

Chapter 8

Hydrogen Storage

8.1 Introduction

Hydrogen is an important *energy carrier*, and when used as a fuel can be considered to be an alternate to the major fossil fuels, coal, crude oil and natural gas, and their derivatives. It has the potential to be a clean, reliable and affordable energy source, and has the major advantage that the product of its combustion with oxygen is water, rather than CO and CO₂, which contain carbon and are considered greenhouse gases. It is expected to play a major role in future energy systems.

It has been shown that hydrogen can be used directly in internal reciprocating combustion engines, requiring relatively minor modifications, if it is raised to a moderately high pressure, as well as in turbines and process heaters.

It can also be used in hydrogen/oxygen fuel cells to directly produce electricity. Again, the only product is water. The energy efficiency of fuel cells can be as high as 60 %. Fossil fuel systems, on the other hand, are typically about 34 % efficient. When hydrogen is used in elevated temperature fuel cells, it is possible to obtain electricity and also to use the heat generated in the fuel cell, related to its inefficiency, for heating purposes. This is called *co-generation*, and in this way it is possible to obtain total energy efficiencies up to 80 %.

Electrically-powered vehicles have the advantage that electric motors can have energy efficiencies of about 90 %, whereas typical internal combustion engines are about 25 % efficient. On the other hand, fuel cells now cost about 100 times as much as equivalent internal combustion engines of comparable power. One can, however, expect some reduction in cost from further development and larger scale production of fuel cells.

Because of these attractive features, a number of people have long advocated the concept of a simple *hydrogen economy*, in which hydrogen is used as the major fuel.

It reacts with oxygen, either by combustion or in fuel cells, to give energy, and the only product is water. It can be regenerated directly from water by electrolysis.

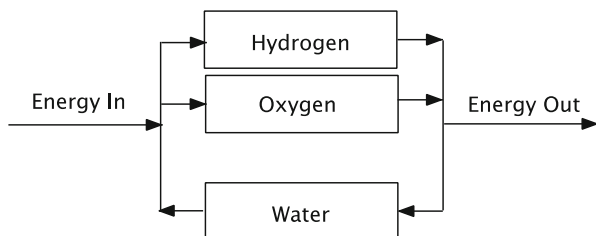


Fig. 8.1 The general concept of the ideal hydrogen economy

This is a closed chemical cycle. No chemical compounds are created or destroyed, but there is a net flow of energy.

This concept is illustrated schematically in Fig. 8.1. It is important to recognize that a full hydrogen economy is not necessary. Even partial implementation would be desirable as a way to reduce environmental pollution problems.

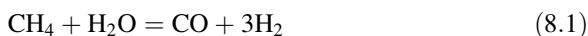
The major use of hydrogen at the present time, however, is not as an energy carrier, but as a reactant in a number of important large-scale chemical processes.

8.2 The Production of Hydrogen

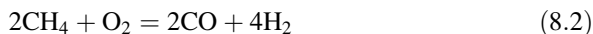
As discussed in the Preface, the major, and least expensive, way to obtain hydrogen is to extract it from natural gas, which is primarily methane. The most common method for the conversion of methane to hydrogen involves the use of the *steam reforming*, followed by the *water-gas shift reaction*. It now provides some 95 % of all the hydrogen produced in the USA. This process, as well as several other methods for making hydrogen, will be briefly discussed in the following sections of this chapter.

8.2.1 The Steam Reforming Process

The first step in this procedure is the elimination of impurities, such as sulfur, from the methane-rich natural gas. The methane is then reacted with steam at a relatively high temperature, using nickel oxide as a catalyst. This process is called *steam reforming*, and was already discussed in Chap. 4. It can be written as



This can be followed by a second step in which air is added to convert any residual methane that did not react during the steam reforming.



This is then followed by the *water–gas shift reaction* at a somewhat lower temperature that produces more hydrogen from the *CO* and steam:



As discussed already, the driving force for any reaction is the standard Gibbs free energy change, ΔG_r^0 that occurs as the result. This is the difference between the sum of the standard Gibbs free energies of formation of the products and the sum of the standard Gibbs free energies of formation of the reactants. In this case, this can be expressed as

$$\Delta G_r^0 = \Delta G_f^0(\text{CO}) + 3\Delta G_f^0(\text{H}_2) - \Delta G_f^0(\text{CH}_4) - \Delta G_f^0(\text{H}_2\text{O}) \quad (8.4)$$

Values of the standard Gibbs free energy of formation of the relevant species for three different temperatures are given in Table 8.1.

From these data it is possible to obtain the standard Gibbs free energy of relevant reactions in this system at those temperatures. These are shown in Table 8.2, and the results for Eqs. (8.1) and (8.3) are plotted in Fig. 8.2.

It can be seen that the steam reforming reaction will only go forward if the temperature is *above* about 900 K. Likewise, the subsequent water–gas shift reaction will only proceed if the temperature is *below* about 1025 K.

Table 8.1 Temperature dependence of the standard Gibbs free energies of formation of species in reaction 1

Species	ΔG_r^0 (400 K) (kJ mol ⁻¹)	ΔG_r^0 (800 K) (kJ mol ⁻¹)	ΔG_r^0 (1200 K) (kJ mol ⁻¹)
CO	-146.4	-182.5	-217.8
H ₂ O	-224.0	-203.6	-181.6
CO ₂	-394.6	-395.5	-396.0
CH ₄	-42.0	-2.1	+41.6

Table 8.2 Standard Gibbs free energies of reaction at several temperatures

Reaction	ΔG_r^0 (400 K) (kJ mol ⁻¹)	ΔG_r^0 (800 K) (kJ mol ⁻¹)	ΔG_r^0 (1200 K) (kJ mol ⁻¹)
CH ₄ + H ₂ O = CO + 3 H ₂	+119.6	+23.2	-77.8
2 CH ₄ + O ₂ = 2 CO + 4 H ₂	-208.8	-360.8	-518.8
CO + H ₂ O = CO ₂ + H ₂	-24.2	-9.4	+3.4
CH ₄ + 2 O ₂ = CO ₂ + 2 H ₂ O	-800.6	-800.6	-800.8
C + H ₂ O = CO + H ₂	+77.6	+21.1	-36.2

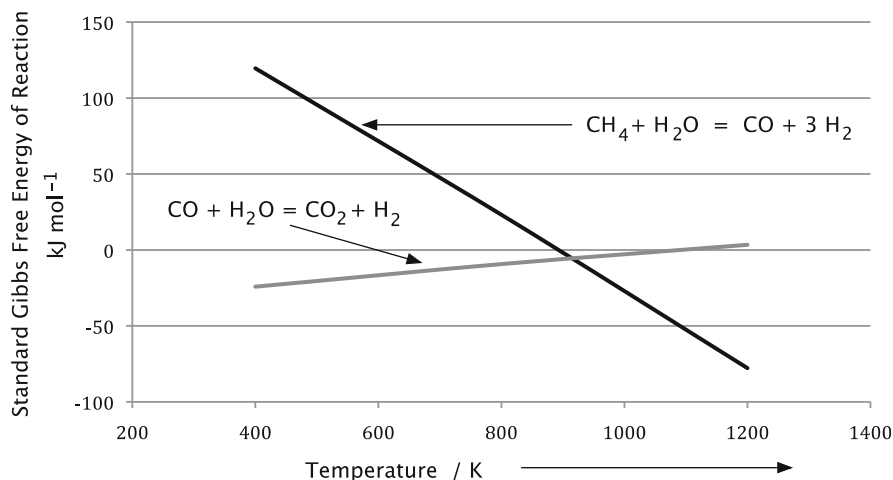


Fig. 8.2 Temperature dependence of the standard Gibbs free energy of reactions involved in extraction of hydrogen from methane

