

Gaseous hydrogen

Hydrogen is a colorless, odorless, tasteless, highly flammable gas. It is also the lightest-weight gas. Hydrogen is noncorrosive; however, materials of construction can be subject to hydrogen damage mechanisms, most commonly hydrogen embrittlement, and hence must be carefully selected and designed. Vessels and piping must be selected and designed to withstand the pressure and temperatures involved and comply with applicable codes and regulations as well as material compatibility..

Table 1 shows physical properties of gaseous hydrogen. As indicated by the specific gravity, hydrogen gas is much less dense than air and can disperse rapidly or accumulate in the upper sections of enclosed spaces.

Flammability

The wide flammability range, 4% to 75% in air, and the small amount of energy required for ignition necessitate special handling including preventing leaks, safe system design, and sizing. Sources of ignition, such as sparks from electrical equipment, static electricity, open flames, or extremely hot objects, should be eliminated.

Hydrogen and air mixtures, if ignited, burn with a low luminosity flame. Often flames are visible as atmospheric contaminants or other substances could be burning, but the flame is most clearly visible at night. Hydrogen released into congested areas may deflagrate or detonate.

Manufacture

Hydrogen is primarily produced by steam methane reforming; however, several methods exist, including electrolysis, biomass gasification and biomass conversion technologies.

The steam reforming process produces syngas, which is a mixture of hydrogen and carbon monoxide. The product stream is separated into its components, and the hydrogen is dried, purified, and compressed into cylinders, pipelines, or tubes for transportation.

Uses

Hydrogen is used in manufacturing processes for producing petroleum, steel, chemicals, foods and electronics. Refineries use hydrogen to produce cleaner burning gasoline and low sulfur diesel fuel, helping to reduce air pollution.

In the metallurgical industry, hydrogen is used to reduce metal oxides and prevent oxidation when heat-treating certain metals and alloys. It is also used as a fuel in alternative energy vehicles and may be used when welding and cutting metals. Hydrogen is also used by semiconductor manufacturers, primarily to form reducing atmospheres, and it is used in the chemical industry to synthesize ammonia and methanol.

Health

Hydrogen gas is odorless and nontoxic but may induce suffocation by diluting the concentration of oxygen in air below levels necessary to support life.

The amount of hydrogen gas necessary to produce oxygen-deficient atmospheres is well within the flammable range, making fire and explosion the primary hazards associated with hydrogen and air atmospheres.

Containers

Gaseous hydrogen may be supplied in cylinders or in tubes that are designed and manufactured according to applicable codes and specifications for the pressures and temperatures involved. The pressure rating and internal volume of a container determines the quantity of hydrogen it can hold. Cylinders may be used individually or can be manifolded together to allow for a larger gas storage volume.

Tubes are mounted on truck-trailer chassis or in ISO frames for transportation and are referred to as tube trailers or tube modules, respectively. Stationary tube (also called hydril tube) modules store large quantities of hydrogen at customer locations.

Table 1: Gaseous Hydrogen Physical and Chemical Properties

Chemical Formula	H ₂
Molecular Weight	2.02
Boiling Point at 1 atm	−423°F (−252.8°C)
Freezing Point at 1 atm	−435°F (−259.2°C)
Critical Temperature	−400°F (−240°C)
Critical Pressure	190.8 psia (13.16 bar, abs)
Density, Gas at 70°F (21°C), 1 atm	0.0052lb/ft ³ (0.083 g/l)
Specific Gravity, Gas (air=1) at 68°F (20°C), 1 atm	0.07
Specific Volume at 70°F (21°C), 1 atm	192.0 ft ³ /lb (11.99 m ³ /kg)
Latent Heat of Vaporization	192 Btu/lb (446 kJ/kg)
Flammable Limits at 1 atm in air	4%–75% (by volume)
Autoignition Temperature at 1 atm	1040°F (560°C)

A bulk gaseous hydrogen customer storage system commonly consists of 3 to 18 tubes with total capacities up to 150,000 standard cubic feet (>4,250 m³) of hydrogen. Stationary storage tubes have individual valves and safety devices and are manifolded together so the customer can withdraw product from a single tube or multiple tubes. Customer storage systems are commonly filled to 2,400 psig (165 barg).

Portable and stationary gaseous hydrogen fueling systems with service pressures to accommodate H35 and H70 fueling systems.

Specifications

In the United States, cylinders and mobile tubes are manufactured according to Department of Transportation (DOT)-3A or DOT-3AA specifications. Cylinders and mobile tubes are hydrostatically tested upon manufacture and tested periodically thereafter at 5/3 times the service pressure as specified by DOT regulations. Hydrogen may be stored in ASME coded and stamped, National Board registered high-pressure gas storage tubes as part of a stationary installation. These tubes are hydrostatically tested by the manufacturer but, unlike cylinders and mobile tubes, they do not require periodic hydrostatic testing.

