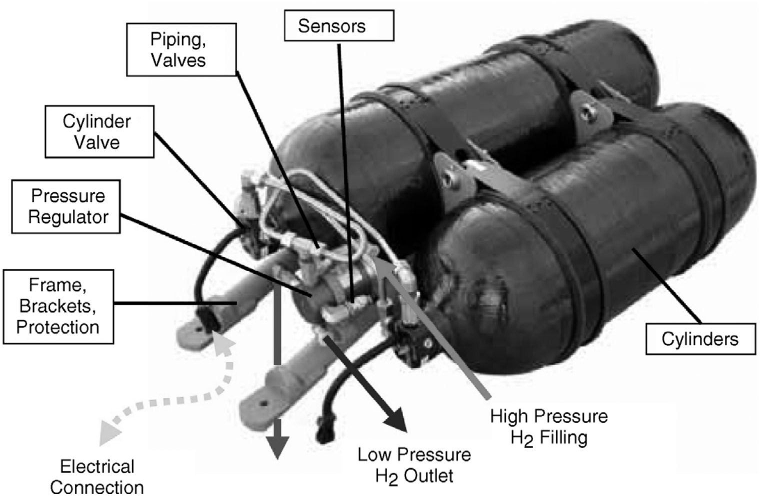


Figure 1.5 Compressed hydrogen tank for automotive application. Source Dynetek [1].

Hydrogen filling stations for vehicles resemble the filling stations for natural gas. Regulations and certification are usually derived from natural gas applications, whilst hydrogen-specific regulations are being developed [13]. As the gas is filled by a pressure gradient, the reservoir pressure has to be considerably higher than the nominal tank pressure to provide a short filling time.

Compressors for hydrogen have to fulfill high technical demands. High pressures of up to 900 bar can be achieved by multi-stage piston compressors. To assure the necessary purity of the compressed hydrogen, the piston rings have to be self-lubricating. Due to safety considerations, these compressors are often operated by hydraulic oil. For lower pressures, diaphragm compressors are also used. In newer concepts and for special applications, mechanical compressors and metal pistons are replaced by ionic liquids, metal hydrides or electrochemical compressors [16].

From the high pressure reservoir, hydrogen is filled into the tank system by a pressure gradient. Overfilling and overheating of the tank systems have to be avoided by adequate safety measures. The dispensers to refuel automotive tank systems resemble the usual dispensers for natural gas. Certificated couplings for 350 and 700 bar are available. After connection, a pressure pulse checks for tightness of the system. If successful, the valves for filling the tank open.

As mentioned before, the temperature of hydrogen increases and causes the tank to warm up during the filling process. After cooling to ambient temperature, the tank pressure would be below the nominal pressure, thus causing a loss of contained mass. This effect has to be accounted for by cooled filling or slow filling with heat dissipation into the external environment. In the second case, a significant increase in the filling time would have to be accepted, something that otherwise only requires a few minutes. Therefore, the gas filling infrastructure for high pressure requires a cold fill device, where hydrogen is cooled by a heat exchanger with liquid nitrogen. If the temperature of the tank system thus decreases below ambient temperature, it is necessary to ensure that, after heating to ambient temperature, the pressure of the tank system does not exceed the allowed maximum pressure, 25% above nominal.

Another important feature of the infrastructure is the filling time. Refueling of an automotive hydrogen gas tank takes a few minutes. The resulting effective energy flow can be estimated as follows: 10 kg of hydrogen contain energy of 1200 MJ. If a vessel is filled within 5 min or 300 s, the filling process corresponds to a power of $1200\,\text{MJ}/300\,\text{s} = 4\,\text{MW}$. This comes close to the values for refueling of gasoline or diesel and clearly exceeds the potential of solid storage or battery recharging.

Being gaseous, hydrogen has a number of features in common with natural gas and can be mixed with it in any ratio. The use of mixtures of hydrogen and natural gas H_2NG offers several advantages in terms of infrastructure, storage, and use, and is the subject of worldwide research. Synergies in infrastructure and customer acceptance can be achieved, for example, by running internal combustion engines on mixtures of hydrogen and natural gas. Alongside the bridging effect between natural gas and hydrogen, such mixing offers advantages in terms of reduced emissions and improvements to the combustion process. The wide ignition limits and high flame speed of hydrogen have as positive an impact on the combustion of H_2NG mixture as does the higher energy density of natural gas on range [2].

1.4
Liquid Storage

The storage of liquefied cryogenic gases is a proven and tested technology. Hydrogen was first liquefied by J. Dewar in 1898. Compared to compressed gases, the density of liquefied gases is considerably higher. On the other hand, liquefaction, storage and handling of the cryogenic boiling liquids require energy input as well as complex tank systems and infrastructure.

After an overview of the liquefaction process, a short thermodynamic analysis of a liquid hydrogen infrastructure with storage tanks and filling processes is presented. The tank systems are sophisticated containers with vacuum insulation and pressure regulation.

1.4.1
Liquefaction

Basic thermodynamic principles of the liquefaction of hydrogen are explained using the *T–s*-diagram, see Figure 1.6. In the hypothetical case of isobaric cooling at ambient pressure p_0 down to condensation at CP and the boiling point BP, the cooling energy would be:

$$q_K = h_2 - h_1 \tag{1.21}$$

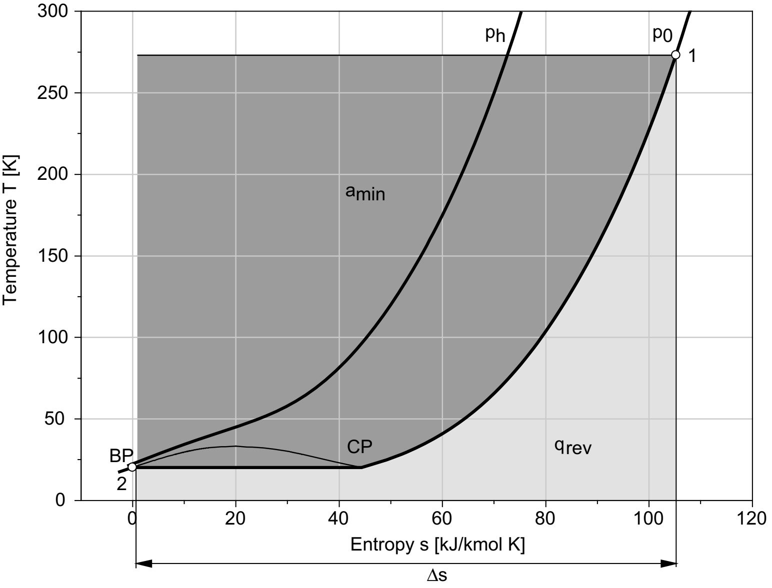


Figure 1.6 Cooling load and work of the cyclic process of liquefaction.

The cooling load for liquefying hydrogen at ambient pressure would correspond with the light gray area in Figure 1.6 and amount to

$$q_K = -0.888 - 3959 = -3960\,\text{kJ kg}^{-1}$$

This is about 3.3% of the calorific value of hydrogen. The only possible cooling medium for this case would be liquid helium, but such a process is technically and economically not viable. Therefore the liquefaction is treated as an ideal cyclic process. The minimum inner work for such a process can be calculated from:

$$a_{\text{min}} = q_{\text{zu}} - q_{\text{ab}} = T_0 \Delta s - q_K \tag{1.22}$$

The work for this case is depicted in dark gray in Figure 1.6 and will amount to

$$a_{\text{min}} = 16092 - 3960 = 12132\,\text{kJ kg}^{-1}$$

This corresponds to about 10% of the calorific value of hydrogen.

Besides this low pressure process, there is also an alternative of a high pressure process at p_h above the critical pressure, see Figure 1.6. In this case the phase transition of the condensation can be avoided. This brings advantages in heat exchanger dimensioning, however, the plant design gets more complex.

