Hydrogen

What is hydrogen?

Hydrogen is one of the elements, as are helium, carbon, nitrogen, oxygen, neon, sodium, aluminum, sulfur, chlorine, potassium, iron, nickel, copper zinc, silver, platinum, gold, mercury, and uranium, to name only twenty of the first ninety two elements, or atomic “building blocks”, of which all matter is composed.

Hydrogen atoms

Hydrogen atoms are the lightest of the atoms, with a relative mass of 1, while, of the atoms just named, uranium atoms are the heaviest, with a relative mass of 238. Between hydrogen and uranium are helium atoms, of relative mass 4; carbon atoms, of relative mass 12; oxygen atoms, of relative mass 16; and so on, as is recorded in any “Periodic Table” of the elements.

Hydrogen molecules

Hydrogen atoms, H, however, actually travel in pairs, as diatomic *molecules*, with a relative *molecular* mass of 2.

H—H

a representation of a hydrogen molecule

A less well known fact is that there are two forms of molecular hydrogen, the “ortho” form and the “para” form. These forms differ by the relationship between a property of each atom called “spin”.

The form of the molecule in which the two hydrogen atoms have their spins aligned is called the ortho form, while the form of the molecule in which the two hydrogen atoms have their spins opposed is called the para form. At room temperature, when hydrogen is present as a gas, 75% of the hydrogen molecules will be in the ortho form, with 25% being in the para form.

At the temperature of liquid hydrogen, however, 99.8% of the hydrogen molecules will be in the para form.

The conversion of ortho hydrogen to para hydrogen during liquefaction is a critical part of the process of liquefaction of hydrogen gas.

Other molecules

Nitrogen atoms and *oxygen* atoms also travel in pairs, as diatomic molecules. The relative molecular mass of a nitrogen molecule, N_2, is 2 x 14, or 28, and the relative molecular mass of an oxygen molecules O_2, is 2 x 16, or 32. *Carbon* atoms appear in even more combinations. *Graphite*, which is pure carbon, has a structure wherein the carbon atoms are connected in layers. The layers are free to move across one another, which accounts for the slippery, or lubricating, properties of graphite. On the other hand *diamond*, which is also pure carbon, has a three-dimensional structure in which all the carbon atoms are connected so as to form a single big molecule. The fact that a perfect diamond is a single molecule accounts for the great strength of diamond. Then there are the more recently discovered allotropic forms of carbon, C_{60} and C_{70}.

In contrast, *helium* atoms never travel in pairs, occurring only as monatomic particles of relative mass 4.

Although *coal* is mostly carbon the presence in coal of atoms of nitrogen, oxygen, and sulfur leads to a complex molecular structure for coal.

Occurrence of hydrogen

We are told that hydrogen is the most abundant element in the universe, with about 87% of all atoms being hydrogen atoms. In second place is helium, with a relative abundance of about 12%. The remaining 1% corresponds to the atoms of all the rest of the elements.

The distribution of these elements, however, is far from even, and the details of their distribution are a story in themselves.

Composition of air

The main constituents of dry air are nitrogen molecules, at 78.084% relative particle concentration, and oxygen molecules, at 20.947% relative particle concentration. Argon atoms come next at 0.934% relative particle concentration. These three elements together account for approximately 999,650 particles, atoms or molecules, out of every million particles of air. Only about 350 particles per 1,000,000 particles are not yet accounted for.

Minor components of air

At this time there are, on the average, about 320 molecules of carbon dioxide per million particles of air. Similarly, there are about 18 atoms of neon, 5 atoms of helium, 2 molecules of methane, 1 atom of krypton, 1 molecule of sulfur dioxide, and about half a molecule each of nitrous oxide and hydrogen in each million particles of air.

There is also a variable amount of water vapor in the air and, on some occasions, small amounts of ozone, nitrogen dioxide, carbon monoxide, or ammonia can be present.

Abundance of elemental hydrogen

As we have just seen, there is no useful amount of elemental hydrogen in air.

Useful amounts of both nitrogen and oxygen are obtained by the liquefaction of air, and, as a byproduct of these efforts, useful amounts of neon, argon, and krypton are also obtained from air.

In contrast, almost all methane is obtained from natural gas, as is all helium, which occurs in low concentration in some sources of natural gas.

Air has never been a source of hydrogen gas.

