

CGA G-5—2024

9TH EDITION

HYDROGEN



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1 Introduction

This publication is one of a series written by the Compressed Gas Association, Inc. (CGA) to provide information on the production, transportation, handling, and storage of compressed gases, cryogenic liquids, and related products.

2 Scope

This publication provides information on the physical and chemical properties of hydrogen and proper handling and use. It is intended to provide background information for personnel involved in the manufacture, distribution, and use of hydrogen. Additional technical information can be obtained from hydrogen gas manufacturers.

Appendix A provides definitions for commonly used terms related to hydrogen.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

4 General Information

4.1 Physical and chemical properties of gaseous hydrogen

Gaseous hydrogen is a colorless, odorless, tasteless, flammable, nontoxic gas. It is the lightest of all gases, having a specific gravity of 0.0696. The hydrogen content of atmospheric air at sea level is 0.5 ppm.

Gaseous hydrogen has two isomers (forms): ortho-hydrogen, in which the two atomic nuclei spin in the same direction and para-hydrogen, in which the two atomic nuclei spin in opposite directions. There are no differences in the chemical properties of the two forms of gaseous hydrogen, but there are slight differences in their physical properties. Gaseous hydrogen is a mixture of 75% ortho-hydrogen and 25% para-hydrogen at room temperature. Gaseous hydrogen is also called normal hydrogen.

Gaseous hydrogen is a flammable gas that burns with an almost invisible bluish flame. The flame is so pale in daylight that a person can feel heat or even be burned by hydrogen that was accidentally ignited without ever having seen a flame.

The flammability limits of gaseous hydrogen in air at atmospheric pressure are approximately 4% to 75%, and the minimum autoignition temperature is 1050 °F (566 °C). The flammability limits of gaseous hydrogen in oxygen range from approximately 4% to 95%, and the minimum autoignition temperature is 1074 °F (579 °C). When handling gaseous hydrogen, personnel shall observe all the precautions necessary for the safe handling of a flammable gas. The minimum ignition energy of gaseous hydrogen is 0.02 mJ, which is an order of magnitude

less than the ignition energy for most hydrocarbons. Gaseous hydrogen can be ignited by an almost imperceptible spark or by static electricity discharge. Hydrogen fires are concentrated, rapid, and only slightly radiative compared to hydrocarbon fires.

At ordinary temperatures and pressures, most common gases, e.g., oxygen, nitrogen, and carbon dioxide, are cooled by throttled expansion from high to low pressure. This is not the case with gaseous hydrogen. Because of its negative Joule-Thomson coefficient, gaseous hydrogen is heated to a slight extent, about 10 °F (5.6 °C), when throttled from 2 000 psi (13 790 kPa) to atmospheric pressure.^{1, 2}

Because of its small molecular size, gaseous hydrogen diffuses rapidly through porous materials. It also dissolves in and slowly diffuses through metals at ambient temperatures and dissolves in and more rapidly diffuses through metals at elevated temperatures. At equivalent pressure, gaseous hydrogen can leak out of a system that is gas-tight for air or other common gases.

Gaseous hydrogen is noncorrosive and considered nonreactive, but hydrogen service will generally reduce the mechanical properties of some metals by the complex process of embrittlement, which can occur in the following ways:

- Environmental hydrogen embrittlement—occurs in metals and alloys plastically deformed in a high pressure hydrogen environment. Deformations under high pressure conditions lead to increased surface cracks, loss in ductility, and decreases in fracture stress;
- Internal hydrogen embrittlement—caused by absorbed hydrogen. Small amounts of dissolved hydrogen can cause embrittlement and allow fractures to occur with little or no warning; or
- Hydrogen reaction embrittlement—caused by the absorption of hydrogen and the reaction of the hydrogen with the base metal, an alloy, or a contaminant. The resulting hydrides are typically very brittle and they lower the metal's ductility.

The physical constants of gaseous hydrogen are listed in Table 1.

4.2 Physical and chemical properties of liquid hydrogen

The boiling point of liquid hydrogen is −423.2 °F (−252.9 °C) at 1 atmosphere pressure.