8.2.2 The Reaction of Steam with Carbon

A number of countries, especially the USA and China, have large amounts of coal that they can use as an energy source. It is possible to react steam with solid carbon instead of with methane. In this case, the product is *syngas*, a mixture of CO and hydrogen. This reaction is included in Table 8.2. The resultant CO can then be reacted with steam in the water–gas shift reaction, just as is done in the case of steam reforming of methane.

The temperature dependence of the standard Gibbs free energies of these two reactions is shown in Fig. 8.3. As was the case with the reaction of steam with methane, the standard Gibbs free energy of the reaction of steam with carbon also decreases as the temperature increases. It can be seen that this reaction will only go forward if the temperature is above about 940 K. Again, the water–gas shift reaction proceeds only at lower temperatures.

The power plants that generate hydrogen from coal by this two-step process have overall efficiencies of about 34 %. But if they capture the effluent CO₂ from the water–gas reaction, the efficiencies can rise to above 40 %.

The thermal behavior of these various reactions can also be determined from data on the standard enthalpies of the species in these reactions. Such data for three temperatures are included in Table 8.3.

From these data for the various species the enthalpy (heat) effects of these reactions can be calculated. The results are included in Table 8.4, and plotted in Fig. 8.4.

It is seen that the water–gas reaction is endothermic, whereas the other reactions are both exothermic.

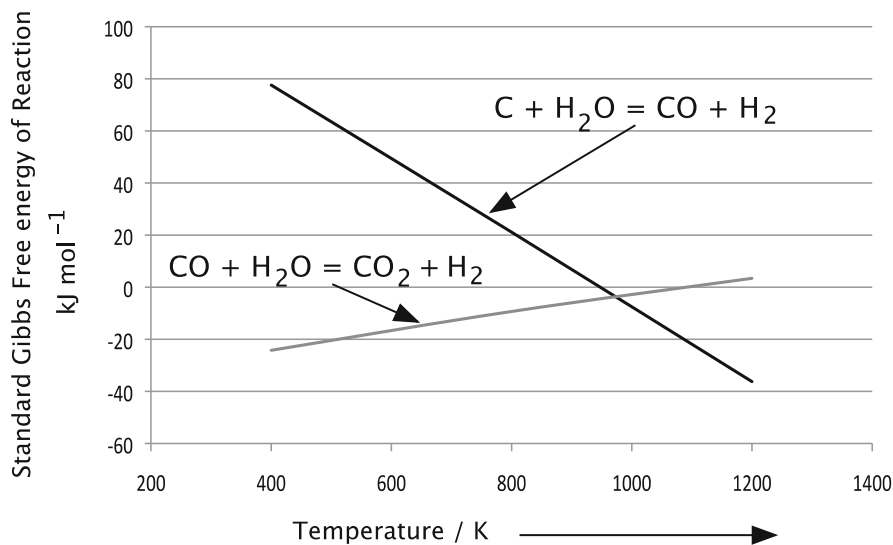


Fig. 8.3 Temperature dependence of the standard Gibbs free energies of reactions involved in reaction of steam with carbon

Table 8.3 Temperature dependence of the standard enthalpies of relevant species

Species	ΔH_f^0 (400 K) (kJ mol ⁻¹)	ΔH_f^0 (800 K) (kJ mol ⁻¹)	ΔH_f^0 (1200 K) (kJ mol ⁻¹)
CO	-110.1	-110.9	-113.2
H ₂ O	-242.8	-246.4	-249.0
CO ₂	-393.6	-394.2	-395.0
CH ₄	-78.0	-87.3	-91.5

Table 8.4 Standard enthalpies of reactions

Reaction	ΔH_r^0 (400 K) (kJ mol ⁻¹)	ΔH_r^0 (800 K) (kJ mol ⁻¹)	ΔH_r^0 (1200 K) (kJ mol ⁻¹)
$C + H_2O = CO + H_2$	+132.7	+135.5	+135.8
$CO + H_2O = CO_2 + H_2$	-40.7	-36.9	-32.8

If the hydrogen is to be used in a low temperature fuel cell, the gas mixture resulting from the water–gas reaction also generally undergoes a further step, called *methanation*, in which the remaining CO is converted back into methane, which is recycled. This is necessary because CO poisons the platinum catalysts that are typically used in such fuel cells.

It should be noted that all of these gas-phase reactions produce products that consist of mixtures of gases. The separation of hydrogen from the other gas

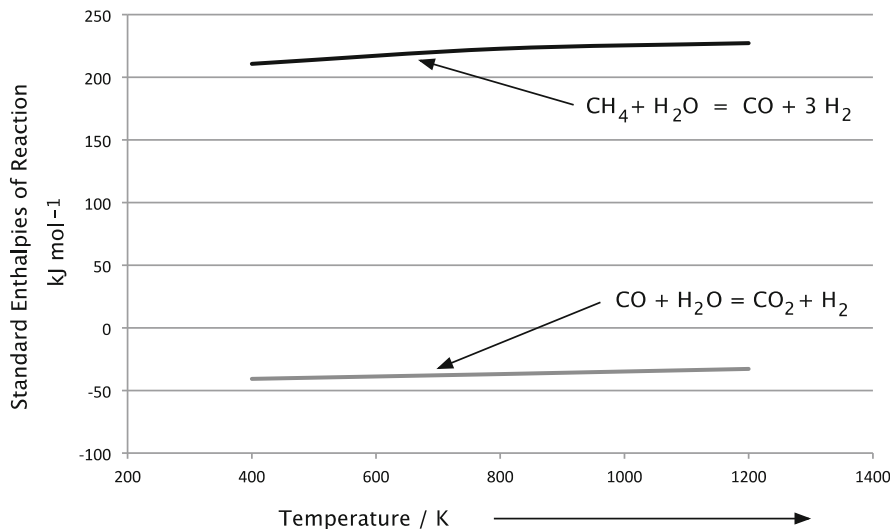


Fig. 8.4 Temperature dependence of the standard enthalpies of reactions

components involves the use of membranes that are permeable to hydrogen, but not to the other species. There is a need for the development of better selective membranes for this purpose.

8.2.3 *Electrolytic Production of Hydrogen*

The second major method for the production of hydrogen involves the electrolysis of water by imposing a voltage between two electrodes within it that exceeds its thermodynamic stability range. The result is the evolution of hydrogen gas at the negative electrode, and oxygen gas at the positive electrode. Both of these gases have a significant commercial value. It is easy to design systems to collect them separately.