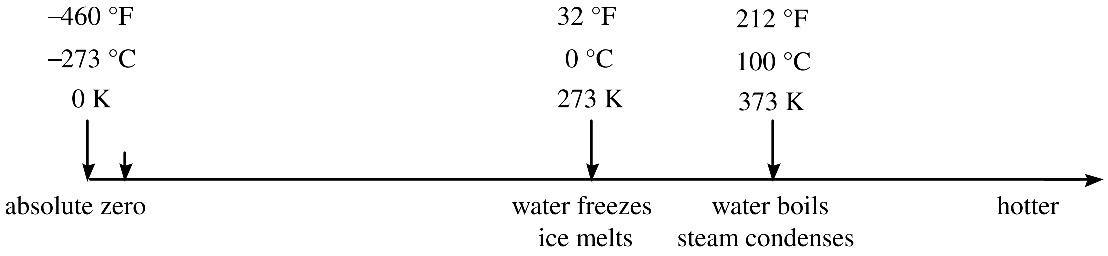
Properties of hydrogen

Under ordinary conditions hydrogen is a gas, as are nitrogen, oxygen, and all the other components of air. Hydrogen can be liquefied, however, and in this way be reduced in volume. For example, 844 gallons of hydrogen gas at room temperature can be reduced to a volume of only 1 gallon of liquid hydrogen. Liquefaction, however, is not easy, however, as the temperature required for liquefaction, 20 degrees Kelvin, is well below even the freezing points for both nitrogen and oxygen.

An aside on temperature scales

The two scales of temperature that are used in “ordinary” life, the Fahrenheit scale and the Celsius scale, differ from the scale of temperature used in “scientific” life. The scientific scale, or Kelvin scale, takes as the zero of temperature the temperature at which no heat remains to be removed. This temperature is 273 degrees below the zero of the Celsius scale, where zero is the temperature at which water freezes and ice melts, and 460 degrees below the zero of the Fahrenheit scale.

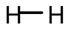
We can represent the relationships among these three temperature scales in this way.



The small arrow indicates the temperature at which hydrogen will become a liquid. You might wonder how you can get hydrogen gas cold enough to condense.

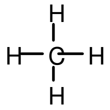
Production of hydrogen

As we have seen, there is no free hydrogen. There are no "hydrogen mines", as there are coal mines; there are no "hydrogen wells", as there are gas wells or oil wells. All hydrogen is found in combination with other elements. The main constituent of natural gas, methane, is carbon in combination with hydrogen, and, of course, water is oxygen in combination with hydrogen.



hydrogen

"free" hydrogen



methane

combined hydrogen

water

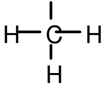
combined hydrogen

If there is to be any free hydrogen it must be obtained from a source of combined hydrogen.

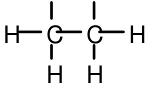
Sources of combined hydrogen

While the most obvious source of combined hydrogen is water, abundantly available in lakes, streams, and oceans, as well as "water wells", only a small amount of hydrogen is produced from water.

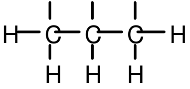
At this time the most widely used source of combined hydrogen is natural gas, mostly methane, and other petroleum hydrocarbons such as ethane and propane.



methane



ethane



propane

The steam reforming reaction

The most common method by which hydrogen gas is produced from petroleum hydrocarbons is *steam reforming*, a process in which the hydrocarbon is treated with water vapor, that is, *steam*, at high temperature and high pressure to give carbon monoxide gas and hydrogen gas.

In the case of methane the steam reforming reaction can be represented in this way.

$$\underset{\textbf{Methane}}{CH_4} + \underset{\textbf{water}}{H_2O} + \underset{\textbf{heat}}{191.7\ \text{kJ/mol}} \xrightarrow{1000\ ^\circ C} \underset{\substack{\textbf{carbon}\\ \textbf{monoxide}}}{CO} + \underset{\substack{\textbf{hydrogen}\\ \textbf{molecules}}}{3\ H_2}$$

steam reforming reaction

Overall, the carbon atom takes the oxygen atom from the water molecule, forming carbon monoxide, and the 6 hydrogen atoms left over combine to form three hydrogen molecules. The reaction requires a high temperature and consumes heat, 191.7 kilojoules of heat per mole, or 16 grams, of methane converted. The high temperature and the heat, or thermal energy, are provided by, in a separate process, the burning of natural gas, which is mostly methane.