Liquid hydrogen is colorless, odorless, noncorrosive, and not significantly reactive. Liquid hydrogen has the lowest density of any liquefied gas: 1 gallon weighs only 0.5906 lb (0.2679 kg), about 1/14 the weight of water. The stable form of liquid hydrogen at low pressure is para-hydrogen. The ortho-para conversion occurs naturally but slowly at low temperatures and generates heat. For each pound of hydrogen converted, the heat of reaction will vaporize 1.5 lb (0.68 kg) of liquid hydrogen. Therefore, in liquid hydrogen production a catalyst is used to accelerate the ortho-para conversion so the heat of this reaction becomes part of the total refrigeration load. The resulting product is 95% para-hydrogen.

The physical constants of liquid hydrogen are listed in Table 2.

4.3 Physiological effects

Hydrogen is nontoxic and is used as a background gas for oxygen used in diving. Hydrogen can act as an asphyxiant by displacing the oxygen in air. Since hydrogen is flammable at 4% in air, it is a flammability hazard well before it can act as an asphyxiant.

¹ psi, bar, and kPa shall indicate gauge pressure unless otherwise noted as (psia; bar, abs; and kPa, abs) for absolute pressure or (psid; bar, dif; and kPa, dif) for differential pressure. All kPa values are rounded off per CGA P-11, *Guideline for Metric Practice in the Compressed Gas Industry* [1].

² References are shown by bracketed numbers and are listed in order of appearance in the reference section.

Upon contact with the skin and other tissues, liquid hydrogen and the cold gas evolving from the liquid can produce severe burns that are similar to thermal burns. Eyes can be injured by a brief exposure to the cold gas or splashed liquid that is too brief to have any effect on the skin of the hands or face. Contact between unprotected parts of the body and uninsulated piping or vessels containing liquid hydrogen can cause the flesh to stick, and the skin can tear when removal is attempted.

Table 1—Physical constants of gaseous (normal) hydrogen ¹⁾

	U.S. Units	SI Units
Chemical formula	H ₂	H ₂
Molecular weight	2.016	2.016
Density of the gas at 70 °F (21.1 °C) and 1 atm	0.00521 lb/ft ³	0.08342 kg/m ³
Specific gravity of the gas at 32 °F (0 °C) and 1 atm (air = 1)	0.06960	0.06960
Specific volume of the gas at 70 °F (21.1 °C) and 1 atm	192.0 ft ³ /lb	11.99 m ³ /kg
Boiling point at 1 atm	−423.0 °F	−252.8 °C
Melting point at 1 atm	−434.55 °F	−259.2 °C
Critical temperature	−399.93 °F	−239.96 °C
Critical pressure	190.8 psia	1316 kPa, abs
Critical density	1.88 lb/ft ³	30.12 kg/m ³
Triple point	−434.55 °F at 1.117 psia	−259.19 °C at 7.7 kPa, abs
Latent heat of vaporization at boiling point	191.7 Btu/lb	446.0 kJ/kg
Latent heat of fusion at triple point	24.97 Btu/lb	58.09 kJ/kg
Specific heat of the gas at 70 °F (21.1 °C) and 1 atm		
C _p	3.425 Btu/(lb)(°F)	14.34 kJ/(kg)(°C)
C _v	2.418 Btu/(lb)(°F)	10.12 kJ/(kg)(°C)
Ratio of specific heats	1.42	1.42
Solubility in water, vol/vol at 60 °F (15.6 °C)	0.019	0.019
Density of the gas at boiling point and 1 atm	0.083 lb/ft ³	1.331 kg/m ³
Density of the liquid at boiling point and 1 atm	4.43 lb/ft ³ (0.5922 lb/gal)	70.96 kg/m ³
Gas/liquid ratio (gas at 70 °F [21.1 °C] and 1 atm, liquid at boiling point, vol/vol)	850.3	850.3
Heat of combustion at 70 °F (21.1 °C) and 1 atm		
Gross	318.1 Btu/ft ³	11 852 kJ/m ³
Net	268.6 Btu/ft ³	10 009 kJ/m ³
¹⁾ Normal hydrogen is a gaseous mixture of 75% ortho-hydrogen and 25% para-hydrogen.		