Relatively pure hydrogen can be produced by the electrolysis of water, and this method appears to be attractive in the long run. There is an enormous amount of water on the earth, with the potential to supply an almost limitless supply of hydrogen. About 4 % of the hydrogen currently used in the world is produced by electrolysis.

The problem with this apparently attractive scenario is that the electrolytic decomposition of water to produce hydrogen is currently quite expensive. Thus it is only a feasible large-scale option where the cost of electricity is relatively low.

An advantage of water electrolysis to produce hydrogen is that, instead of requiring large central facilities, there can be distributed generation using smaller units. They can be located at places near where the hydrogen will be used in order to reduce storage and transportation costs.

The equilibrium (zero current) cell voltage E_{eq} required to decompose water can be found from the value of the standard Gibbs free energy of the formation of water, ΔG_f^0 , a thermodynamic quantity. Data of this type for many materials over a range of temperatures can be found in [1]:

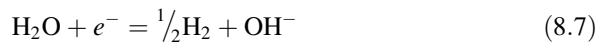
$$E = -\Delta G_f^0 / 2F \quad (8.5)$$

F is the Faraday constant, or 96,500 J per volt equivalent. The value 2 is present because the formation of water from hydrogen and oxygen involves two electronic charges (two equivalents):

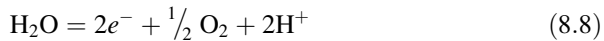


The value of ΔG_f^0 is -237.1 kJ/mol for water at 298 K, or 25 °C. Thus the voltage needed to exceed the stability range of water is above 1.23 V at that temperature. If there is a bit of a salt present to provide ionic conductivity, the application of sufficiently higher voltages causes current to flow, and the hydrogen and oxygen bubble off at the electrodes.

The reactions at the electrodes when water is being electrolyzed can be written as



on the negative side, and



on the positive side of the cell. Inside the water the result is the formation of OH^- ions at the negative electrode, and H^+ ions at the positive electrode.

But it must be realized that in order for these reactions to occur there must be ionic transport through the water. This would normally be either by the transport of H^+ ions to the other electrode in acid solutions, or the transport of OH^- ions in alkaline solutions.

But where does the water actually disappear? It cannot go away at both electrodes. If the water is acidic, it disappears from the solution at the positive electrode. The protons formed on that side, along with the O_2 gas, are transported to the negative side. When they reach the negative electrode, they react with the OH^- ions that are generated there to form H_2O . Thus there is a net loss of H_2O at the negative side in this case, not at the positive side.

The total cell voltage E_t when current is flowing is

$$E_t = E_{eq} + E_{neg} + E_{pos} + iR_{\text{electrolyte}} \quad (8.9)$$

where E_{neg} is the voltage loss at the negative electrode, E_{pos} is the voltage loss at the positive electrode, and $iR_{\text{electrolyte}}$ is the voltage loss across the water electrolyte.

This can also be written as

$$E_t = E_{\text{eq}} + iZ_{\text{neg}} + iZ_{\text{pos}} + iR_{\text{electrolyte}} \quad (8.10)$$

where i is the current, and the Z values are the impedances at the two electrodes. These can be thought of as resistances whose values depend upon the value of the current. On the other hand, the resistance of the electrolyte, $R_{\text{electrolyte}}$, is essentially current-independent.

The energy consumed during the electrolysis of the water is

$$\text{Energy} = iE, \quad (8.11)$$

and the energy efficiency is

$$\text{Efficiency} = \frac{iE_{\text{eq}}}{iE_t} \quad (8.12)$$

As mentioned already, although electrolytic production of hydrogen is significantly more expensive than obtaining it from natural gas, it has the advantage that the resulting gas can be of significantly greater purity. This can be especially important when the hydrogen is used in low-temperature fuel cells with polymeric solid electrolyte membranes. Even minor amounts of impurity species, such as CO, can cause problems by adsorbing on the surfaces of the platinum catalysts that are typically used to assist the conversion of H_2 molecules to H^+ ions and electrons at the negative electrode.

This requires additional treatment, and results in higher costs. The degree of CO adsorption on the catalyst surface decreases as the temperature is raised, so that this type of poisoning is not present in high-temperature fuel cells. That is one of the reasons for interest in the further development of this type of fuel cell.

Current low-temperature fuel cells actually operate at temperatures somewhat above ambient temperature in order to increase the overall kinetics.

As with any fuel, in addition to its acquisition, there must also be methods to transport hydrogen to the locations at which it will be used. Because such matters are typically not fully synchronized, there must also be methods for its storage.

Large commercial electrolyzers now produce hydrogen at a pressure of about 30 bar and a temperature of 80 °C, and have energy efficiencies of 80–90 %. The major source of loss is connected with the processes that take place at the positive electrode, where oxygen is evolved.

The decomposition of water requires that the oxygen species change from oxide ions in the water, that carry a charge of -2 , to oxygen molecules, O_2 , in which the charge on the oxide ions is effectively zero. An intermediate state, with peroxide O^{-1} ions, must be present on or near the catalyst surface.

High-surface-area nickel or nickel alloy electrodes are typically used on the oxygen side of water electrolysis cells. They have a surface layer of nickel oxy-hydroxide, NiOOH . The properties of this material, which plays an important role in a number of battery systems, will be discussed in a later chapter.

For kinetic reasons, electrolysis cells generally operate at about 2 V, which is substantially greater than the open circuit thermodynamic value for the decomposition of pure water of 1.23 V, and there is a continual effort to reduce the magnitude of this excess voltage.

8.2.4 Thermal Decomposition of Water to Produce Hydrogen

An additional method that can be used to produce hydrogen from water is to thermally decompose it by heating to a very high temperature. The stability of water relative to its two components, hydrogen and oxygen, is expressed in terms of its standard Gibbs free energy of the formation, ΔG_f^0 , as mentioned above. This value is temperature-dependent, and can be expressed as

$$\Delta G_f^0 = \Delta H_f^0 - T\Delta S_f^0 \quad (8.13)$$

where ΔH_f^0 and ΔS_f^0 are the enthalpy and entropy values for the formation of water, respectively. The values of both of these terms are relatively independent of the temperature. Using values from [1], the temperature dependence of the standard Gibbs free energy of formation of water is shown in Fig. 8.5.

It is seen that water does not become thermodynamically unstable until the temperature reaches about 4300 K. Thus this method is hardly a practical alternative for splitting water into hydrogen and oxygen, for the required temperature is very high.