The water-gas shift reaction

Additional hydrogen can be obtained by treating the carbon monoxide formed in the steam reforming reaction with lots more water at a lower temperature. This reaction, the *water-gas shift reaction*, can be represented as follows.

$$\underset{\substack{\textbf{carbon}\\ \textbf{monoxide}}}{CO} + \underset{\substack{\textbf{water}\\ \textbf{(in excess)}}}{H_2O} \xrightarrow{130\ ^\circ C} \underset{\substack{\textbf{carbon}\\ \textbf{dioxide}}}{CO_2} + \underset{\substack{\textbf{hydrogen}\\ \textbf{molecule}}}{H_2} + \underset{\textbf{heat}}{40.4\ \text{kJ/mol}}$$

water-gas shift reaction

Again, the carbon atom takes the oxygen atom from the water molecule, this time forming carbon dioxide gas, and the left over hydrogen atoms again combine to form a hydrogen molecule. This second reaction is run at a relatively low temperature and is slightly exothermic.

At this time, about 95% of the hydrogen produced in this country is made by this combination of reactions: steam reforming followed by water-gas shift. The overall process, for methane, can be represented in this way.

$$CH_4 + 2\ H_2O + 151.3\ \text{kJ/mol} \longrightarrow CO_2 + 4\ H_2$$

Energy efficiency

Although the energy content of the hydrogen produced in these two reactions is greater than the energy content of the methane converted, the overall "energy efficiency" of the process drops to about 70% when the calculation includes *both* the energy of the methane used to provide the heat for the steam reforming step *and* the energy of the methane converted to hydrogen in the reaction.

An aside on energy efficiency

Energy efficiency is a fraction. This fraction is the energy that is produced divided by *both* the energy consumed by the process (energy of agency) *and* the energy of the materials that are transformed (energy transformed). The more nearly the fraction is to one the greater the energy efficiency.

$$\text{energy efficiency} = \frac{\text{energy produced}}{\text{energy of agency} + \text{energy transformed}}$$

In the production of hydrogen just described the energy efficiency equals the energy of the hydrogen that is produced divided by the energy of the methane burned to provide the required heat (energy of agency) *and* the energy of the methane that was converted to hydrogen (energy transformed).

The energy efficiency can never be greater than one. The only time that energy efficiency comes close to 1 is in the production of heat, thermal energy, from any other form of energy.

If someone suggests that an energy conversion process has an energy efficiency of greater than one you know that they are leaving out some of the energy consumed in the process. It's like currency exchange: you can never come out ahead, and you usually lose.

An aside on energy balance

It appears that energy balance is not the same as energy efficiency. Whereas energy efficiency divides energy produced by *all* energy used, including that of the material transformed, energy balance divides the energy produced by only the energy requirements of the agency (energy of agency) that causes the transformation. In this reckoning the energy content of the material transformed is not included. The energy balance can be greater than 1.

$$\text{energy balance} = \frac{\text{energy produced}}{\text{energy of agency}}$$

An aside on "heating value"

A common way of estimating the energy content of a substance is to determine how much heat will be produced when a given amount of the substance is burned.

For example, the chart in front of me says that a gallon of "reformulated gasoline" will produce 113,602 Btu (British thermal unit) of heat when burned, and that a gallon of ethanol, ethyl alcohol, will produce 76,330 Btu of heat when burned.

The same chart, however, also says that a gallon of "reformulated gasoline" will produce 121,848 Btu of heat when burned, and that a gallon of ethanol, will produce 84,530 Btu of heat when burned.

The first set of numbers is *Lower Heating Values*, LHV, while the second set of numbers are *Higher Heating Values*, HHV.

Why are they different? The reason for the difference is that the LHV, or gross calorific value, is defined as the amount of heat released by burning a specified quantity, initially at 25 °C, and lowering the temperature of the combustion products, which contain steam, only to 150 °C. In this reckoning the heat that could have been recovered by condensing the steam to water *is not* counted.

In contrast, the HHV, or net calorific value, is defined as the amount of heat released by burning a specified quantity, initially at 25 °C, and returning the temperature of the combustion products, which contain steam, to 25 °C. In this reckoning the heat released by the condensation of steam to water *is* included. Thus the LHV (smaller number) and HHV (larger number) differ by the energy of vaporization/condensation of the water produced upon burning.