Real-world efficiencies for liquefaction lie around 30%, which means, about 20% to 30% of the energy content of hydrogen is needed for its liquefaction. In the process, hydrogen is first compressed to about 30 bar. The gas is then cooled with liquid nitrogen to about 80 K. Between 80 and 30 K hydrogen is cooled by expansion turbines, where hydrogen is compressed, cooled and expanded. In this stage also the

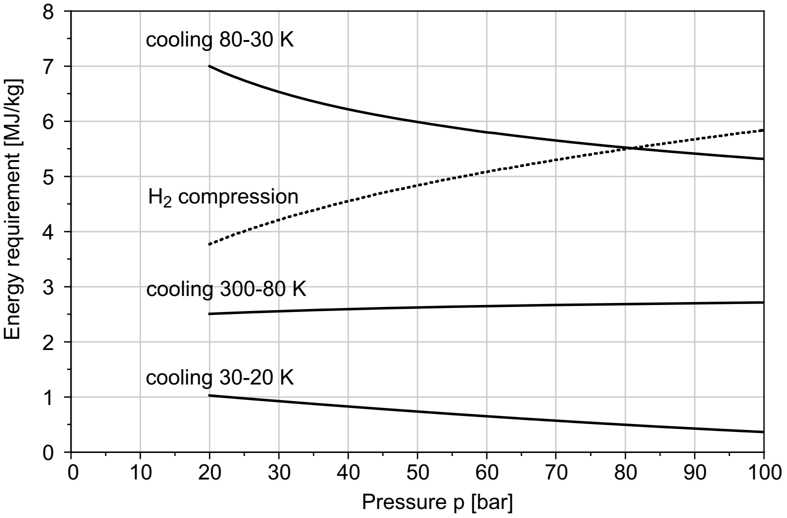


Figure 1.7 Energy required for different stages of liquefaction.

transition from ortho-hydrogen to para-hydrogen is effected, which means additional energy has to be dissipated. The last part of the cooling process from 30 to 20 K is done by Joule–Thomson valves. The positive Joule–Thomson effect is used here to cool during an expansion. Figure 1.7 with the energy required for the different stages of the liquefaction shows that the compression and the cooling from 80 to 30 K need most energy [24].

1.4.2
Thermodynamic Analysis

A thermodynamic analysis of a liquid hydrogen infrastructure will be given on the basis of the equipment at HyCentA Research GmbH in Graz [14]. The main storage tank, see Figure 1.8a, has a volume of 17 600 l and can store 1000 kg of hydrogen at a temperature of −253 °C at a pressure between 6 and 9 bar. The conditioning container, see Figure 1.8b, serves to adjust the pressure of the hydrogen to 2 to 4 bar to be used in the test stands or for filling tank systems.

The main tank is filled with liquid hydrogen from a trailer. Despite the sophisticated heat insulation in any container for cryogenic liquids, the small amount of remaining heat input will trigger off a warming process in the tank which causes the liquid in the container to evaporate and the pressure to rise. After a certain *pressure build-up* time the maximum operating pressure of the tank is reached. The pressure relief valve has to be opened. From this point onwards, gas must be released (*boil-off*). The container now acts as an open system with gas usually being lost to the environment.

Pressure build-up and boil-off of the main tank will be analyzed on the basis of the measurement of pressure and filling level over time, see Figure 1.9. From the

(a)

Figure 1.8 (a) Reservoir tank and (b) conditioning container at the HyCentA Graz.

(b)

Figure 1.8 (*Continued*)

measurements, heat input can be calculated. Simple thermodynamic models will be developed to simulate pressure build-up, boil-off and filling processes, including the cooling down of components.

The following characteristics are of interest:

Filling: Before filling, the pressure in the tank is reduced to enable liquid hydrogen to flow into the container from the trailer along a pressure gradient. As the blow-off valve remains open during the process, pressure drops till the end of the filling after about 50 min, see Figure 1.9b.

Pressure build-up: in spite of the insulation, due to the unavoidable heat input, hydrogen evaporates in the tank. Thus the pressure rises in the vessel. Pressure rise can be regarded as being linear over time, see Figure 1.9c. Pressure build-up continues until the maximum pressure p_{tank} in the vessel is reached and a blow-off valve has to be opened. The pressure build-up time in this case is nearly 30 h.

Boil-off: From reaching maximum system pressure of 6.7 bar in our case, the tank is an open system and hydrogen is blown out. From then, the pressure remains constant, the filling level decreases constantly. The vaporization rate and/or the rate of the effusing hydrogen is about 0.5 kg H_2 per hour.

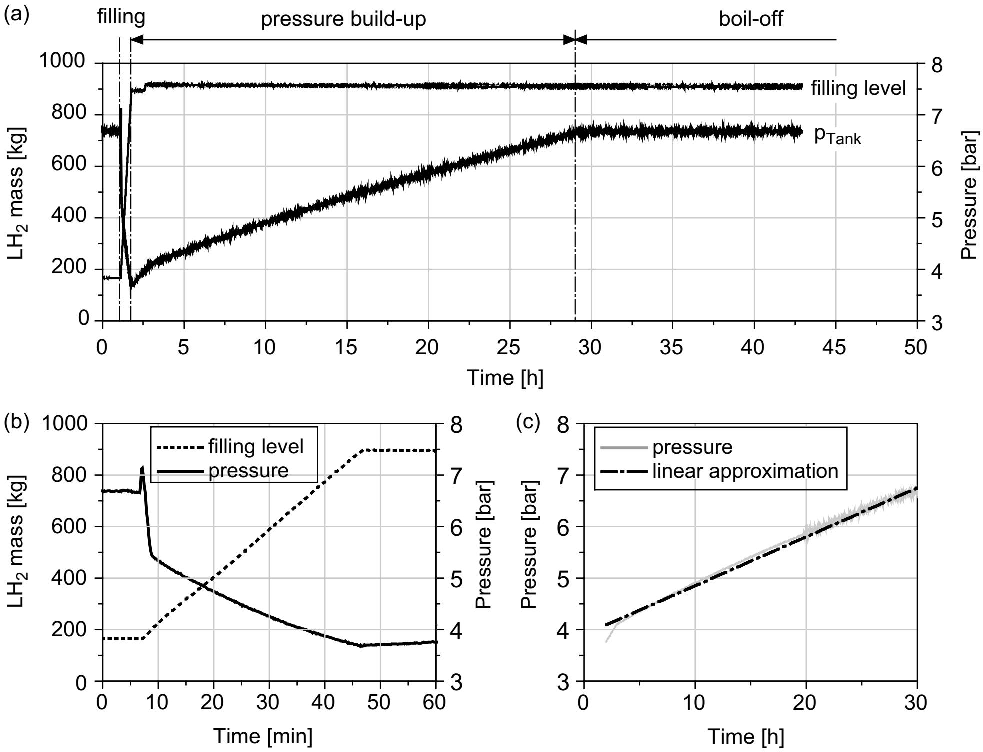


Figure 1.9 (a) Measurement of pressure and filling level in the tank versus time and in more detail: (b) during filling process, (c) during pressure build-up.

For a general illustration, we shall look first at a cryo-container with an in-flowing mass flow rate m_e and an out-flowing mass flow rate m_a as an open system, see Figure 1.10. It is assumed that this system is in thermodynamic equilibrium, that is, all state variables are equally distributed within the system. In particular, we find the same pressure throughout the system and the same temperature of the boiling liquid hydrogen and the saturated hydrogen vapor. This system can be described by applying the first law of thermodynamics and the law of conservation of mass. Despite the simplifying assumptions underlying the model, it can describe the principles of the relevant processes in the tank system, that is, the pressure build-up resulting from heat input, the evaporation resulting from heat input (boil-off), the effusion in order to decrease pressure, and the refueling process, see, for instance, [3, 9, 11, 12, 17, 27].

The first law of thermodynamics for open systems applies: the transport of work dW, heat dQ_a and mass dm_i with its enthalpy h_i and external energy e_{ai} (kinetic and potential energy) across the system boundaries equals the change in internal energy dU and external energy dE_a in the system.

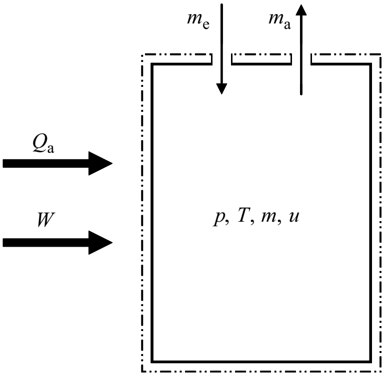


Figure 1.10 System of a cryo-container.

$$dW + dQ_a + \sum dm_i.(h_i + e_{ai}) = dU + dE_a \tag{1.23}$$

There is no work transferred. Neglecting kinetic and potential energy yields:

$$dQ_a + \sum dm_i \cdot (h_i) = dU \tag{1.24}$$

The conservation of mass states that added mass minus relieved mass equals the increase in mass of the system:

$$dm_e - dm_a = dm \tag{1.25}$$

1.4.2.1 **Pressure Build-Up**

In order to simulate the pressure increase and pressure build-up time in the storage system, we shall first assume a closed system in thermodynamic equilibrium with a constant heat input Q_a, see Figure 1.11. We assume that the pressure and temperature of the boiling liquid hydrogen and the gaseous saturated hydrogen vapor are the same throughout the whole system.