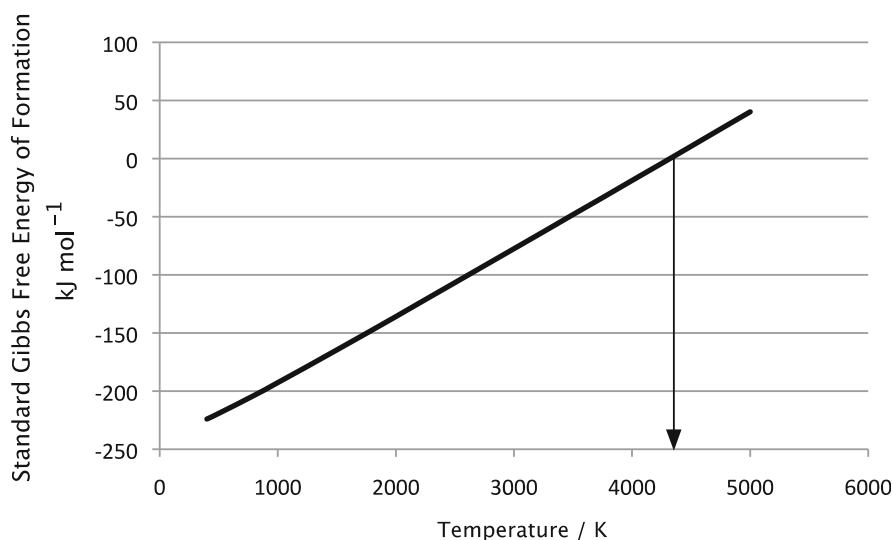


Fig. 8.5 Temperature dependence of the standard Gibbs free energy of formation of water

8.2.5 Chemical Extraction of Hydrogen from Water

It is also possible to produce hydrogen by chemically decomposing water. Many species form oxides when in contact with water. In general, however, the oxide that forms produces a protective surface layer that prevents further reaction with the water. There are a few exceptions in which a non-protective product is formed. One of these is lithium, which forms soluble LiOH . Another is aluminum, that can form soluble aluminum hydroxide, or hydrated oxide, instead of the simple oxide Al_2O_3 , in basic solutions. This has led to the development of the so-called aluminum/air battery, which utilizes air as the reactant in the positive electrode.

The chemical reaction of aluminum with water can also be used to produce hydrogen, as was first shown by Cuomo and Woodall at the IBM Laboratory in 1968 [2]. This is accomplished by the use of a solution of aluminum in a low-melting-point liquid alloy based on gallium. The aluminum-gallium phase diagram is shown in Fig. 8.6. It can be seen that the melting point of gallium is 30°C , and slightly below that, there is an eutectic reaction at 26°C . There is a gradual increase in the solubility of aluminum in the liquid phase as the temperature increases, reaching complete miscibility at the melting point of aluminum at 660°C . There is also a modest amount of solubility of gallium in solid aluminum all the way up to the melting point.

When this alloy is in contact with water at slightly above room temperature the dissolved aluminum will not form a protective skin, but reacts vigorously to form

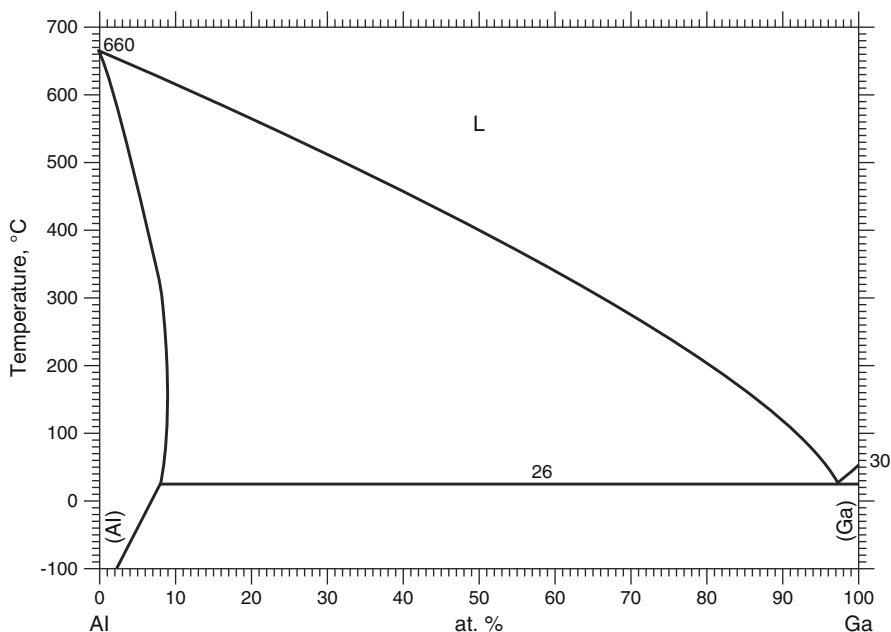


Fig. 8.6 The aluminum-gallium phase diagram

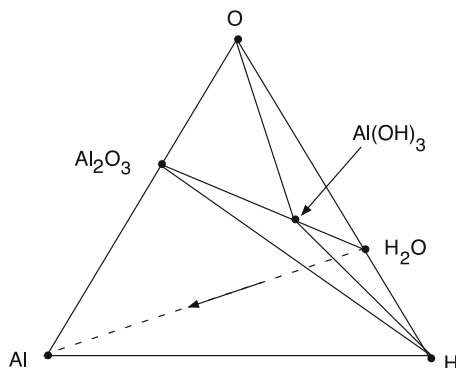


Fig. 8.7 Ternary phase stability diagram for the H–Al–O system

Table 8.5 Thermodynamic data related to the formation of Gibbsite

Species	ΔG_f^0 at 300 K (kJ mol)	ΔH_f^0 at 300 K (kJ mol)
H ₂ O	–236.8	–285.8
Al ₂ O ₃	–1581.7	–1675.7
Al ₂ O ₃ · 3 H ₂ O	–2308.4	–2586.6

hydrogen and finely dispersed aluminum oxide, which floats on the top of the liquid gallium alloy, according to the equation



Aluminum hydroxide is generally described as a hydrated version of Al₂O₃, called Gibbsite, Al₂O₃·3 H₂O. There is also a version with a slightly different crystal structure, called Bayerite.

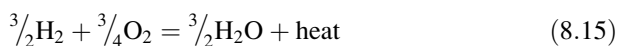
The behavior of this ternary system can be understood by use of the ternary phase stability diagram for the H–Al–O system shown in Fig. 8.7. The principles and methods that can be used to draw and quantitatively interpret such figures will be described in Chap. 12.

The driving force for this reaction, assuming that all species are at unit activity can be calculated from the values of their Gibbs free energy of formation. Using the data in Table 8.5, this is found to be –443.8 kJ per mol of aluminum at 300 K. This value will vary somewhat with temperature, of course.

Similarly, the magnitude of the heat produced by this reaction at 300 °C can be calculated from the respective values of their standard enthalpies. This is found to be 435.9 kJ per mol of aluminum.

In addition to the heat released in this reaction, the hydrogen product can also be subsequently oxidized to produce further heat. This can be done either at the same location or elsewhere, of course.

This second reaction, the combustion of the hydrogen formed, is simply



From the enthalpy data in Table 8.5 it can be found that the heat released in this second reaction is 428.7 kJ for the 1.5 mol of hydrogen produced at 300 °C. Thus the overall amount of heat produced from the aluminum is 864.6 kJ per mol of aluminum.