Formation of hydrogen from coal

If coal is a form of carbon how can coal give hydrogen? First, hard coal, or anthracite, contains about 3% hydrogen, and soft coal, bituminous coal, contains somewhat more than 3% hydrogen. Second, and more important, coal can be subjected to the water-gas reaction by heating it with steam. The consequent formation of hydrogen can be represented in this way.

$$\underset{\textbf{coal}}{\mathrm{C}} + \underset{\textbf{water}}{\mathrm{H_2O}} \xrightarrow{1000\ ^\circ\mathrm{C}} \underset{\substack{\textbf{carbon}\\\textbf{monoxide}}}{\mathrm{CO}} + \underset{\substack{\textbf{hydrogen}\\\textbf{molecule}}}{\mathrm{H_2}}$$

Then, in the water-gas shift reaction, more hydrogen is formed.

$$\underset{\substack{\textbf{carbon}\\\textbf{monoxide}}}{\mathrm{CO}} + \underset{\substack{\textbf{water}\\\textbf{(in excess)}}}{\mathrm{H_2O}} \xrightarrow{130\ ^\circ\mathrm{C}} \underset{\substack{\textbf{carbon}\\\textbf{dioxide}}}{\mathrm{CO_2}} + \underset{\substack{\textbf{hydrogen}\\\textbf{molecule}}}{\mathrm{H_2}}$$

Thus in the formation of “hydrogen from coal” most of the hydrogen actually comes from water.

However, so long as methane and natural gas are cheap and available, “hydrogen from coal” will account for only a few percent of hydrogen production in this country. At this time it is much cheaper and easier to make hydrogen from methane and natural gas.

Hydrogen as a byproduct

Some industrial processes produce hydrogen gas as a byproduct. Typically this hydrogen is captured and used in another process by the same company that produced it. The amount of hydrogen produced in this way exceeds, in this country, the amount of hydrogen produced from coal.

Electrolysis of water

The methods for the production of hydrogen just presented all start with a “fossil fuel”, either natural gas, other petroleum hydrocarbons, or coal. All, therefore, necessarily give carbon dioxide as a byproduct.

We now turn to a method of production of hydrogen gas that does not form carbon dioxide as a byproduct. This method is the electrolysis of water.

Normal chemical reactions

In chemical reactions as they are normally carried out the exchange of electrons that takes place occurs directly between the participants.

Batteries

In a battery, however, the electrons flow through an external wire, and, in doing so, the electrons can do something useful like run your calculator, or run your cell phone, rather than just produce heat.

When your battery runs down, you put it in the “recharger”, and the recharger forces the electrons to flow in reverse, “recharging” the battery for reuse.

Electrolysis of water

The electrolysis of water is the “recharging” of a gas battery in which the materials are not, for example, a pair of metals but a pair of gases, hydrogen and oxygen. The hydrogen-oxygen “gas battery”, was, in fact, one of the first batteries invented, by William Grove, in 1837, and at this point we are interested in the recharging of this battery.

In the recharging, or *electrolysis*, process electrons are pushed into one part of the “battery”, and drawn out of another part of the battery.

The cathode reaction

At the point in the battery where electrons are pushed in, the *cathode*, the electrons combine with protons in the battery to produce hydrogen gas. The process can be represented in this way.

$$\underset{\textbf{protons}}{4\ H^+} + \underset{\textbf{electrons}}{4\ e^-} \longrightarrow \underset{\textbf{hydrogen gas}}{2\ H_2}$$

cathode reaction

The anode reaction

At the point in the battery where electrons are pulled out, the *anode*, the electrons are removed from water molecules to produce oxygen gas and protons. The process can be represented in this way.

$$\underset{\textbf{water}}{2\ H_2O} \longrightarrow \underset{\textbf{oxygen gas}}{O_2} + \underset{\textbf{protons}}{4\ H^+} + \underset{\textbf{electrons}}{4\ e^-}$$

anode reaction

The overall electrolysis reaction

The overall reaction for the electrolysis of water is the sum of these two “half reactions”.

$$2\ H_2O \longrightarrow 2\ H_2 + O_2$$

What is special about electrolysis

The electrolysis of water differs in two important ways from “ordinary” chemical reactions. First, in an “ordinary” chemical reaction the electrons are transferred directly, by physical contact between the reacting species. In the electrolysis reaction, however, the electrons are transferred indirectly, by passage through a wire. Second, in electrolysis the direction of transfer of the electrons is opposite to that which would occur naturally. The electrons have to be “pushed” onto the protons and “pulled” from the water molecules. A minimum electron “pressure” or voltage of 1.23 volts is required to move the electrons to force the electrolysis of water. A higher voltage makes the process go faster, and a voltage of about 1.75 volts might be used in practice.

The reaction of hydrogen with oxygen

If left to itself water would never spontaneously separate into hydrogen gas and oxygen gas. The “natural” course of events is for hydrogen and oxygen to combine to form water; the tendency, that is, for hydrogen to burn. It is this tendency that is the basis of the hydrogen-oxygen engines of the space shuttle, the explosive nature of a mixture of hydrogen and oxygen in a balloon, the hydrogen-oxygen gas battery, and the hydrogen-oxygen fuel cell. The hydrogen-oxygen fuel cell is actually a type of battery. When an non-rechargeable battery runs down, you throw it away. When a rechargeable battery runs down, you put it in the recharger. When a fuel cell battery “runs down”, you add more fuel.