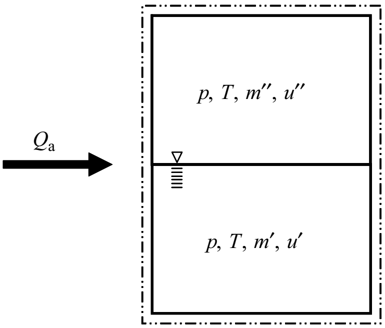


Figure 1.11 Cryo-storage system in a thermodynamic equilibrium system.

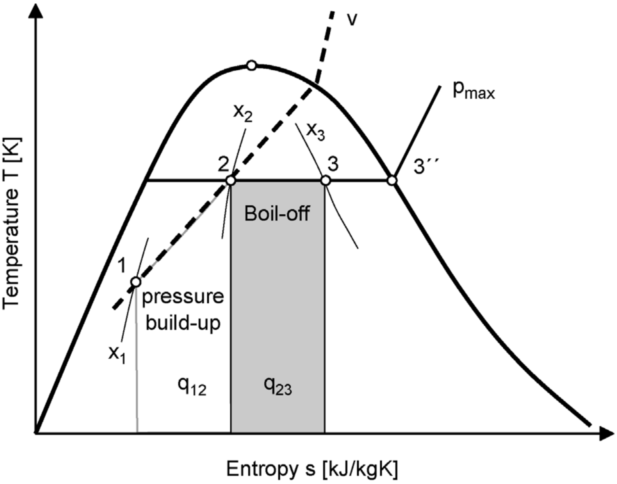


Figure 1.12 *T*–*s*-diagram for pressure build-up and boil-off due to heat input.

With a given container volume of 17 600 l and a given total hydrogen mass m, specific volume v (or density ϱ) is determined in the total system. All possible states move along an isochoric line in the *T*–*s*-diagram from starting point 1 to the highest permissible pressure in point 2, see Figure 1.12. If a pressure between points 1 and 2 is specified, the state of the system is clearly determined.

The constant container volume V consists of the variable shares for the liquid V' and gaseous hydrogen volume V'', in which the following applies:

$$V = \frac{m}{\varrho} = mv = V' + V'' = m'v' + m''v'' \tag{1.26}$$

The distribution of the mass in the boiling liquid m' and saturated vapor m'' is described by the vapor fraction x:

$$x = \frac{m''}{m} = \frac{m''}{m' + m''} \quad m'' = x \cdot m \quad m' = (1-x) \cdot m \tag{1.27}$$

Thermophysical property tables give the specific volumes for liquid v' and saturated vapor v'' for each pressure so that the vapor fraction and the mass distribution can be determined:

$$x = \frac{v-v'}{v''-v'} \tag{1.28}$$

With the vapor fractions of two states defined by a pressure increase Δp, the evaporated hydrogen mass $\Delta m''$ is also determined.

$$\Delta m'' = \Delta x \cdot m \tag{1.29}$$

The reason for the pressure build-up is the heat input. The specific heat quantity can be read from the *T*–*s*-diagram as the area below the constant-volume change in

Table 1.4 Pressure rise $\Delta p/\Delta t$ and resulting heat input Q_a.

FL [%]	p_1 [bar]	p_2 [bar]	Δp [bar]	Δt [h]	$\Delta p/\Delta t$ [mbar h^{-1}]	Q_a [kJ]	$\dot{Q}_a$ [W]
15.5	8.83	9.69	0.85	23.51	36.4	3271.89	38.65
38.0	9.10	9.72	0.62	16.14	38.5	5206.66	89.62
78.0	5.45	6.58	1.14	17.63	64.4	16146.41	254.42

state, see Figure 1.12. During the pressure build-up, the system can be described by means of the first law of thermodynamics for closed systems:

$$\mathrm{d}Q_a = \mathrm{d}U = \mathrm{d}(mu) = m\mathrm{d}u \tag{1.30}$$

The internal energy u of the system consists of the internal energy of the liquid u′ and of the vapor u″ and is determined at two points 1 and 2 with the help of the vapor fractions as

$$\begin{aligned} u_1 &= u_1' + x_1 \cdot (u_1'' - u_1') \\ u_2 &= u_2' + x_2 \cdot (u_2'' - u_2') \end{aligned} \tag{1.31}$$

With the filling level FL given through the measurement of the liquid hydrogen mass in the tank, the hydrogen mass is fixed. From the volume of the container, the constant specific volume is given. With this variable and a second property like pressure, all state variables of the hydrogen are given and can be read from the *T*–*s*-diagram or a property data base [21]. From two pressure measurements at two times, the vapor fractions and thus the internal energies of the hydrogen can be found, thus giving the heat input Q_a. For our example of the main tank, pressure rise and heat input for a number of cases are shown in Table 1.4.

1.4.2.2 **Boil-Off**

When the maximum operating pressure has been reached after pressure build-up to point 2, hydrogen is released by a valve in order to keep the pressure constant. From now on, saturated hydrogen vapor is released. The thermodynamic state in the tank is determined by the pressure and the vapor fraction x and moves from point 2 to point 3 in the *T*–*s*-diagram Figure 1.13 shows the relevant details from the measurements in Figure 1.9, the constant pressure in the tank and the liquid hydrogen mass in the tank, which decreases due to the boil-off without hydrogen being taken from the tank deliberately.

The first law of thermodynamics (1.24) for the now open system becomes:

$$\mathrm{d}Q_a = \mathrm{d}U + h''\mathrm{d}m \tag{1.32}$$

Integration between the two states 2 and 3 gives:

$$Q_a = \int_2^3 \mathrm{d}U + \int_2^3 h''\mathrm{d}m = u_3 m_3 - u_2 m_2 + h''(m_2 - m_3) \tag{1.33}$$

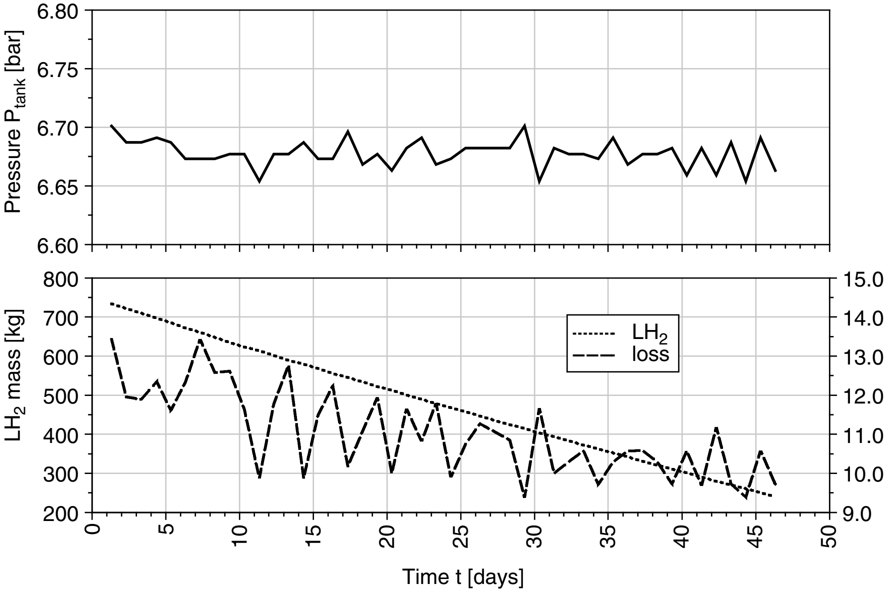


Figure 1.13 Tank pressure and filling level during boil-off.

The evaporated mass is the difference between the masses at two times:

$$\Delta m = m_3 - m_2 \tag{1.34}$$

With the fixed boil-off pressure and the measurement of the filling level, that is, of the hydrogen mass, all state variables of the hydrogen (u_2, u_3, h'') are known from the T–s-diagram or a data base. From two measurements of the filling level at two times, the evaporating mass can be calculated and thence the heat input Q_a. For our example of the main tank, evaporating mass and heat input for two cases are shown in Table 1.5. Evaporation losses of the tank here are between 1 and 1.2% per day.

1.4.2.3 **Cooling and Filling**

After the pressure build-up and boil-off behavior of a hydrogen container, the cooling and filling of a container will be analyzed. Generally, containers are filled using a pressure gradient. First, liquid hydrogen from the main container is filled into the conditioning vessel by a pressure gradient to adjust the hydrogen pressure there. All connecting pipes, valves and fittings have to be vacuum insulated. For each filling process, all pipelines, valves and fitting also have to be cooled to −253 °C.