Valves

Stainless Steel or Brass valves are typically used on cylinders and tube trailers. The standard hydrogen cylinder valve outlet connection in North America is the CGA 350 for pressures up to 3,000 psig. Different connections are used for hydrogen in other locations based on national or regional standards. Further information on valves and valve outlet connections is provided in Air Products' Safetygram 23, "Cylinder Valves," and Safetygram 31, "Cylinder Valve Outlet Connections."

Pressure relief devices

Pressure Relief Devices (PRDs) and Thermally-activated Pressure Relief Devices (TPRDs) are employed to reduce the likelihood of container failure in fire situations. These devices take the form of frangible disks, fusible metal plugs or pressure relief valves.

In North America and Asia, pressure relief devices are commonly integral parts of the cylinder valves and are installed on both ends of portable and stationary tubes. Current standards in the US reduce the requirements for PRDs or TPRDs, and many trailers in the US no longer have PRDs or TPRDs. In Europe, PRDs are not commonly used on gaseous hydrogen cylinders or on portable or stationary bulk containers.

For further information on PRDs, consult Safetygram 15, "Cylinder Pressure-Relief Devices."

Shipment: hydrogen

Compliance with applicable Dangerous Goods regulations is required for all shipments by motor freight, rail, air and water. These regulations describe the marking, labeling, placarding, and shipping papers required. International shipments by air must comply with International Air Transport Association/International Civil Air Organization (IATA/ICAO) Dangerous Goods regulations. Final acceptance for air transport is at the discretion of the airline. International shipments by water must comply with International Maritime Organization (IMO) regulations.

Safety considerations

The hazards associated with handling gaseous hydrogen are fire, explosion, and pressure. Although hydrogen tends to dissipate quickly, its minimum ignition energy is extremely low, allowing relatively easy ignition of hydrogen mixtures in the flammable range. Hydrogen is easily ignited by open flames, electrical sparks and static electricity. Hydrogen may detonate and ignite when rapidly vented into the air. Hydrogen burns with an almost invisible flame, and severe burns may result from unknowingly walking into a hydrogen fire; however, large leaks are generally clearly audible. The fire and explosion hazards can be controlled by appropriate design and operating procedures. Preventing the formation of combustible fuel-oxidant mixtures and removing potential sources of ignition (electric spark, static electricity, open flames, etc.) in areas where the hydrogen will be used are essential. Adequate ventilation will help reduce the possible formation of flammable mixtures in the event of a hydrogen leak.

Hydrogen's autoignition temperature (AIT) is 1040°F (560°C). The AIT is the minimum temperature required to initiate self-sustained combustion. The relatively high autoignition temperature makes ignition of a hydrogen/air mixture unlikely from heat alone without an additional ignition source.

Purging

To prevent the formation of flammable mixtures, gaseous hydrogen systems must be purged of hydrogen before opening the system to the atmosphere, and purged of air, oxygen, or other oxidizers prior to admitting hydrogen to the systems. If the piping systems are extensive or complicated, multiple purging and evacuation cycles may be required for optimum results. Purging can be done using system evacuation, inert gas pressurizing-depressurizing cycles (cycle purging), flowing inert gas through the equipment or combinations of these methods. System configuration considerations, including total volume, inclusion of piping “dead ends,” and availability of evacuation capability, should all be taken into account when selecting the purging methods to be used.

Before opening a hydrogen-filled system to the air, the hydrogen concentration should be reduced to well below the lower flammable concentration (4%). The hydrogen concentration should be reduced to well less than 25% of the lower flammable concentration (below 1% actual).

Before introducing hydrogen into systems that were open to air, the oxygen concentration in the system should be reduced to less than 1% (well below the minimum oxygen concentration needed for hydrogen ignition). Additional purging will often be needed to meet higher-purity application requirements.

Cylinder handling and use

Compressed gas cylinders must be stored properly, handled correctly, and used with the appropriate equipment to reduce the risk of incidents and injuries. Safetygram 10, “Storage, Handling and Use of Compressed Gas Cylinders,” describes good practices. CGA’s publication P-1, “Safe Handling of Compressed Gases in Cylinders,” also provides safe handling guidance. EIGA training modules TM 4/23 “Introduction to Hydrogen” and TM 5/23 “Further Information on Hydrogen” also provide information on hydrogen storage and handling.

Be aware that refilling and shipping a compressed gas cylinder without consent of the owner is not allowed.