Table 2—Physical constants of liquid hydrogen ¹⁾

	U.S. Units	SI Units
Boiling point at 1 atm	−423.2 °F	−252.9 °C
Melting point	−434.8 °F	−259.3 °C
Critical temperature	−400.31 °F	−240.17 °C
Critical pressure	187.5 psia	1293 kPa, abs
Critical density	1.96 lb/ft ³	31.43 kg/m ³
Triple point	−434.8 °F at 1.021 psia	−259.3 °C at 7.040 kPa, abs
Latent heat of vaporization at boiling point	191.6 Btu/lb	445.6 kJ/kg
Latent heat of fusion at triple point	25.06 Btu/lb	58.29 kJ/kg
Specific heat of the gas at 70 °F (21.1 °C) and 1 atm		
C_p	3.555 Btu/(lb)(°F)	14.88 kJ/(kg)(°C)
C_v	2.570 Btu/(lb)(°F)	10.76 kJ/(kg)(°C)
Ratio of specific heats	1.38	1.38
Density of the gas at boiling point and 1 atm	0.084 lb/ft ³	1.338 kg/m ³
Density of the liquid at boiling point and 1 atm	4.42 lb/ft ³ (0.5907 lb/gal)	70.78 kg/m ³
Gas/liquid ratio (gas at 70 °F [21.1°C] and 1 atm, liquid at boiling point, vol/vol)	848.3	848.3
NOTE—The physical constants for liquid hydrogen are different from the physical constants for normal hydrogen (see Table 1 for the physical constants of normal hydrogen). ^{1), 2)}		
¹⁾ Liquid hydrogen is 100% para-hydrogen.		
²⁾ Normal hydrogen is a gaseous mixture of 75% ortho-hydrogen and 25% para-hydrogen.		

4.4 Manufacture

4.4.1 Production

Most hydrogen is consumed at or within pipeline distance of the production site. Hydrogen can be produced directly or recovered as a by-product from various chemical processes. Hydrogen is produced industrially by several methods including:

- as a by-product of cracking hydrocarbon feedstocks in oil refineries;
- through the reaction of natural gas or light hydrocarbons with steam in the presence of a catalyst;
- through the electrolysis of water or aqueous acid or alkali solutions; and

NOTE—The electrolysis of water or aqueous acid or alkali solutions is a major source of hydrogen. Considerable amounts of hydrogen are obtained as a by-product of the electrolytic production of chlorine and alkali. Some electrolytic plants operate solely to produce oxygen and hydrogen from water.

- by the cracking (dissociation) of ammonia.

4.4.1.1 Steam reformation

Steam reformation is a chemical reaction between hydrocarbons and steam with the assistance of catalysts to produce hydrogen and carbon monoxide according to the following equation:

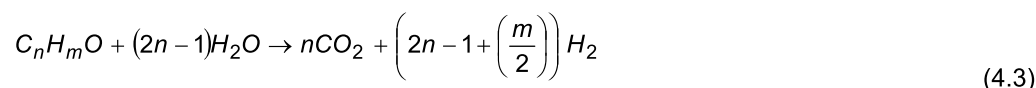


The reactions are typically endothermic and kinetically favorable at high temperatures between 1000 °F and 1900 °F (537.8 °C and 1073.8 °C). The steam reforming reaction is typically coupled with a lower temperature, exothermic reaction called water gas shift (WGS) to convert the carbon monoxide to carbon dioxide and produce more hydrogen according to the following equation:



The product gases then pass through a pressure swing adsorption (PSA) bed to purify the hydrogen product. The product hydrogen's purity is typically 99% or greater at the end of the purification process. When natural gas or methane is used for the feed, the process is called steam methane reforming (SMR). Figure 1 is a schematic of SMR.

When alcohol is used as a feed, the steam reforming reaction occurs according to the following equation:



As with equation 4.2, the product gases pass through a PSA bed where the hydrogen gas is purified.