Table 1.5 Evaporating mass $\Delta m/\Delta t$ and resulting heat input Q_a.

Pressure [bar]	m_1 [kg]	m_2 [kg]	Δm [kg]	Δt [h]	$\Delta m/\Delta t$ [kg h^{-1}]	Q_a [kJ]	$\dot{Q}_a$ [W]
6.67	689.02	603.05	85.97	169.8	0.51	43809.53	71.67
6.67	831.92.	523.15	308.77	709.16	0.44	38253.62	67.42

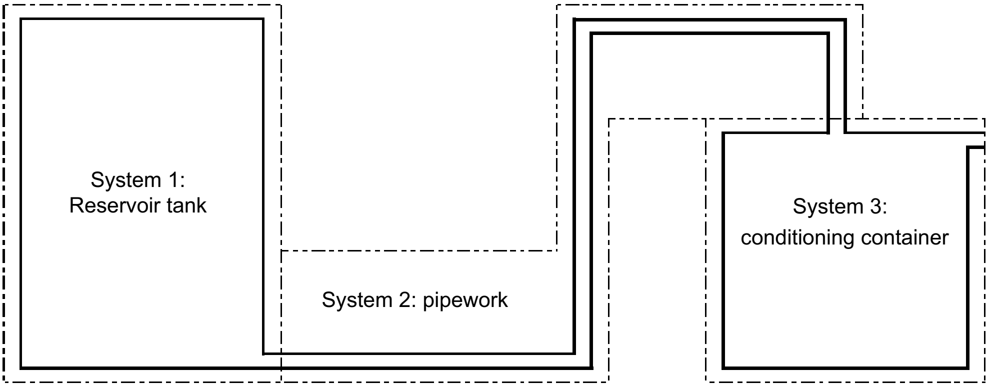


Figure 1.14 Filling system.

Figure 1.14 shows the complete system, which is divided into three subsystems.

For the main tank and the conditioning container subsystems 1 and 3, the relations of the general homogeneous model described above apply. It is assumed that both containers contain liquid hydrogen, that is, they are at low temperature. As the heat input into the reservoir tank can be neglected for the time the filling takes, the change in the internal energy $\mathrm{d}U_1$ depends only on the effusing mass $\mathrm{d}m$ and its specific enthalpy h_1. The mass flow $\dot{m}$ coming from the reservoir tank eventually flows through system 2. If the temperature of system 2 (pipelines) is higher than the boiling temperature according to pressure – which is usually the case – the pipeline system must first be cooled before liquid hydrogen can be transported. The liquid hydrogen coming from the reservoir tank evaporates in the pipelines and chills them through enthalpy of evaporation.

The liquid mass inflow $\dot{m}$ leaves the system at the beginning of the filling process as gaseous mass flow $\dot{m}_g$. If the thermal mass of the pipelines reaches a temperature below the respective boiling temperature according to pressure, a liquid mass flow $\dot{m}_l$ manifests itself. A segment of the pipeline shows the chilling process in greater detail, see Figure 1.15 [4].

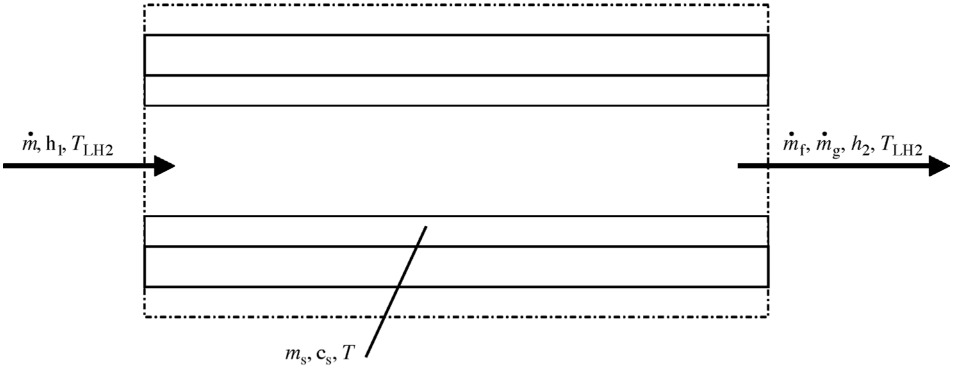


Figure 1.15 Chilling of the pipeline.

Energy balance of the chilling process:

$$m_{\mathrm{s}} \cdot c_{\mathrm{s}} \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = -\dot{m}_{\mathrm{LH_2}} \cdot r_{\mathrm{H_2}} + \alpha \cdot A \cdot (T_0 - T) \tag{1.35}$$

The term $\alpha \cdot A \cdot (T_0 - T)$ corresponds with the transferred heat flow from radiation and convection and is much smaller than the term of the evaporation enthalpy $\dot{m}_{\mathrm{LH_2}} \cdot r_{\mathrm{H_2}}$ and can thus be disregarded. The following differential equation results:

$$T(t) = -\frac{\dot{m}_{\mathrm{LH_2}} \cdot r_{\mathrm{H_2}}}{m_{\mathrm{s}} \cdot c_{\mathrm{s}}} \cdot t + C \tag{1.36}$$

Boundary condition: $t = 0,\ T = T_0$

This results in the following temperature progression:

$$T(t) = T_U - \frac{\dot{m}_{\mathrm{LH_2}} \cdot r_{\mathrm{H_2}}}{m_{\mathrm{s}} \cdot c_{\mathrm{s}}} \cdot t \tag{1.37}$$

Energy balance for the pipelines:

$$\mathrm{d}m_{12} \cdot h_1 - \mathrm{d}m_{23} \cdot h_2 = \mathrm{d}U_2 \tag{1.38}$$

The system of the conditioning container is represented in Figure 1.16. The inflowing mass consists either of gaseous or liquid hydrogen, depending on the temperature of the pipes.

Energy balance for the conditioning container:

$$\mathrm{d}m_{23} \cdot h_2 = \mathrm{d}U_3 \tag{1.39}$$

The chilling process usually requires several minutes and the evaporating hydrogen must generally be considered as a loss. It is disposed of into the environment via a

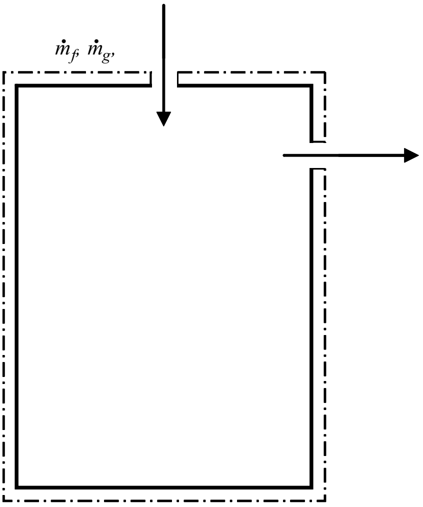


Figure 1.16 System 3: conditioning container.

flue at the HyCentA. There are further losses during the filling process that will be dealt with now.

1.4.2.4 **Back-Gas**

To fill a tank system in the test stand or in a car, liquid hydrogen is first transferred from the main tank to the conditioning container. There the pressure can be adjusted. From the conditioning container, the test tank is filled again by a pressure gradient. The whole system is shown in Figure 1.17.

Before liquid hydrogen can be transported and filled, all parts have to be cooled to −253 °C. During the filling process, a certain amount of gaseous hydrogen has to be transferred back from the test tank system, the so called back-gas m_{bg}. This will be analyzed in more detail, compare [5].

The back-gas is determined indirectly as the difference between the mass taken from the conditioner Δm_{condi} and the mass filled into the test tank Δm_{tank}. The relative amount of back-gas is defined as the rate of back-gas $\beta := \frac{m_{\text{bg}}}{\Delta m_{\text{tank}}} = \frac{\Delta m_{\text{condi}} - \Delta m_{\text{tank}}}{\Delta m_{\text{tank}}}$.

The back-gas consists of three kinds of losses:

1) Loss of heat input: The largest share of hydrogen is lost by evaporation to cool down the pipelines as described above. In spite of the vacuum insulation heat input cannot be avoided completely and causes hydrogen to evaporate also after the system has been cooled down.
2) Loss of filling volume: in order to fill a liquid hydrogen mass m′ into the tank, a volume V of hydrogen gas is replaced by liquid hydrogen $V = v'' \, m'' = v' \, m'$. The gaseous mass m'' has to be removed from the tank, the increase of mass in the test tank is $m' - m''$. The rate of back-gas thus becomes

$$\beta_v = \frac{m''}{m' - m''} = \frac{v'}{v'' - v'} \tag{1.40}$$

Even though the ratio of the densities between the gaseous and liquid phase is much smaller with hydrogen than with other gases, this loss is relatively small.