It is useful to consider why it is possible to produce hydrogen and Gibbsite by the reaction of aluminum with water, rather than forming Al_2O_3 , which would block further reaction. This can be seen by looking at the ternary phase stability diagram in Fig. 8.7. As will be discussed in Chap. 12, the overall composition during the reaction of aluminum with water moves along the dashed line in Fig. 8.7, starting at the point representing the composition of water.

As aluminum is added, the overall composition first moves into the composition triangle that has H, H_2O and $\text{Al}(\text{OH})_3$ at its corners. In this composition regime the activity of the aluminum is low. When the overall composition crosses the line between $\text{Al}(\text{OH})_3$ and hydrogen and enters the triangle whose corners are Al_2O_3 , $\text{Al}(\text{OH})_3$ and H, the aluminum activity is much greater. Upon crossing into the triangle Al, Al_2O_3 , and H, the aluminum activity becomes unity. The phase Al_2O_3 is present in either of the latter triangles, and will form, blocking further reaction.

Thus the condition for the absence of a protective layer of Al_2O_3 is that the aluminum activity must be smaller than a critical value. This is accomplished by dissolving it into the liquid alloy.

The use of this very powerful approach to understanding reactions in ternary phases will be discussed much more completely in Chap. 12, and used in both understanding and predicting the potentials and compositional ranges of electrodes in battery systems in subsequent chapters.

Since aluminum from the alloy is consumed in the reaction to form hydrogen and Gibbsite, it must be replenished in order for the reaction to continue. This can easily be done merely by putting solid aluminum in contact with the alloy. The protective Al_2O_3 skin is decomposed, and aluminum dissolved into the liquid alloy.

Subsequent to the discovery that dilute low temperature liquid aluminum alloys can react with water to produce hydrogen gas, it has been found that solid aluminum alloys containing some 5 % of a ternary Ga–In–Sn alloy will also react with water to form hydrogen and finely divided Gibbsite [3–6].

Although gallium dissolves somewhat in solid aluminum, this is essentially not true in the cases of indium and tin. On the other hand, aluminum dissolves slightly in a liquid solution containing all three of these elements. By use of compositions in this ternary system it is possible to obtain aluminum-containing liquids at ambient temperature.

When used as components in alloys that are mostly aluminum, this low-melting phase resides at the aluminum grain boundaries. This grain boundary region becomes liquid at temperatures not far above ambient. When such alloys are in contact with water, it is believed that aluminum in the liquid grain boundary phase

reacts with water, forming hydrogen and Gibbsite. As the grain boundary aluminum is reacted, it is replenished by the solution of more of the adjacent solid aluminum phase of the alloy, allowing this reaction to proceed further.

The use of such solid aluminum alloys, instead of aluminum-containing low-melting metals, has significant practical advantages. Such alloys can be readily stored and transported, so that hydrogen and heat can be generated at any location where water is available. The weight of the water is about twice that of the alloy per unit of hydrogen produced.

There are a number of aspects of this method for the production of hydrogen that are quite favorable. It is not necessary that either the aluminum or the alloy constituents be of high purity. No additional materials or electrical power are required. It can also be used as a reserve system to generate hydrogen (and heat) only when needed.

Aluminum is relatively abundant and inexpensive. It is used in many products. This results in the accumulation of a large amount of scrap aluminum. This scrap is generally not reprocessed, for it is generally cheaper to produce more aluminum from the alumina (aluminum oxide) that is extracted from bauxite ore. The result is that there is an immense, and growing, amount of inexpensive scrap aluminum in the world. One estimate was that this currently amounts to about 400 billion kilograms [6].

The Al_2O_3 that is formed by this process can be recycled by electrolysis in the same way that aluminum is produced from its natural oxide ore, bauxite. The Ga-In-Sn alloy is not consumed in this reaction, so that it is completely recoverable.

The specific energy of this system is attractive, 1170 Wh/kg, counting the alloy and water weights, but not considering the weight of the container and any other system components.

However, because of the weights of the aluminum and water, the weight efficiency of the production of hydrogen is not especially attractive—only 3.6 % hydrogen by weight, so such a system is not interesting for on-board vehicle use.

8.2.6 Additional Approaches to the Production of Hydrogen

Another option that has been pursued somewhat has involved the processing hydrocarbons through an electric arc, whereby they decompose to form carbon and hydrogen at temperatures over 1600 °C.

In addition, there has been a considerable amount of research on the possibility of the use of *photoelectrolysis*, in which solar energy is used to decompose water directly, or *photoelectrochemical cells*, in which solar energy is employed to reduce the necessary applied voltage in electrically-driven cells. Although these are very active areas of investigation [7–11], they will not be discussed here.

8.3 Governmental Promotion of the Use of Hydrogen

In 2003 the President of the USA announced a major Hydrogen Fuel Initiative to accelerate the research and development of technologies needed to support hydrogen-powered fuel cells for use in transportation and electricity generation. The underlying objective of this program was to decrease air pollution resulting from the use of petroleum. This program resulted in a significant increase in the amount of research and development on both hydrogen-based fuel cells and on-vehicle hydrogen storage. The proposed budget was \$ 1.2 billion over a span of five years, to be used to develop hydrogen production, delivery, storage and fuel cell technologies to enable the automobile and energy industries to commercialize fuel cell vehicles and the hydrogen fuel infrastructure. The general assumption was that hydrogen-powered vehicles should have performance equal or superior to current gasoline-consuming vehicles.

One aspect of this was the achievement of a practical driving range of at least 300 miles for light-duty vehicles. This resulted in the development of targets for the performance of on-board hydrogen storage systems in terms of weight, volume and cost, as well as operating parameters. The more important targets for 2010 are shown in Table 8.6. It has been assumed that meeting these goals would make it possible for some smaller and lighter vehicles to achieve the desired performance. Even more challenging targets have been proposed for the year 2015 that would be appropriate for the full range of light-duty vehicles in North America.

In arriving at these targets it was assumed that fuel cell power plants would have a factor of 2.5–3 times greater efficiencies than current gasoline-powered vehicles. It was also assumed that 5–13 kg of hydrogen would be necessary for fuel cell-driven vehicles, and that 1 kg of hydrogen can contribute about the same amount of energy as 1 gal of gasoline.

Consideration of the magnitudes of some of these parameters is instructive. For example, if hydrogen is stored on board in metal hydrides instead of in high-pressure tanks, care must be taken when recharging them because the reaction of hydrogen with metal hydride materials is typically highly exothermic.