The energy efficiency of electrolysis

The minimum electron “pressure” required to cause hydrolysis is 1.23 volts. At this voltage the electrons will just barely start to flow. In order to have a useful rate of flow the electron pressure must be increased.

It’s like pumping water from the well up into the water tower. You can pump the water with just enough pressure to start the flow, but if you really want to fill the tower you need to increase the pumping pressure so as to overcome the resistance to flow and to pump the water faster. Thus, whether you are pumping electrons or pumping water, you must invest more energy to do the pumping than will be present in either the pumped electrons or the pumped water. The energy stored, as electrons or water at higher energy will be less than the energy of agency. The efficiency of the energy storage will be less than 1.

For the electrolysis of water the efficiency is the threshold voltage of 1.23

volts divided by the actual voltage used, typically about 1.75 volts. Thus the energy efficiency of electrolysis will be only about 70%. Only 70% of the electrical energy consumed by electrolysis will be present in the hydrogen and oxygen formed by hydrolysis. Thirty percent of the electrical energy consumed had to be used to overcome resistance so as to provide a reasonable rate of electrolysis.

$$\text{energy efficiency of electrolysis} = \frac{\text{threshold voltage}}{\text{actual voltage}} = \frac{1.23}{1.75} = 0.70$$

At this time in this country electrolytic hydrogen accounts for only one or two percent of all the hydrogen produced.

Use of hydrogen

About half of the hydrogen produced in this country is converted to ammonia, as indicated in this equation.

$$3\ H_2 + N_2 \xrightarrow[\text{high temperature}]{\text{high pressure}} 2\ NH_3$$

hydrogen **nitrogen** **ammonia**

The ammonia is then used as fertilizer, either by direct injection as anhydrous ammonia gas, “anhydrous”, into the soil, or by application as ammonium nitrate, other ammonium salts, or urea.

Most of the rest of the hydrogen is used in the “hydrocracking” operations of the petroleum industry. In “hydrocracking” some of the less easily processed fractions of crude oil are heated to a very high temperature, conditions under which larger molecules break into pieces, or “crack”, and then hydrogen atoms are put onto the ends of the new pieces. These new, and smaller, molecules are then sorted and sold as additional petroleum products.

Smaller amounts of hydrogen are used to make “partially hydrogenated” cooking oils.

The price of products made from hydrogen

In the case of ammonia and ammonia based fertilizers, where hydrogen is a major ingredient, any increase in the price of hydrogen will result in a similar increase in the price of the product.

In contrast, when hydrogen is a minor ingredient, as in hydrocracking or in the partial hydrogenation of cooking oils, an increase in the cost of hydrogen is not necessarily passed on to the consumer.

The price of hydrogen as fuel

The idea that hydrogen might be used as a fuel is, except for the space program, a new idea. If hydrogen does become a fuel that is sold directly by the public, the price of hydrogen to the consumer will vary with the cost of production of hydrogen plus the costs of storage, transportation, and delivery.

Thus for these reasons the price of hydrogen as a fuel will be greater and more variable than is now the case with hydrogen sold as a commodity.

We consider next the storage, transportation, and delivery of hydrogen.

Storage of hydrogen

Hydrogen, under normal conditions of temperature and pressure, is a gas. Under these same normal conditions gasoline is a liquid. Since gases are much less dense than liquids you might expect that it will take a larger volume of hydrogen gas to contain the same amount of energy as a smaller volume of gasoline. You would be right. An amount of hydrogen gas under normal conditions that would be equivalent in its energy content to one gallon of gasoline would require a volume of 3,107 gallons. Yes, that's right. The gasoline-energy-equivalent volume of hydrogen *gas* at atmospheric pressure is about 3,000 times larger than the volume of the gasoline.

In contrast, the gasoline-energy-equivalent volume of ethyl alcohol, another *liquid*, is only 1.35 times the volume of the gasoline.

Compressed hydrogen at 200 bar

Gases, for good reason, as you have just seen, are typically compressed and then stored under pressure.