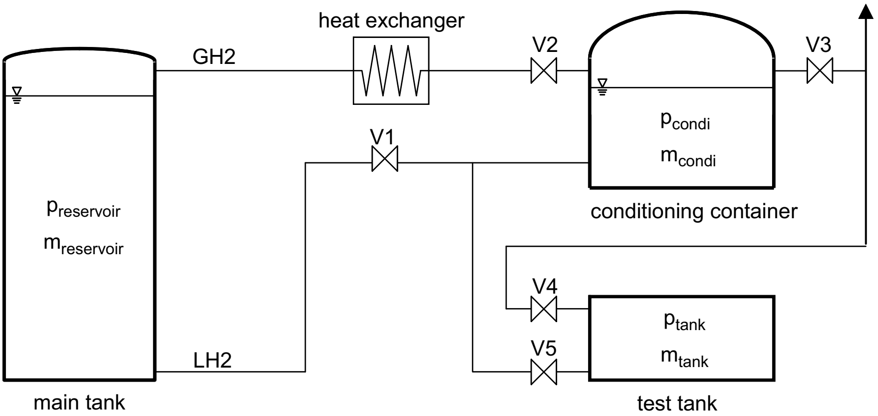


Figure 1.17 Experimental set-up at HyCentA.

Table 1.6 Back-gas losses for different filling processes [5].

Test	A	B	C	D	E
βtot	0.63	0.46	0.25	1.00	0.20
β_{heat1}	0.40	0.17	0.10	0.80	0.08
β_{heat2}	0.04	0.13	0.04	0.11	0.05
β_v	0.05	0.06	0.06	0.04	0.04
β_p	0.14	0.10	0.05	0.05	0.03

3) Loss of pressure drop: due to restrictions and friction, the pressure drops in the pipelines. This causes the boiling temperature to decrease and thus a fraction of hydrogen to evaporate. This part can be calculated in dependency of the vapor fraction x:

$$\beta_p = \frac{1}{1-x} \tag{1.41}$$

With a sophisticated experimental set-up, the back-gas was analyzed at HyCentA for different conditions. The results are shown in Table 1.6.

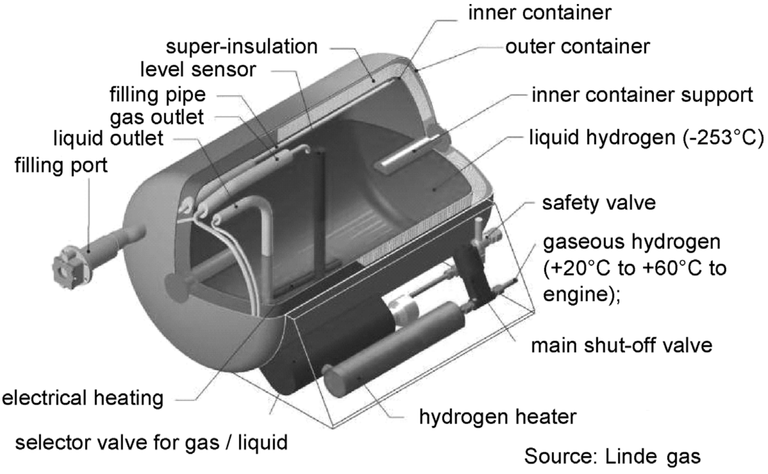
Total losses vary from 20% to 100%. Losses of filling volume and losses of pressure drop are relatively small, the largest contribution is the loss through heat input. This part decreases with repeated filling processes. To minimize losses, the filling process should meet the following requirements:

- Pipelines and system should be short and well isolated
- Pressure in the conditioner should be as high as possible, which shortens the filling time
- The higher the filling amount, the smaller the (relative) losses
- Undercooling the liquid in the conditioner will reduce losses.

The pressure in the conditioner can be regulated by valves V2 and V3, see Figure 1.17. After some time, thermodynamic equilibrium can be assumed in the container, so that the boiling temperature corresponds to the pressure according to the saturated lines in the T–s-diagram. If the pressure is varied quickly in the conditioner and not enough time is allowed for the temperature to reach equilibrium, the fluid will be in thermodynamic non-equilibrium in an undercooled or overheated state. If pressure is decreased and liquid hydrogen is undercooled, it will consume some additional heat to reach thermodynamic equilibrium without evaporating and in that way losses are minimized.

1.4.3
Tank Systems

Liquid storage requires highly sophisticated tank systems. Heat transfer into the tank through conduction, convection and radiation has to be minimized. Therefore, the specially insulated vessels consist of an inner tank and an outer container with an



Source: Linde gas

Figure 1.18 Liquid hydrogen tank [18].

insulating vacuum layer between them, see Figure 1.18. The vacuum layer should inhibit heat conduction and heat convection. The evacuated space between the nested containers is filled with multilayer insulation (MLI) having several layers of aluminum foil alternating with glass fiber matting to avoid heat radiation.

Nevertheless, due to the inevitable inward heat leakage, hydrogen evaporates in the container leading to an increase in pressure. Liquid hydrogen containers must therefore always be equipped with a suitable pressure relief system and safety valve. Liquid storage thus takes place in an open system in which released hydrogen has to be dealt with by means of catalytic combustion, dilution or alternative consumption. Evaporation losses on today's tank installations are somewhere between 0.3% and 3% per day, though larger tank installations have an advantage as a result of their lower surface area to volume ratio [16].

Active cooling with liquid nitrogen is used for large vessels for transportation. To avoid embrittlement and diffusion, appropriate materials like stainless steel and aluminum alloys have to be chosen. The austenitic stainless steel most commonly used for such tanks retains its excellent plasticity even at very low temperature and does not embrittle. Apart from cylindrical tank systems, flat shapes help to save volume in automotive applications. To release the appropriate amounts of hydrogen for acceleration, a hydrogen heater has to be installed. With this adjustable heat input, the hydrogen is evaporated and brought to the energy converter.

Liquid hydrogen tank systems reach today's highest energy densities with 0.06 kg $H_2\,kg^{-1}$ or $2\,kW\,h\,kg^{-1}$ and $0.04\,kg\,H_2\,dm^{-3}$ or $1.2\,kW\,h\,dm^{-3}$. The liquid storage system for the first small series hydrogen vehicle with internal combustion engine, BMW Hydrogen 7, was built by MAGNA STEYR in Graz [20]. Each system was tested for functionality, insulation, pressure build-up and so on, at HyCentA, see Figure 1.19. The tank system for about 9 kg of hydrogen has a volume of about $170\,dm^3$ and a weight of about 150 kg, which allows a maximum driving range of about 250 km. Costs for the system are not published [6].

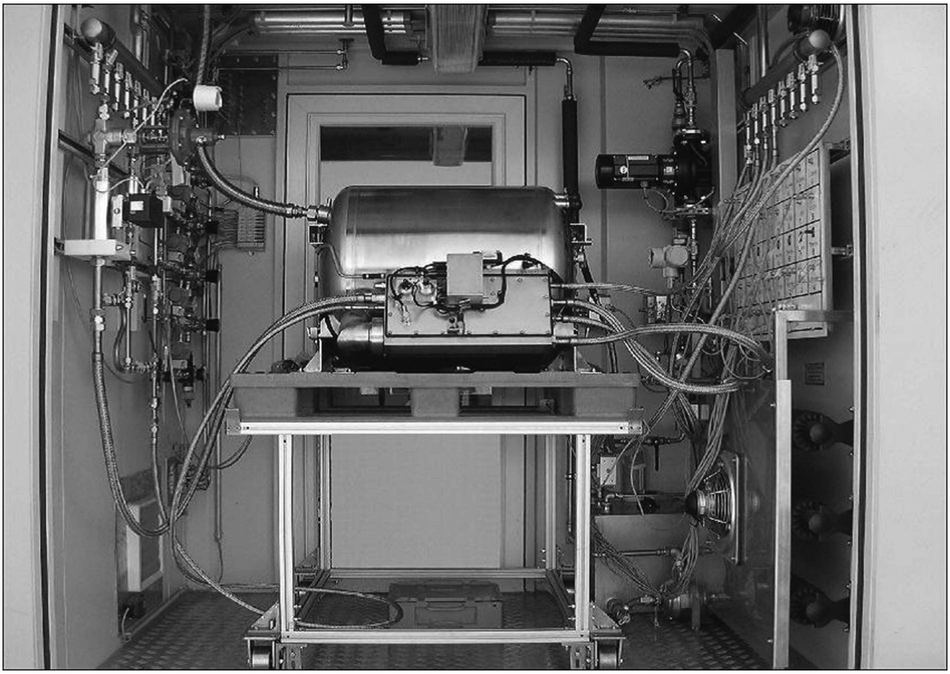


Figure 1.19 Testing of a LH_2-tank system at HyCentA.