Table 8.6 US Dept. of Energy hydrogen storage system performance targets for year 2010

System parameters	Year 2010 targets
Specific energy from H ₂	2 kWh/kg or 6 wt% H ₂
Energy density from H ₂	1.5 kW/l
Operating ambient temperature	–30 to 50 °C
H ₂ delivery temperature	–40 to 85 °C
Cycle life (25–100 %)	1,000 cycles
Minimum delivery pressure	4 atm (fuel cell) or 35 atm (ICE)
Recharging time (for 5 kg H ₂)	3 min
Minimum flow rate	0.02 g/s per kW

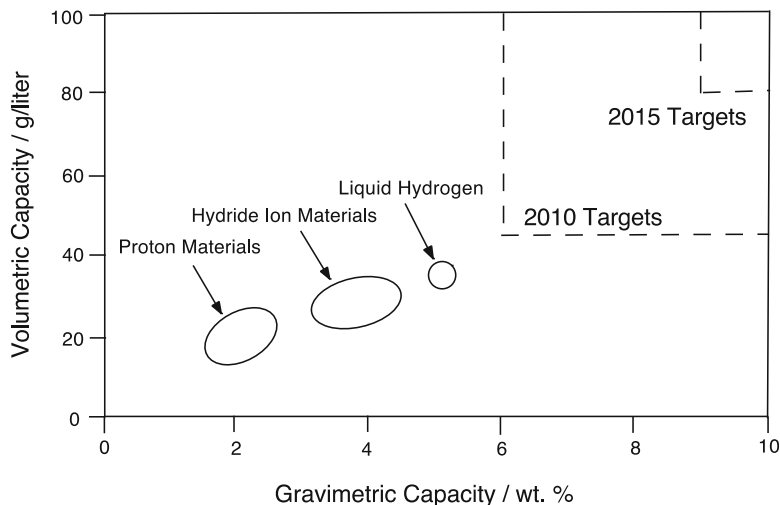


Fig. 8.8 Parameters of current hydrogen storage technologies, related to DOE targets

A material that has a reaction enthalpy of 30 kJ/mol of hydrogen will generate 400 kW of heat if it reacts with 8 kg of hydrogen in 5 min. This heat would obviously have to be removed somehow.

In addition, a fuel cell operating at 80 kW requires a hydrogen flow rate of 1.6 g/s. Therefore the generation of this hydrogen from metal hydrides, which is discussed below, will require an equivalent amount of heat input. As a result, system thermal management can become critical.

These Department of Energy targets are very ambitious, and will require materials with properties significantly better than those presently available, as well as innovative system designs. A rough picture of the current status and future targets is given in Fig. 8.8.

As will be discussed in Chap. 21, it is likely that serious attention will have to be given to compromises that are similar to some of those presently being considered for battery-propelled vehicles, such as plug-in hybrids.

As mentioned above, one of the problems that could limit the rapid expansion of the use of hydrogen-propelled vehicles is the current lack of a large-scale hydrogen support infrastructure. Another is the amount of hydrogen that would be needed if a significant number of vehicles were to be converted to hydrogen propulsion. It was estimated [12] that one million fuel cell-propelled vehicles would consume about 0.4 million tons of hydrogen per year. The magnitude of this becomes evident when it is compared with the fact that the total hydrogen production in the USA is currently about ten million tons. It should also be remembered that the production of hydrogen from natural gas causes about as much pollution as burning it directly.

8.4 Current On-Board Hydrogen Storage Alternatives

It has become recognized that the problem of carrying the hydrogen fuel in the vehicle is the critical issue. Three different approaches have been pursued by the auto industry to date. Each of these has potential advantages and disadvantages, as will be discussed below.

8.4.1 *Storage of Gaseous Hydrogen in High-Pressure Tanks*

An obvious method for storing hydrogen involves containment at high pressure in tanks. Although such tanks have traditionally been made of steel, fiber-reinforced composite materials have recently been developed that can withstand internal pressures up to 5,000–10,000 psi (340–680 atm). Hydrogen gas, even at these high pressures, has a relatively large volume, about twice that of liquid hydrogen.

This topic was discussed briefly in Chap. 6, where it was pointed out that, according to the ideal gas law, the amount of gas that is stored in a fixed-volume tank is proportional to the pressure. In addition, attention must be given to the thermal effects. Rapid charging of a tank with hydrogen is almost adiabatic (without heat exchange with the surroundings), so that a large amount of heat can be generated, giving rise to high temperatures. If the discharge of the gas from the tank into a fuel cell, for example, is relatively slow, so that heat transfer to the environment can occur, this reverse process is not so adiabatic, and the resulting cooling may not be important.

8.4.2 *Storage of Liquid Hydrogen in Insulated Tanks*

Hydrogen can be liquefied by cooling. Its boiling point at 1 atm is 20.3 K.

It can be contained and transported in liquid form in thermally-insulated containers.

Hydrogen gas can be readily obtained by applying heat so as to raise the local temperature above the liquid/gas transition. Demonstration vehicles were constructed by the auto firm BMW some years ago in which this method was used for the storage of hydrogen. The hydrogen was combusted in a slightly modified internal combustion engine. A significant disadvantage in this approach is that the process of liquefaction requires some 30–40 % of the final energy content of the hydrogen.

8.4.3 *Storage of Hydrogen as Protons in Solids: Metal Hydrides*

The third approach is to reversibly absorb hydrogen in solid metal-hydrogen compounds, called *metal hydrides*.

Hydrogen reversibly dissolves in a number of solids, and in some cases to surprisingly high concentrations. The reason why this is possible is that the hydrogen is present in them as protons (H^+) ions, not as hydrogen atoms or hydride (H^{-1}) ions. The electrical charge in solids must always be balanced, so the charged due to the presence of protons is balanced by the presence of an equal number of extra electrons. Thus these materials are always good electronic conductors.

The capacities of such materials depend upon the amount of hydrogen that they can absorb in their crystal structures. This is directly analogous to the absorption of lithium into the electrode materials commonly used in lithium batteries, a topic that is discussed in Chap. 18.

Protons are very small, and easily fit into the interstices (spaces) between the other atoms present. An example of this is the metal alloy $LaNi_5$. It can absorb up to six hydrogen atoms per mol, to form $LaNi_5H_6$. Another example is the alloy $FeTi$, which can absorb two hydrogen atoms per mol, forming $FeTiH_2$. The hydrogen densities of these materials, which can absorb up to one hydrogen atom per metal atom, are 5.5×10^{22} and 5.8×10^{22} atoms of hydrogen per cm^3 , respectively. These are greater than the density of liquid hydrogen, which is 4.2×10^{22} atoms cm^{-3} . Thus the storage of hydrogen in such materials is very attractive from a volumetric standpoint.

Despite the fact that the hydrogen is present as positively charged ions (protons) such hydrogen-containing metallic alloys are generally called metal hydrides. A number of them are widely used as negative electrode reactants in aqueous electrolyte batteries. The most common examples are the hydride/"nickel" cells that are used in many small applications, as well as the battery component of some hybrid automobiles. One of their especially attractive properties is the high rate at which they can be charged and discharged. This topic will be discussed in some detail in Chap. 16.

Such metal alloy hydrides are certainly candidates for use for hydrogen storage in vehicles. Their major disadvantage, however, is that the presently known materials are too heavy, and do not meet the weight requirements for use in vehicles. As an example, the solid hydride materials that are now employed in the ubiquitous small hydride/"nickel" batteries used in many electronic devices store only about 2–3 % hydrogen by weight. This is far from the 6 % target of the Department of Energy mentioned earlier. There is also some concern about the cost and large-scale availability of some such materials.