When hydrogen is compressed to 200 bar, or to about 200 atmospheres, its volume is reduced by a factor of about 200. Thus the gasoline-energy-equivalent volume of hydrogen at 200 atmospheres should be only about 3,000/200 = 15 times the volume of the gasoline. However, the tank that holds this hydrogen must now resist a pressure of at least 200 atmospheres, or at least 200 x 15 = 3,000 pounds (1.5 tons) per square inch, not counting a safety margin of at least a factor of 2.

Tube tankers transport compressed hydrogen at this pressure.

Compressed hydrogen at 800 bar

If some compression is good, more compression might be better. The ultimate compression for hydrogen gas will be about 800 bar, or 800 times atmospheric pressure. At this pressure compressed hydrogen will have about the same density as liquid hydrogen, which is the limit for compression. At this density the gasoline-energy-equivalent volume of hydrogen is 3.6 times the volume of the gasoline.

Another way to say this is that the smallest possible gasoline-energy-equivalent volume for hydrogen is about 3.6 times greater than the volume of the gasoline. The hydrogen tank for a car that contains the gasoline-energy-equivalent of 15 gallons of gas will have to contain about 54 gallons of hydrogen gas at 800 bar, a pressure equivalent to 800 tons per square foot.

An aside on pressure

Just as the air around us can be characterized by its temperature, so the air can be characterized by its pressure. Just as a weather map will sometimes present lines that connect points of equal temperature, or *isotherms*, so a weather map will sometimes present lines that connect points of equal barometric pressure, or *isobars*.

Also, just as temperature can be reported in more than one way, in degrees Fahrenheit, or in degrees Celsius, or in Kelvins, so pressure can be reported in more than one way.

While there is considerable agreement that, as scientists, we will express temperature in Kelvins, there is no similar agreement about a standard expression of pressure.

If we were to talk about the weather we would express the pressure at various points on the earth as “millimeters of mercury” or “inches of mercury”.

To understand what we read about hydrogen, however, we need to know about four other commonly used expressions of pressure, and a fifth for emphasis.

The most familiar of these is the *atmosphere*, the typical, standard, or normal pressure of the air around us. We then need know that a *bar* is practically the same as an atmosphere, a *megapascal*, Mpa, is about one tenth of an atmosphere or bar, and that the pressure of the atmosphere corresponds to a force of 14.70 pounds applied to one square inch, 14.70 *psi*, or a force of 1.058 tons applied to one square foot, 1.058 *tsf*.

The first line of the following table presents “atmospheric pressure” in all five units. The conversion factors are given to four significant digits.

The other four rows of the table give *approximate* equivalents for commonly mentioned pressures. Thus: 200 bar is about 200 atmospheres, 20 megapascals, 3,000 pounds per square inch, and 200 tons per square foot.

Atm	**bar**	**Mpa**	**psi**	**tsf**
1.000	1.013	0.103	14.70	1.058
1	1	0.1	15	1
5	5	0.5	75	5
200	200	20	3000	200
700	700	70	10,000	700
800	800	80	12,000	800

Atm = atmosphere; bar = bar; Mpa = megapascal; psi = pounds per square inch; tsf = tons per square foot

Cryogenic , or liquid, hydrogen

Compression is not the only way to reduce the volume of a gas. The other way to reduce the volume of a gas is to make the gas colder. Cooling hydrogen from room temperature, 300 K, to 150 K will reduce its volume by half. Going half the remaining “distance” to absolute zero, or to 75 K, will reduce the volume by half again, to 1/4 of the original volume.

The good news is that when the temperature of hydrogen reaches 20 K the hydrogen molecules will clump together and become a liquid, *liquid hydrogen*. However, as we said just above, even when clumped together as a liquid the gasoline-energy-equivalent volume of liquid hydrogen is 3.6 times greater than the volume of the gasoline. The hydrogen tank for a car that contains the energy equivalent of 15 gallons of gas would have to contain about 54 gallons of liquid hydrogen at 20 K, a temperature 280 degrees C below room temperature. At this temperature all other gases, except helium, would not only have condensed but would also have solidified.

This is a very low temperature.

We will consider later the costs of compression and liquefaction of hydrogen.

Transport of hydrogen

Hydrogen is similar to electricity. Neither electricity nor hydrogen exists in a free form in nature. Both electricity and hydrogen must be produced from another source of energy. Neither electricity nor hydrogen is easily or cheaply transported.

Location of producers of electricity

Electrical generating stations are built close to the points where electricity is in greatest demand. The reason for this is that it is cheaper to ship the fuel to the power plant than it is to transport the electricity to the customer.

Location of producers of hydrogen

At this time almost all hydrogen is produced close to the consumer of the hydrogen. Indeed, most hydrogen is either used by its manufacturer and its business partners, or is sold "over the fence".