1.4.4
Distribution Facilities

As was explained in the thermodynamic analysis, the infrastructure for liquid hydrogen is sophisticated. It has to meet high safety requirements. All valves, pipelines, fittings and couplings have to be vacuum isolated and are made of appropriate materials. Backgas from cooling and filling causes loss of hydrogen to the environment. Filling of tank systems is usually effected by a pressure gradient, whilst cryo-pumps for liquid hydrogen are under investigation [16].

1.5
Hybrid Storage

By applying the term *hybrid* for a system combining two technologies, a number of hybrid storage systems for hydrogen are currently discussed. By cooling pure hydrogen below the freezing point at −259 °C, a mixture of solid and liquid hydrogen, called slush, can be produced. This promises higher energy densities, but needs more effort for production. Also cryo-compressed storage of hydrogen as a supercritical fluid in cryogenic tank systems for high pressures is under consideration. Combinations of liquid or compressed storage with solid storage technologies are

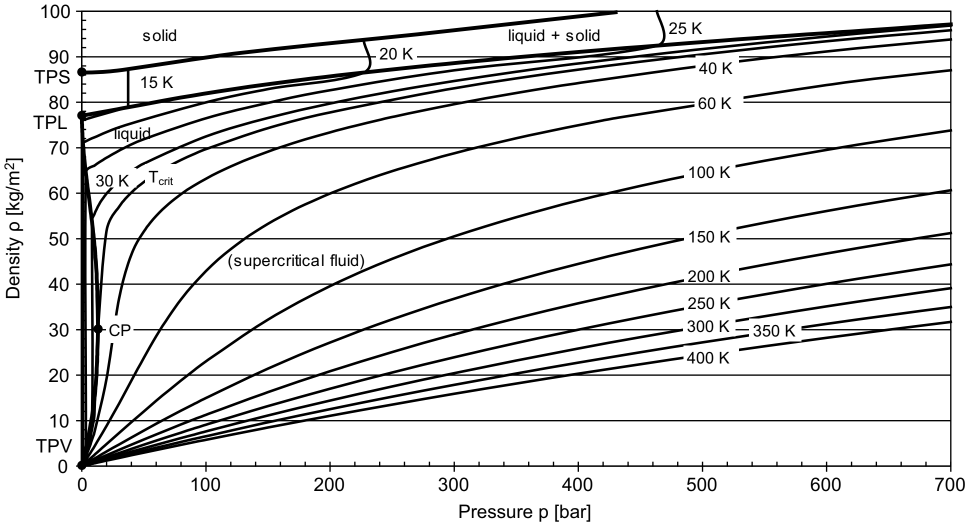


Figure 1.20 Density of hydrogen as a function of pressure and temperature.

also being investigated, for example, to store the boil-off of a liquid tank system in solid state absorbers.

The density of any substance depends on pressure and temperature. For gases at ambient conditions the influence of the pressure prevails, but with temperatures approaching the critical value, the influence of temperature increases. The potential and limits in terms of density can be judged from the state diagrams for hydrogen. Figure 1.20 shows density versus pressure with lines of constant temperature, Figure 1.21 density versus temperature with lines of constant pressure, both especially for low temperatures. The diagrams with critical point CP, triple point for solid TPS, liquid TPL and vapor TPV, and lines of phase transition show the potential for high hydrogen densities at low temperatures and high pressures.

1.5.1
Supercritical Storage

The state of a substance at temperatures and pressures above the critical values is called supercritical fluid. The properties are in between those of the liquid and gaseous state. Hydrogen is a supercritical fluid at temperatures above 33.2 K and pressures above 31.1 bar. As can be seen in Figure 1.21, the density at 350 bar and 35 K lies around 80 kg m^{-3} and thus above the density for the saturated liquid. The hybrid storage technology combining elements of cryogenic liquid and compressed storage is called cryo-compressed storage. It promises high energy densities. As there is no change of phase, evaporation can be avoided, pressure build-up time is assumed to increase, boil-off losses to diminish [7]. Due to heat input and warming, pressure will, nevertheless, rise in the tank and eventually reach a limit, where a boil-off valve has to open. Challenges for tank system design and refueling infrastructure are high.

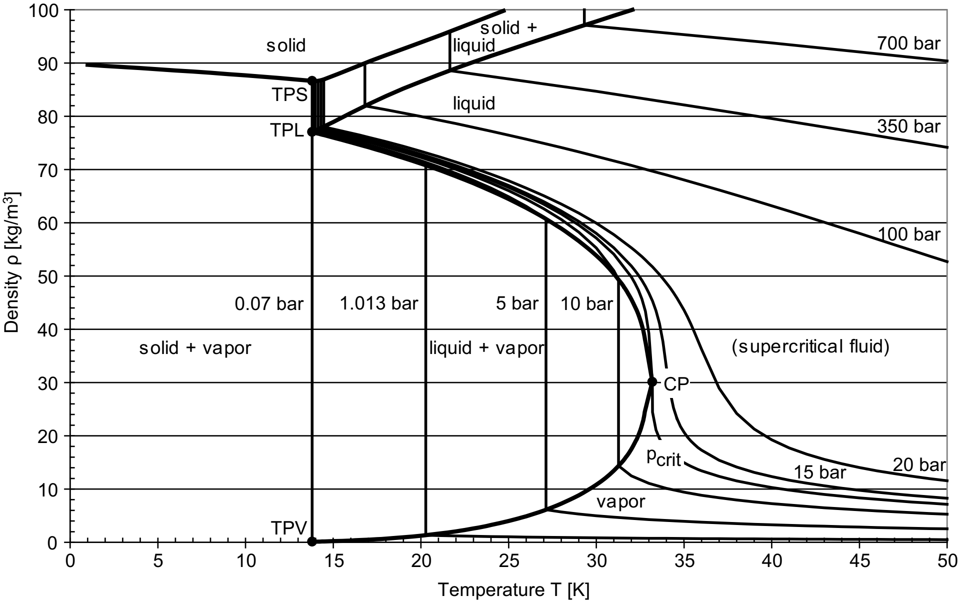


Figure 1.21 Density of hydrogen as a function of temperature and pressure.

1.5.2
Hydrogen Slush

Slush hydrogen is a two-phase solid–liquid cryogenic fluid consisting of solid hydrogen particles in liquid hydrogen at the triple point (0.07 bar, 13.8 K). The density of hydrogen slush at a solid mass fraction of 50% is halfway between the density of the liquid at the triple point and that of solid hydrogen, and thus about 16% higher than the density of the liquid [22]. As the energy for sublimation exceeds the energy for vaporization, a container of hydrogen slush has a much longer pressure build-up time compared with a container of liquid hydrogen. Due to its higher density, slush has been investigated as a rocket fuel, other applications are under consideration. Production of hydrogen slush is complicated, a number of production technologies based on liquid helium and cooling by expansion are known [10], all being on a laboratory scale.