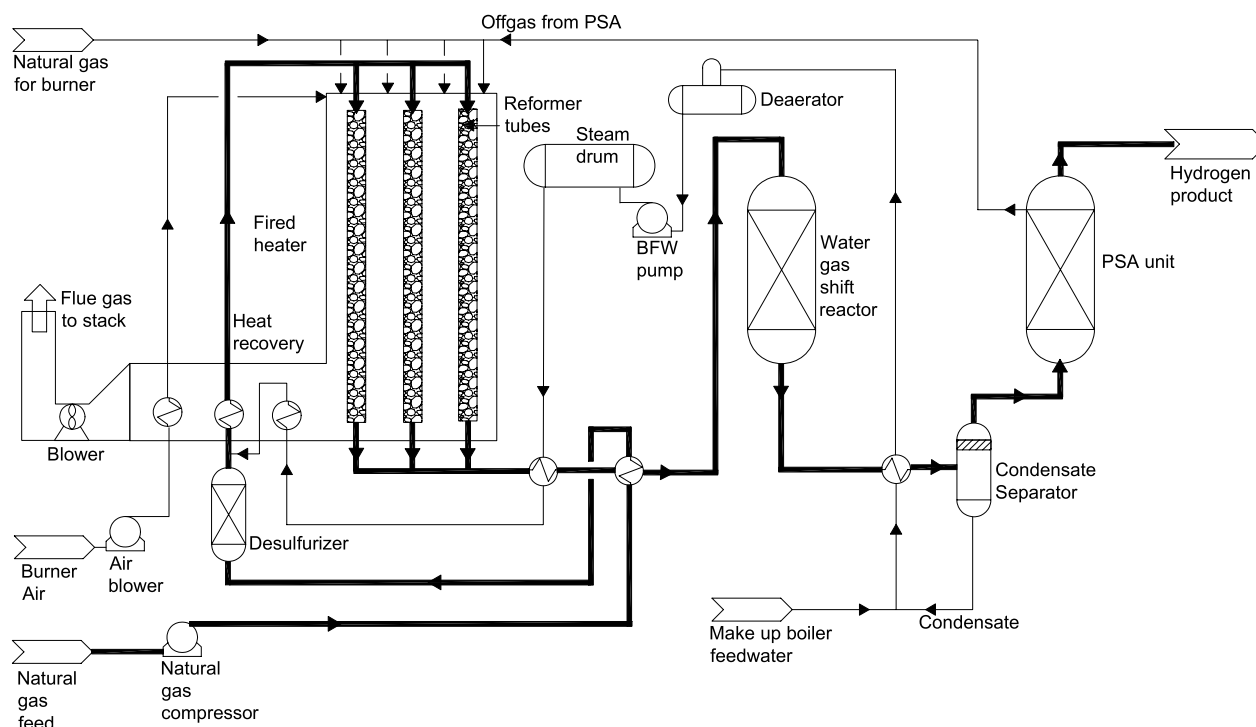


Figure 1—Typical steam methane reforming schematic

4.4.1.2 Partial oxidation

Partial oxidation is an incomplete combustion reaction where hydrocarbons or hydrogen-containing compounds are reacted with a substoichiometric amount of oxygen to produce a mixture of hydrogen and carbon monoxide. The reactions are highly exothermic and follow the equation:



When the reactions are assisted by the use of catalyst, they are called catalytic partial oxidation (CPOX). CPOX has the advantage of a lower reaction temperature, the ability to use air as oxidant, shorter reaction times, and thus a smaller reactor.

4.4.1.3 Autothermal reforming

Autothermal reforming is a combination of exothermic partial oxidation and endothermic steam reforming reactions. It integrates the heat produced by the partial oxidation reactions and uses it to sustain the steam reforming reactions. The products of the reactions are mixtures of hydrogen and carbon monoxide. When the reactions are balanced, the process only requires heat input during the initial stage. Once a steady state is achieved, external heat input is not required to sustain the reactions.

4.4.1.4 Gasification

Gasification is a chemical reaction that produces hydrogen by injecting steam into a hot bed of coal or coke. Similar to the steam reforming process, the reaction is coupled with a WGS reaction to produce more hydrogen according to the following equations:



4.4.1.5 Water electrolysis

Water electrolysis is an electrochemical process that uses electricity to separate water molecules into gaseous hydrogen and oxygen according to the following equation:



The reaction at the anode proceeds according to the following equation:



The reaction at the cathode proceeds according to the following equation:



The water electrolysis process requires energy for the dissociation of water. The typical system power demand is 0.13 kWh/scf to 0.18 kWh/scf (4.6 kWh/Nm³ to 6.4 kWh/Nm³).

4.4.2 Purification

Hydrogen is purified to required levels using methods such as scrubbing, gas adsorption beds, cryogenic adsorption traps, purifiers, and filters. The quality verification levels (grades) of hydrogen can be found in CGA G-5.3, *Commodity Specification for Hydrogen* [2].