Transport of hydrogen by pipeline

When the volumes are large and the distances are small, as with the examples above, hydrogen is distributed by pipeline. While there are more than a million miles of gas pipeline present today in the United States, there are now only about 700 miles of hydrogen pipeline; there are fewer than four feet of hydrogen pipeline for every mile of gas pipeline.

Transport of hydrogen as a compressed gas

Compressed hydrogen at 200 bar (about 200 atmospheres) can be delivered by tube trailers. This method of transport, however, is extraordinarily inefficient in that a 80,000 pound gross weight (40 ton) tube trailer can deliver only about 1% of that weight, or 800 pounds of hydrogen. In contrast, a similar 80,000 pound gross weight (40 ton) gasoline tanker can deliver 52,000 pounds of gasoline.

Even though the gasoline-energy-equivalent *weight* of hydrogen is only one third that of gasoline, it would take more than 20 tube trailers to deliver as much energy as can be delivered by one gasoline tanker.

Transport of hydrogen as a cryogenic liquid

Liquid hydrogen at atmospheric pressure but very low temperature can also be delivered by truck. While high pressure tubes are not needed for liquid hydrogen, its low boiling point, 20 K, or –253 °C, requires that liquid hydrogen be stored and transported in extremely well insulated tanks.

The low density of liquid hydrogen, just a little greater than that of heavy duty Styrofoam, means that these tanks must also be big. If 8,000 pounds of liquid hydrogen is to be delivered (10 tube trailers worth of hydrogen), the cryogenic tank must have a volume, not counting insulation, of at least 2,000 cubic feet.

For comparison, a gasoline tanker has a volume of about 1,250 cubic feet, needs no insulation, and carries twice as much energy as the cryogenic hydrogen tanker.

Delivery of hydrogen

We have considered the production, storage, and transportation of hydrogen. We now consider the *delivery* of hydrogen, the last step in the trip from the source of hydrogen to the individual consumer of hydrogen.

Consumption of energy

We consume energy in several forms. For heating we used to consume coal, delivered to our coal chute by truck. We then changed to oil, delivered, again by truck, to the fill tube on our oil tank. We now use natural gas, or methane, delivered to our furnace by a pipe through the basement wall.

We also consume energy carried by electrons. The electrons come to us through a pair of wires, less than 1/4 inch in diameter, that also come through our basement wall. These wires go to our fuse box where the electrons delivered to the fuse box are directed to all parts of our house.

To get the energy for our cars we drive to the “filling station” where we fill our tank with gasoline, delivered at room temperature and normal pressure through a small pipe right into the fill tube of the tank in our car. It takes less than two minutes to run in 10 gallons, and we can do it ourselves.

Delivery of hydrogen

At this time we are not considering delivery of hydrogen to our home. We are considering only delivery of hydrogen to our car.

Hydrogen at normal temperature and pressure

We could go to a “hydrogen gas at normal temperature and pressure” station. We would need, however, a 3,000 gallon tank in order to take delivery of a volume of hydrogen equivalent in energy to 1 gallon of gas. We would need a tank one third the size of a gasoline tanker. And that's for only one "gallon-of-gasoline" equivalent of hydrogen, at NTP.

Hydrogen at normal temperature and 200 bar

How about a "hydrogen gas at normal temperature and 200 bar" station? This time we would need only a 15 gallon tank to hold our volume of hydrogen equivalent in energy to 1 gallon of gas. Again, the 15 gallon tank is for only one "gallon-of-gasoline" equivalent of hydrogen. What if we wanted to drive more than, say, 50 miles?

Hydrogen at normal temperature and 800 bar

How about a "hydrogen gas at normal temperature and 800 bar" station? This time we would need only a 4 gallon tank, but it would have to be strong enough to hold hydrogen at a pressure of 6 tons per square inch, not counting any safety factor. And again, the 4-gallon tank is for only one "gallon-of-gasoline" equivalent of hydrogen.

Cryogenic hydrogen

How about a "liquid hydrogen at 20 K but atmospheric pressure" station? How about the cryogenic hydrogen station? This time the volume requirement would also be 4 gallons, but the tank would have to be "super insulated". And, again, the 4 gallon tank is for only one "gallon-of-gasoline" equivalent of hydrogen.

Other features of hydrogen delivery

Refueling with hydrogen would be much more complicated than refueling with gasoline. First, there would have to be a strong mechanical connection between the hydrogen supply and the car; no more just sticking the nozzle into the fill tube. Second, any air in the line would have to be pumped out. This precaution would be taken so as to remove any possibility of forming an explosive mixture with air, and, in the case of the transfer of liquid hydrogen, to avoid the possibility of frozen air later clogging the lines.