1.6
Comparison of Energy Densities

Figure 1.22 shows the dependence of density and of volumetric energy density on pressure for cryogenic liquid and gaseous compressed hydrogen. It is obvious that the density of liquid hydrogen stored at pressures between 2 and 4 bar is at least 50% higher than the density of gaseous hydrogen stored at 700 bar. At the same time this

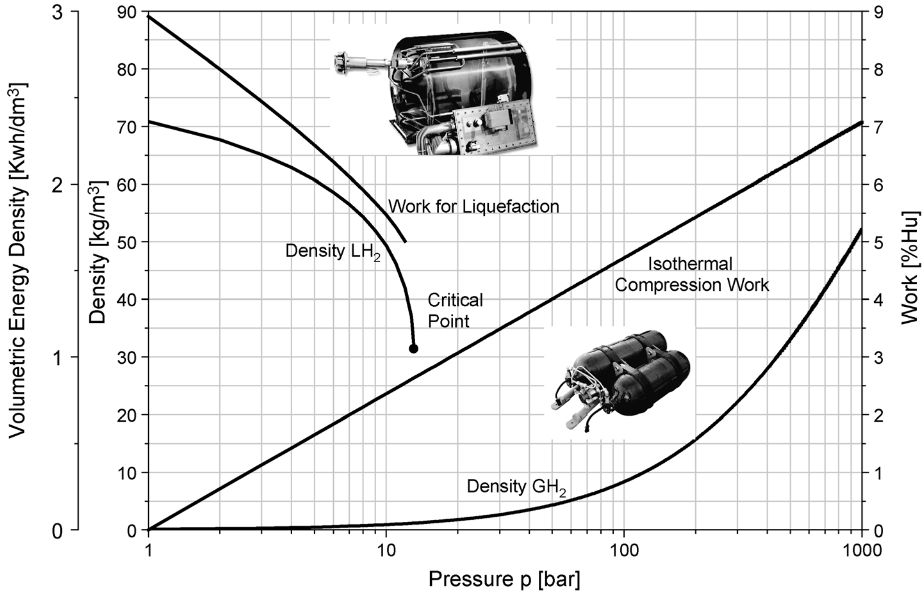


Figure 1.22 Density of LH_2 and GH_2 dependent on pressure.

denotes the physical limits of the storage densities of pure hydrogen. Without counting the volume of the storage system, the maximum volumetric energy density of liquid hydrogen at 2 bar is 2.3 kW h dm^{-3}, of gaseous hydrogen at ambient temperature and 700 bar 1.3 kW h dm^{-3}. The graph also shows the minimum work required for the liquefaction and isothermal compression of hydrogen in percentages of the calorific value H_u of 120 MJ kg^{-1}. The liquefaction and compression work represented here does not take into account the process efficiencies that lie around 50% for compressors and around 30% for liquefaction.

A comparison between the volumetric and gravimetric energy densities of state-of-the-art available energy storage systems is given in Figure 1.23 and Figure 1.24 [7].

Figure 1.23 shows the volumetric energy densities for compressed hydrogen at 350 and 700 bar, for liquid hydrogen, for solid hydrogen storage in metal hydrides, for Li ion batteries, for compressed and liquefied natural gas, and for gasoline. Where available, values are given for the pure substance and for the whole storage system. Liquid hydrocarbons like diesel and gasoline with their light and cheap tank systems allow by far the highest energy densities and thus longest driving ranges in a vehicle.

The corresponding comparison of gravimetric energy densities is given in Figure 1.24. Even though hydrogen has the highest gravimetric energy density of all pure fuels at 33.3 kW h kg^{-1}, because of the heavy tank systems it is still far from reaching the high gravimetric energy density of gasoline storage. Energy densities of available solid hydrogen storage systems or batteries are smaller by an order of magnitude.

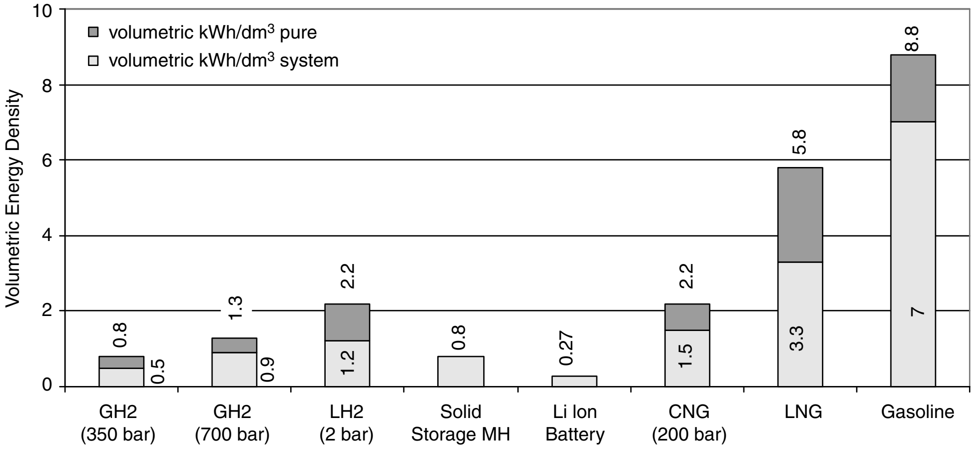


Figure 1.23 Volumetric energy density of storage systems.

If a CO_2-free energy conversion is required, only hydrogen and electrical energy can fulfill this demand. In spite of progress in battery technology, at present electrical energy densities are still quite low. Of course, both hydrogen and electricity would have to be produced in a CO_2-free way.

Another comparison of volumetric versus gravimetric storage density including solid storage systems is given in Figure 1.25 [26]. It is obvious that, with regard to volumetric storage density, storage of hydrogen in compounds has the greater potential. More hydrogen per unit can be stored in compounds than in the pure form. Gasoline and diesel actually are chemical hydrogen compounds with high volumetric and gravimetric energy densities, but hydrogen cannot easily be separated from the carbon.

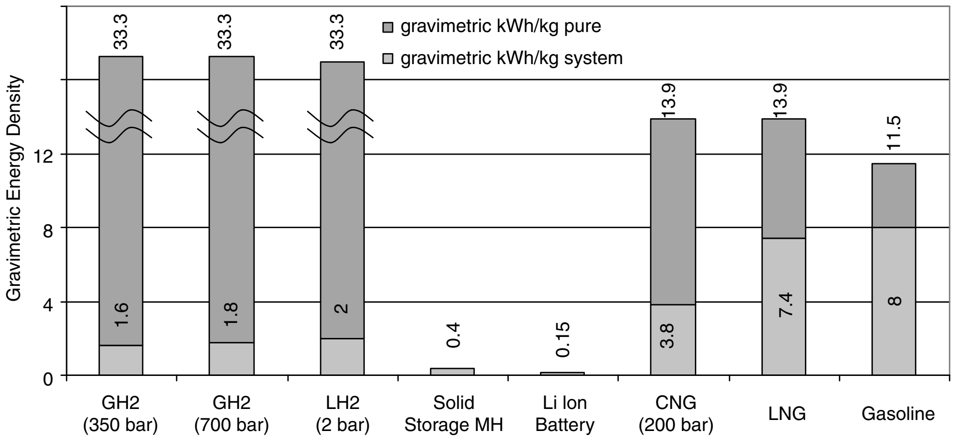


Figure 1.24 Gravimetric energy density of storage systems.

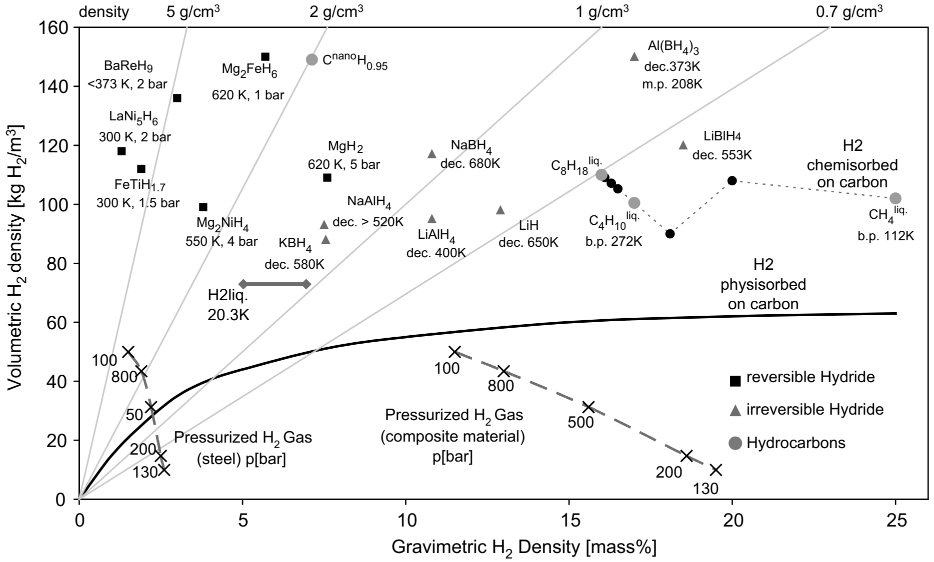


Figure 1.25 Density of hydrogen storage technologies.

Until now most solid storage systems have been on a laboratory scale only. Apart from the weight and volume of the storage systems, topics of research are the conditions of charging and discharging the system (pressure, temperature, heat transfer, time), the potential number of charging cycles (lifetime) and of course costs.

1.7
Conclusion

Hydrogen in a pure form can be stored as a highly compressed gas at up to 700 bar, cryogenically liquefied at −253 °C or in hybrid form.