Gaseous hydrogen siting recommendations

General

- Air Products can provide site-specific location recommendations for bulk gaseous hydrogen installations. Air Products follows the “Hydrogen Technologies Code” (NFPA 2) for systems in North America.
- The system should be located so it is readily accessible to delivery equipment and to authorized personnel.
- It is preferable to locate all bulk gaseous hydrogen systems outdoors. Total storage capacity of an indoor hydrogen system should be limited as much as possible and should not exceed 3,000 ft³ (85 m³) of hydrogen without additional engineering safety analysis.
- Systems must be located above ground.
- Systems should not be located beneath electric power lines.
- Systems should not be located close to flammable liquid or other flammable gas piping.
- It is advisable to locate the system on ground higher than flammable liquid storage or liquid oxygen storage. Where it is necessary to locate the system on ground that is lower than adjacent flammable liquid storage or liquid oxygen storage, suitable protective means (such as diking, diversion curbs, or grading) should be employed. For hydrogen storage requirements, see the latest edition of NFPA 2 “Hydrogen Technologies Code”^{*} or equivalent local codes.
- Electrical equipment within 15 feet (4 meters) shall be in accordance with Article 501 of the National Electrical Code for Class 1, Division 2, Group B locations or in compliance with alternate codes where used.
- Gaseous hydrogen storage vessels and associated piping must be electrically bonded and grounded.
- If protective walls or roofs are provided, they should be constructed of noncombustible materials. If the enclosing sides adjoin each other, the area should be properly vented.
- The area within 15 feet (4 meters) of any hydrogen container should be kept free of dry vegetation and combustible material.
- Adequate lighting shall be provided for nighttime transfer operations where appropriate.
- The hydrogen storage location should be permanently placarded: “Hydrogen – Flammable Gas – No Smoking – No Open Flames,” or equivalent.

Indoor storage systems

- Hydrogen systems generally should be located outdoors in well ventilated and properly sited areas. If there is a need for an indoor system or hydrogen equipment enclosure, the design should be reviewed in detail and consideration given to the following including compliance with NFPA 2.
- Provide adequate ventilation, particularly near roof areas where hydrogen might collect. Forced ventilation may be necessary in some applications.
- All vents should be piped to the exterior of the building and must be installed in accordance with local regulations.
- The atmosphere in areas where hydrogen gas may collect should be monitored with portable or continuous flammable gas air monitors calibrated for hydrogen.
- Where large quantities of hydrogen can be released indoors, provide an explosion-venting surface or vents, taking care to vent a pressure wave to areas where people or other equipment will not become involved. Explosion vents may not be required where small quantities of hydrogen are involved.
- Electrical equipment must conform to electrical codes in any area classified as hazardous (where elevated hydrogen gas concentrations can exist).
- Building materials should be noncombustible.
- Hydrogen storage inside a building should not be near oxidants or other combustible materials storage.

^{*} Publication is available from NFPA, 1 Batterymarch Park, Quincy, MA 02169-7471

Personal protective equipment

Flame retardant protective clothing meeting NFPA standards should be worn where possibility of fire exists. Safety glasses, safety shoes, hard hats, personal gas monitors, and sturdy work gloves should be worn when handling cylinders or as the work scope would dictate.

Emergency response

Only trained and qualified emergency personnel should respond to emergencies. For emergencies, a fire-resistant suit and gloves should be worn. Supplied air respirators or self-contained breathing apparatus (SCBA) is also recommended to reduce possible fire or heat injury to the face and airway. Responders must NOT enter or work in areas with hydrogen concentrations in the flammable range or where flammable/explosive atmospheres may be formed.

Firefighting

Hydrogen is easily ignited by open flames, electrical sparks, and static electricity. Hydrogen may detonate and ignite when rapidly vented into the air. It will burn with an almost invisible flame. Most hydrogen fires have the flame characteristic of a torch or jet and originate at the point where the hydrogen is discharging. If a leak is suspected in any part of a system, a hydrogen flame can be detected by cautiously approaching with an outstretched broom, lifting it up and down.

The most effective way to fight a hydrogen fire is to shut off the flow of gas. If the fire is extinguished without stopping the flow of gas, an explosive mixture may form, creating a more serious hazard than the fire itself should reignition occur.

The usual firefighting practice is to prevent the fire from spreading and let it burn until the hydrogen is consumed or can be closed off. An adequate water supply should be available to keep surrounding equipment cool in the event of a hydrogen fire. If water is used to fight the fire, it should not be directed at any cold vents. The local fire department should be advised of the nature of the products handled and made aware of the appropriate methods for combating hydrogen fires.

Air Products has trainings available upon request for hydrogen emergency response.

Additional information

If more information is needed on hydrogen, please contact the Air Products Technical Information Center at 800-752-1597 or 610-481-8565. Safety data sheets are available at airproducts.com/MSDS.

Emergency Response System

T 800-523-9374 (Continental U.S. and Puerto Rico)
T +1-610-481-7711 (other locations)
For regional ER telephone numbers, please refer to the local SDS 24 hours a day, 7 days a week
for assistance involving Air Products and Chemicals, Inc. products

Technical Information Center

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T +1-610-481-8565 (other locations)
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