Vehicles with hydrogen-powered internal combustion engines, in which the hydrogen was stored in metal hydrides, were demonstrated some years ago by Mercedes Benz. In addition to the matter of cost, the primary problem with hydrogen storage in metal hydrides is the relatively small amount of hydrogen

that they can store per unit weight. Brief mention was also made in Chap. 1 of the use of such metal hydrides as hydrogen storage media in fuel cell-propelled submarines. In that case, the volume of the hydrogen-absorbing material, a titanium-manganese alloy, is important, but the weight is not.

8.5 Other Approaches to Hydrogen Storage

In addition to the approaches that have been followed to date in the automobile industry, there are some other approaches to hydrogen storage that might deserve some consideration, for either the vehicle, or other, applications. Two of these are described briefly below.

8.5.1 *Hydrogen from the Decomposition of Materials Containing Hydride Anions*

Another alternative strategy that is being employed for hydrogen storage involves materials in which the hydrogen is present in the form of hydride (H^-) ions, instead of protons. Whereas protons are very small, and can readily dissolve in a number of metal alloys, hydride ions are large, with an ionic radius of 146 pm, which is close to the size of oxide (O^{2-}) ions. Materials containing hydride ions are quite ionic, rather than metallic, in character, and thus have low values of electronic conductivity. The large hydride ions typically have very low mobilities within their crystal structures.

There are two families of materials containing hydride ions that have received a lot of attention as possible hydrogen storage media. One of these is the *borohydride* family, which can be represented by the general formula M^+BH_4^- , where the species M^+ can be Li^+ , Na^+ , or K^+ or NH_4^+ . LiBH_4 can theoretically store 13.9 wt% hydrogen, whereas NaBH_4 contains 7.9 wt% hydrogen.

There is an analogous family of materials, in which the boron is replaced by aluminum. These materials are called *alanates*. A further group of materials are the boranes, which have the general formula NH_nBH_n , where n can range from 1 to 4. One member of this group is amine borohydride, NH_4BH_4 , which has a hydrogen mass ratio of 24 % has received attention [12–14]. This material decomposes in several stages as it is heated, giving off about 6 % of its mass in each step. This is shown in Table 8.7.

Although their hydrogen capacities are quite high, there is a serious practical problem with materials of this general type, for they are not reversible. Hydrogen cannot be simply reacted with them so as to return them to their initial state, as can be done with the common proton-containing metal hydride materials. There is some

Table 8.7 Multi-step decomposition of amine borohydride

Reaction	Wt % H ₂ change	Temperature/°C
$\text{NH}_4\text{BH}_4 = \text{NH}_3\text{BH}_3 + \text{H}_2$	-6.1	<25
$\text{NH}_3\text{BH}_3 = \text{NH}_2\text{BH}_2 + \text{H}_2$	-6.5	<120
$\text{NH}_2\text{BH}_2 = \text{NHBH} + \text{H}_2$	-6.9	<155
$\text{NHBH} = \text{BN} + \text{H}_2$	-7.3	>500

hope that a method might be found for this, however, based on some recent work on titanium-based catalysts [15].

If that cannot be done, they must undergo a chemical reconstitution. This will require their removal from the vehicle and replacement by a new chemical charge. The chemical process to regenerate such hydride-ion materials will probably most effectively be done in large central chemical plants. But then there must also be a system for the transportation of the spent and renewed materials. This requirement for external chemical regeneration constitutes a major disadvantage of this approach.

A similar chemical regeneration requirement led to the demise of the highly touted proposal to use zinc/air batteries for vehicle propulsion some years ago. Although the reaction between zinc and oxygen to form ZnO provides a lot of energy per unit weight, a method for this cell to be electrically recharged was not known. The result was that the discharged battery electrodes had to be shipped to a chemical plant for the conversion of the ZnO product back to elemental zinc. The shipping and chemical processes used to reconstitute the zinc electrodes combined to make this approach unfeasible.

The major problem has traditionally been the ready formation of zinc dendrites when zinc is electrochemically recharged. There has been some recent work aimed at avoiding this problem that involves the use of a solid polymer electrolyte, rather than the conventional aqueous electrolyte.

8.5.2 Ammonia and Related Materials as Hydrogen Storage Media

Another possible approach to consider is the use of ammonia, NH₃, which is 17 % hydrogen by weight. It is possible to thermally decompose ammonia at modest temperatures. This is seen from the data shown in Fig. 8.9, where it can be seen that, at one atmosphere pressure, ammonia decomposes into its elements at about 460 K (187 °C).

Consideration is also being given to the use of more complex materials that can decompose to form NH₃, which can then be further decomposed to provide hydrogen. Metal amines, in which ammonia is coordinated to a metal ion, are one type of such materials. An example is Mg(NH₃)₆Cl₂ [16].

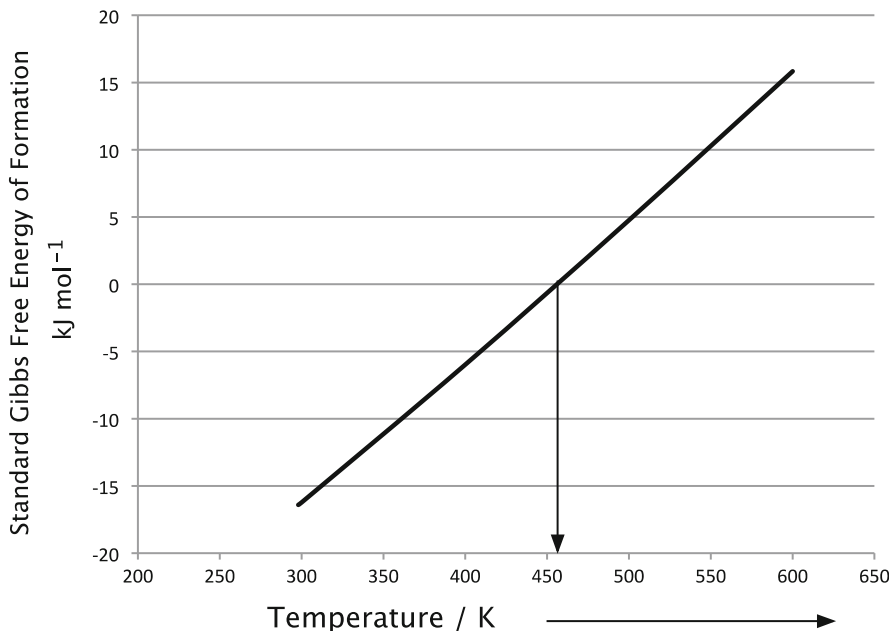


Fig. 8.9 Temperature dependence of the standard Gibbs free energy of formation of ammonia, NH_3

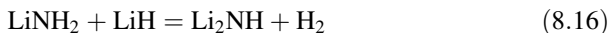
Table 8.8 Standard Gibbs free energy of formation data for phases in the Li–H–N system

Phase	ΔG_f^0 at 298 K (kJ mol^{-1})
Li_3N	-122.2
LiH	-70.0
NH_3	-16.4
Li_2NH	-169.9
LiNH_2	-140.6
H_2	0

Another concept is the use of a material containing hydrogen that might react with another material and give off hydrogen as one of the reaction products. One example of this type that has been proposed is lithium amide, LiNH_2 , with the expectation that it would react with LiH to form lithium imide, Li_2NH and hydrogen.