Gaseous hydrogen storage takes place in a closed system without losses for extended periods. Tank vessels and infrastructure require consideration of questions regarding material choice, component dimensioning and safety, but resemble established technologies applied to compressed natural gas. Type IV containers of composite materials are commercially available for 350 and 700 bar. The hydrogen density is 23.3 $\mathrm{kg\,m^{-3}}$ at 350 bar and 39.3 $\mathrm{kg\,m^{-3}}$ at 700 bar and 25 °C. System energy densities of 1.8 $\mathrm{kW\,h\,kg^{-1}}$ and 0.9 $\mathrm{kW\,h\,dm^{-3}}$ at 700 bar can be achieved. The physical limit of the volumetric energy density at 700 bar is 1.3 $\mathrm{kW\,h\,dm^{-3}}$ for pure hydrogen. The energy required for compression is up to 15% of the fuel energy content.

Higher storage densities are possible with liquid hydrogen: the density at 2 bar is 67.67 $\mathrm{kg\,m^{-3}}$. The physical limit of the volumetric energy density at 2 bar is thus 2.3 $\mathrm{kW\,h\,dm^{-3}}$ for pure hydrogen. However its very low boiling point at −253 °C means that the generation of liquid hydrogen is complex and requires 20 to 30% of its energy content. The storage of liquid hydrogen is technically challenging. Containers with high levels of insulation are used, consisting of an inner tank and an outer container with an insulating vacuum between them. Nevertheless, heat transfer cannot be ruled out completely. As a result of inevitable inward heat leakage, hydrogen evaporates in the container leading to increases in pressure and temperature. Liquid hydrogen containers must therefore always be equipped with a suitable pressure relief system and safety valves. Liquid storage takes place in an open system in which released hydrogen has to be dealt with by means of catalytic combustion, dilution or alternative consumption. Evaporation losses on today's tank installations are between 0.3 and 3% per day. A highly sophisticated and expensive production and processing system is necessary in order to minimize losses caused by diffusion, evaporation and impurity. With today's available liquid hydrogen storage systems energy densities of $2\,\mathrm{kW\,h\,kg^{-1}}$ and $1.2\,\mathrm{kW\,h\,dm^{-3}}$ can be achieved.

From the application point of view storage of compressed hydrogen at 700 bar offers an acceptable energy density at affordable costs. Type IV tank systems are quite mature but also do not offer much potential for further improvement. With a higher effort in production and storage, higher energy densities can be achieved with liquid hydrogen storage. This is applied if driving range is decisive or if large quantities are used, as in centralized production and distribution or in space applications as rocket fuel. Hydrogen slush and cryo-compressed storage are issues of research.

In order to proceed with the application of CO_2-free energy carriers in vehicles, both compressed and liquid hydrogen applications are ready for the market from the technical point of view. They can complement electric drive trains that may be convenient for short ranges. Both electricity and hydrogen have to be produced, a forceful expansion of regenerative energy production is mandatory. Due to higher costs compared with fossil fuels, the widespread use of hydrogen requires political support, for example, through CO_2 taxation.

References

1 Dynetek Industries Ltd., http://www.dynetek.com.

2 Eichlseder, H., Klell, M., Schaffer, K., Leitner, D., and Sartory, M. (2009) Potential of Synergies in a Vehicle for Variable Mixtures of CNG and Hydrogen, SAE paper 2009-01-1420.

3 Eichlseder, H. and Klell, M. (2008) *Wasserstoff in der Fahrzeugtechnik, Erzeugung, Seicherung und Anwendung [Hydrogen in Vehicle Technology, Production, Storage and Application]*, Vieweg + Teubner Verlag, Wiesbaden, ISBN 9783834804785.

4 Eichner, Th. (2005) Kryopumpe für Wasserstoff [Cryo-pump for Hydrogen]. Diploma thesis, Technische Universität Graz.

5 Emans, M., Mori, D., and Krainz, G. (2007) Analysis of back-gas behaviour of an automotive liquid hydrogen storage system during refilling at the filling station. *Int. J. Hydrogen Energy*, **32**, 1961–1968.

6 Enke, W., Gruber, M., Hecht, L., and Staar, B. (2007) Der bivalente V12-Motor des BMW Hydrogen 7 [Bivalent V12 Engine of the BMW Hydrogen 7]. *Motortechnische Zeitschrift MTZ 68*, **06**, 446–453.

7 EU FP6 Integrated Project STORHY, http://www.storhy.net.

8 Gstrein, G. and Klell, M. (2004) *Stoffwerte von Wasserstoff [Properties of Hydrogen]*, Institute for Internal Combustion Engines and, Thermodynamics, Graz University of Technology.

9 Gursu, S., Sherif, S.A., Veziroglu, T.N., and Sheffield, J.W. (1993) Analysis and optimization of thermal stratification and self-pressurization effects in liquid hydrogen storage systems – Part 1: Model development. *J. Energy Resources Technology*, **115**, 221–227.

10 Haberbusch, M. and McNelis, N. (1996) Comparison of the Continuous Freeze Slush Hydrogen Production Technique to the Freeze/Thaw Technique. NASA Technical Memorandum 107324.

11 Kindermann, H. (2006) Thermodynamik der Wasserstoffspeicherung. [Thermodynamics of Hydrogen Storage]. Diploma thesis, HyCentA Graz, Montanuniversität Leoben.

12 Klell, M., Brandstätter, S., Jogl, C., and Sartory, M. (2008) Werkstoffe für Wasserstoffanwendungen [Materials for Hydrogen Application]. Report 3a2008 HyCentA Research GmbH, http://www.hycenta.at.

13 Klell, M. and Sartory, M. (2008) Sicherheit und Standards für Wasserstoffanwedungen [Safety and Standards for Hydrogen Applications]. Report 4a2008 HyCentA Research GmbH, http://www.hycenta.at.

14 Klell, M., Zuschrott, M., Kindermann, H., and Rebernik, M. (2006) Thermodynamics of hydrogen storage. 1st International Symposium on Hydrogen Internal Combustion Engines, Report 88, Institute for Internal Combustion Engines and Thermodynamics, Graz University of Technology, Graz.

15 Kurzweil, P. (2003) *Brennstoffzellentechnik [Fuel Cell Technology]*, Vieweg Verlag, Wiesbaden, ISBN 3528039655.

16 Léon, A. (ed.) (2008) Hydrogen technology, in *Mobile and Portable Applications*, Springer-Verlag, Berlin, Heidelberg, ISBN 9783540790273.

17 Lin, C.S., Van Dresar, N.T., and Hasan, M. (2004) A pressure control analysis of cryogenic storage systems. *J. Propul. Power*, **20** (3), 480–485.

18 Linde Gas Gmbh, http://www.linde-gas.at.

19 Mackay, K.M. (1973) The element hydrogen, ortho- and para-hydrogen, atomic hydrogen, in *Comprehensive Inorganic Chemistry*, **1** (ed. A.F., Trotman-Dickinson), Pergamon Press, Oxford, pp. 1–22.

20 MAGNA STEYR Fahrzeugtechnik AG & Co KG, http://www.magnasteyr.com.

21 National Institute of Standards and Technology NIST, http://www.nist.gov.

22 Ohira, K. (2004) Development of density and mass flow rate measurement technologies for slush hydrogen. *Cryogenics*, **44**, 59–68.

23 Pischinger, R., Klell, M., and Sams, Th. (2009) *Thermodynamik der Verbrennungskraftmaschine [Thermodynamics of the Internal Combustion Engine]*, 3rd edn, Springer Verlag, Wien New York, ISBN 978-3-211-99276-0.

24 Quack, H. (2001) Die Schlüsselrolle der Kryotechnik in der Wasserstoff-Energiewirtschaft [Key Role of Cryotechnology in Hydrogen Energy Sector]. Wissenschaftliche Zeitschrift der Technischen Universität Dresden, 50 Volume 5/6, 112–117.

25 Riedel, E. and Janiak, Ch. (2007) *Anorganische Chemie [Inorganic Chemistry]*, Walter de Gruyter, Berlin New York, ISBN 9783110189032.

26 Schlapbach, L. and Züttel, A. (2001) Hydrogen storage-materials for mobile applications. *Nature*, **414**, 23–31.

27 Scurlock, R. (2006) *Low-Loss Storage and Handling of Cryogenic Liquids: The Application of Cryogenic Fluid Dynamics*, Kryos Publications, Southampton, UK, ISBN 9780955216605.

28 Turns, St. (2006) *Thermodynamics, Concepts and Applications*, Cambridge University Press, New York, ISBN 9780521850421.

29 Züttel, A., Borgschulte, A. and Schlapbach, L. (eds) (2008) *Hydrogen as a Future Energy Carrier*, Wiley-VCH Verlag, Weinheim, ISBN 9783527308170.