Refueling with compressed hydrogen

The strong mechanical connection will ensure that pressure is not lost during transfer. Establishing a tight system is just the beginning, however.

Gasses behave differently from liquids. With a gas you cannot empty one container into another. When two tanks of gas are connected, they come to the same pressure. Gas flows from the tank at the higher pressure into the tank at the lower pressure until the pressures are equal. If, when the pressures are equal, one tank is three quarters full the other tank will also be three quarters full. If one tank is nine times larger than the other and the pressure in each tank is the same the larger tank will contain 90% of the hydrogen and the smaller tank will contain 10% of the hydrogen.

It will, therefore, be impossible to fill the 200 bar tank in your car from a 200 bar tank at the hydrogen station. If the tank at the station is really big and full (200 bar pressure), and your car's tank is relatively small, the pressure in the two tanks, after the hydrogen stops flowing, might be fairly high, but it will not be 200 bar in either tank. The problem becomes worse with each succeeding car because the tank at the station will always have less pressure for the next car.

The same problem exists for the station's tank when the station's tank is refueled by the tube truck.

The solution to the problem is to move hydrogen gas with pumps, pumps that can push hydrogen along in the face of pressures up to 200 bar (3,000 psi), or more. These pumps will be considerably bigger and more expensive than those that push air into your tires, which resist with a pressure of about 30 psi. In contrast, the gasoline pump that pushes gasoline into the fill tube of your gas tank works in the face of a pressure of no more than two or three pounds per square inch.

Refueling with liquid hydrogen

Refueling with liquid hydrogen will be more difficult than refueling with gaseous hydrogen. With liquid hydrogen not only must the refueling system be closed but the refueling system must also be kept cold, colder than any liquid other than liquid helium. It will be kept cold by the evaporation of a small amount of the liquid hydrogen that is transferred.

Here is part of a supplier's statement about the transfer of liquid hydrogen. "Withdrawal of liquid from a tanker, tank, or liquid cylinder requires the use of a closed system, with proper safety relief devices, which can be evacuated and/or purged to eliminate the possibility of creating a flammable atmosphere or explosive mixture of liquid air and liquid hydrogen. Purging should be done with helium since liquid hydrogen can solidify other gases, such as nitrogen, and cause plugging and possible rupture of the transfer line or storage vessel. Liquid transfer lines must be vacuum insulated to minimize product loss through vaporization or the formation of liquid air on the lines with subsequent oxygen enrichment. All equipment must be electrically grounded and bonded before transferring liquid."

Loss on standing

While it is possible to completely prevent the escape of hydrogen from a tank at room temperature it is impossible to completely prevent the entry of heat into a tank at 20 K by insulation alone. Therefore, on standing, liquid hydrogen will evaporate and, unless allowed to escape through a relief valve, the increase in pressure will cause the tank to burst.

At a boil-off rate of, say, 3% per day 3% of the initial amount of liquid hydrogen will evaporate each day. The rate of evaporation will be *independent* of the amount of liquid helium in the tank since the rate of evaporation depends entirely on the rate at which heat enters the tank. After standing in the garage for 33 days, the tank will be empty.

If the design of the tank will allow retention of some hydrogen vapor, and the car is driven a certain minimum number of miles each day, usage can keep up with evaporation. It is truly a "use it or lose it" situation. Use it or not, the tank will have to be refilled at least once a month.

Summary

In this chapter we have considered the properties, production, storage, transportation, and distribution of hydrogen.

Properties: gas at room temperature and pressure; liquid at 20 K.

Production: from fossil fuels (gas, oil, coal): steam reforming followed by water-gas shift. From water: electrolysis.

Storage: as a gas at normal temperature and pressure; as a compressed gas; as a cryogenic liquid.

Transportation: by tube truck; by cryogenic tanker

Delivery: as a gas at normal temperature and pressure; as a compressed gas; as a cryogenic liquid.

Size of one-gallon-of-gas equivalent of hydrogen:

Room temperature and pressure ("standard conditions"): 3,100 gallons.

Room temperature and 200 atmospheres (3,000 psi): 15 gallons.

Room temperature and 800 atmospheres (12,000 psi): 3.6 gallons; same density as liquid hydrogen.

Twenty K and 1 atmosphere (liquid hydrogen): 3.6 gallons.

In the next chapter we consider the energy efficiencies, or energy costs, of these processes.