The feasibility of this concept can be evaluated from thermodynamic data related to the phases concerned. Values of the standard Gibbs free energy of formation for the pertinent phases in the lithium-hydrogen-nitrogen system at 298 K [17] are included in Table 8.8.

The proposed reaction can be written as



The sum of the ΔG_f^0 values of the phases on the left is $-210.6 \text{ kJ mol}^{-1}$, and of the phases on the right is $-169.9 \text{ kJ mol}^{-1}$. Therefore this reaction will tend to go to the left, not the right. Thus this concept makes no sense at that temperature.

8.5.3 Storage of Hydrogen in Reversible Organic Liquids

In addition to solid materials that absorb hydrogen as protons to become metal hydrides, or already contain hydrogen in the form of hydride anions, it is reasonable to also consider the use of liquids. Many organic liquids have large, and often variable, amounts of hydrogen present in their structures.

If everything else were the same, one potential advantage of the use of liquids as hydrogen-carriers is the assumption that such materials could be inexpensively stored in tanks, and pumping them in and out should be no great problem.

In some countries, such as Switzerland, that have surplus hydropower during part of the year, a large-scale method for the storage of some of this energy for use at other times of the year could be valuable. One possible method for such large-scale and long-term energy storage by the use of organic hydrides was proposed some time ago [18]. This concept involves the electrolytic production of hydrogen when electricity is readily available and inexpensive, and reacting it with a simple organic molecule to produce a product containing more hydrogen. The species with the higher hydrogen content could later be treated such that the hydrogen is released.

The simplest example would be the conversion of benzene (C_6H_6) to form cyclohexane (C_6H_{12}). Benzene is a simple aromatic molecule, in which each of the carbon atoms in the 6-member ring is bonded to one hydrogen atom. In cyclohexane each carbon has two hydrogen neighbors. This possibility cannot be seriously considered for actual use, however, because benzene is considered to be a carcinogen.

Thus it is preferable to use toluene (C_7H_8), and to produce methylcyclohexane (C_7H_{14}) by the reversible addition of six hydrogen atoms per molecule. Both of these liquids can readily be stored in large tanks. They are inexpensive and convenient liquids that are easy to transport and store, with freezing temperatures that are convenient, 178 K and 146.4 K, respectively.

It can readily be seen that the weight of the hydrogen stored in this case is 6.5 % of the weight of its carrier, the toluene. This is substantially better than the comparable values for the solid metal hydrides.

The volumetric density of hydrogen is also important. Methylcyclohexane contains 47.4 g of H_2 per liter. The hydrogen density in gaseous hydrogen varies with the pressure and temperature according to the ideal gas equation, of course. At 200 bar it is only 18 g H_2 per liter.

Both the hydrogen-addition and the hydrogen-deletion processes require catalysts. The conversion of toluene to methylcyclohexane, a well-known large-scale

industrial process, is exothermic, and the reverse reaction, which takes place at 400 °C, is endothermic, so heat has to be supplied at a relatively high temperature when extracting the hydrogen. This hydrogenation cycle has a round trip efficiency of about 80 %.

An example of the use of this concept [19] involved installation in a 17-ton truck in Switzerland. The hydrogen obtained from the onboard catalytic splitting of methylcyclohexane was used as the fuel for its 150 kW internal combustion engine. Hydrogen was injected at 10 bar pressure, and resulted in an engine efficiency of 32 %. In an analysis of costs some years ago [20], this scheme for the storage and use of energy was found to be economically competitive with other carbon-free large-scale energy storage methods, as well as with the cost of the construction of additional hydro-power facilities at that time.

Other covalent organic materials with larger molecular structures can also be considered for this purpose, including perhydrofluorene and several species in the carbazole family [21].

An additional interesting feature of the reversible liquid hydrogen systems has to do with their potential use for the transmission of energy over long distances using simple, low-cost pipelines. This has been pioneered as a method to get energy to geographically remote areas in Russia and Brazil, and is illustrated schematically in Fig. 8.10.

Electrical power transmission through wires involves both resistive and capacitive losses that increase linearly with distance, reducing the overall efficiency of the electrical transmission system. These losses can be appreciable if energy is sent over long distances. On the other hand, the losses that are involved in the transport of liquids through pipelines are relatively small.

As a result, there is a critical distance over which energy can be transmitted more economically by fluids in pipelines than by electrical lines. In one study, the breakeven point was at 1400 km. At longer distances the use of the reversible liquid cycle is more effective.

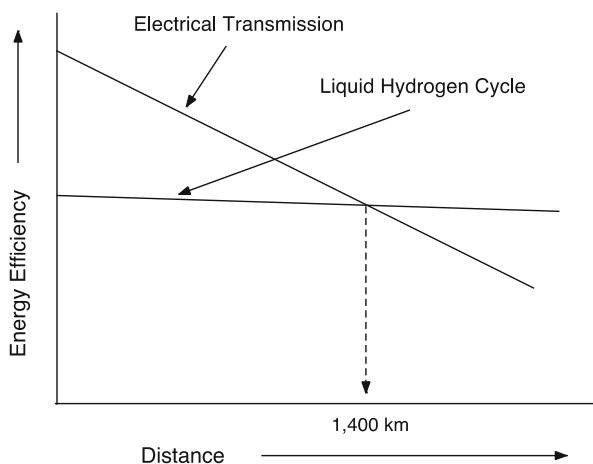


Fig. 8.10 Energy transmission efficiency vs. distance

8.6 The Question of Safety

Almost everyone knows that hydrogen readily burns in air, and with a flame that is almost colorless. Those working with hydrogen are always cautioned to keep it away from open flames. Attention to this potential problem rapidly became widespread after the widely publicized burning of the large Hindenburg zeppelin in New Jersey in 1937.

It is important to give this potential safety problem some attention. The ignition temperature of hydrogen in air is 585 °C at one atmosphere pressure. Thus there is no problem with having a mixture of these gases at ambient temperature. At elevated temperatures the composition range within which flammability is possible is between 4 and 75 % hydrogen by volume.

The density of hydrogen gas is low, only 0.08, so that it rises rapidly in air. This reduces the possibility of reaching the flammability compositional range in open spaces. In enclosed spaces hydrogen tends to accumulate at the highest locations, i.e., near the ceilings of rooms.

The safety question was raised some years ago, when BMW was demonstrating a hydrogen-powered demonstration auto in which the hydrogen was carried as a liquid in an insulated tank. It was contended that any hydrogen that got free would rise so rapidly that its possible combustion would not be a threat.

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