4.4.3 Liquefaction

Hydrogen is liquefied in a production plant using a process cycle that refrigerates a precooled gas stream to form a liquid phase. Adsorption traps provide the high purity levels required by the liquefaction equipment. Catalysts in the product stream convert the hydrogen into the para form to quickly achieve equilibrium conditions in the liquid.

4.5 Commercial uses

Large quantities of hydrogen are consumed in chemical syntheses, primarily in the synthesis of ammonia and methanol. Hydrogen is also used as a reducing agent in chemical processes.

In the organic chemical field, hydrogenation of edible liquid oils such as soybean, fish, cottonseed, and corn converts these oils to semisolid materials such as shortenings, margarine, and peanut butter. Alcohols are produced by hydrogenation of the corresponding acids or aldehydes. Hydrogen is also used to hydrogenate non-edible oils for soaps, insulation, plastics, ointments, and other specialty chemicals.

Industrial applications of hydrogen as a fuel primarily involve its use with oxygen in oxy-hydrogen welding and cutting. Because of the relatively low temperature of the oxy-hydrogen flame, its use is largely restricted to certain brazing operations, to the welding of aluminum and magnesium (especially in thin sections), and to the welding of lead. It is also used in underwater cutting because it can be safely compressed to the pressures required for marine salvage and offshore construction.

Atomic hydrogen welding is particularly applicable in fabrication of thin stock and can be used on practically all nonferrous metals and alloys as well as ferrous alloys, e.g., the fabrication of nickel and Monel® tanks, the fabrication of aluminum aircraft parts and propellers, and the repair of steel molds and dies. This is an arc-welding process in which the arc is maintained between two nonconsumable metal electrodes. At the arc temperature of about 11 000 °F (6 093 °C), the molecular hydrogen is rapidly transformed to atomic hydrogen, which is the vehicle transmitting the heat energy from the arc to the weld zone. At the relatively colder surface of the weld area, the atomic hydrogen recombines to molecular hydrogen with the release of heat. The hydrogen also shields the weld area from the surrounding air.

Hydrogen either alone or mixed with other gases is used to provide a reducing atmosphere in annealing, heat-treating, furnace brazing, production of parts from sintered carbides and other metals, and in the metallurgy of special metals such as molybdenum.

Hydrogen may be used as a lifting medium for meteorological and other balloons.

Hydrogen's high heat capacity allows it to remove heat more efficiently than other heat transfer media. Large electrical generators are often run with an internal hydrogen atmosphere to remove heat. Hydrogen has a low viscosity which reduces the internal friction and allows the generators to run at higher capacities.

Hydrogen may also be used as a fuel to power fuel cell generators that create electricity through an electrochemical process in combination with oxygen.

Electronics manufacturers use controlled hydrogen atmospheres to grow crystals, deposit crystalline layers, and form thin films when manufacturing integrated circuits.

Pharmaceutical manufacturers use hydrogen to produce sorbitol, which is used in vitamins, cosmetics, and medications.

The oxy-hydrogen flame is also used in the production and fabrication of quartz and glass.

Glass manufacturers use hydrogen as a protective atmosphere in the float glass process where molten glass is floated on a surface of molten tin. A hydrogen atmosphere prevents oxidation of the molten tin.

Liquid hydrogen is an important fuel for powering missiles and rockets. Liquid hydrogen is used in laboratory research on the properties of materials at cryogenic temperatures, for example, the superconductivity of metals. Liquid hydrogen is also used in bubble chambers for accelerators in high-energy physics research.

The fuel cell is an electrochemical device that uses the strong attraction of hydrogen and oxygen to its advantage to produce electrical energy. Unlike a combustion process in which hydrogen is burned with oxygen, electrical energy is produced by breaking down hydrogen into protons and electrons, using the electrons to produce power, then recombining the electrons with the protons and oxygen to form water.

Fuel cell systems are being developed for many applications. Fuel cells operate at higher efficiency than internal combustion engines (ICEs), most are low polluting, and some types discharge only water and heat. Many of the fuel cells being developed use gaseous hydrogen as fuel.

Hydrogen can be used as fuel in an ICE either as a pure gas or mixed with natural gas (or other hydrocarbon fuels). Hydrogen has been shown to reduce exhaust emissions under controlled conditions when added to natural