AIR PRODUCTS

Safetygram #4
Gaseous Hydrogen

General

Hydrogen is a colorless, odorless, tasteless, highly flammable gas. It is also the lightest-weight gas. Since hydrogen is noncorrosive, special materials of construction are not usually required. However, embrittlement occurs in some metals at elevated temperatures and pressures. Stationary vessels and piping should be designed to the American Society of Mechanical Engineers (ASME) code and the American National Standards Institute (ANSI) Pressure Piping code for the pressures and temperatures involved. Vessels used for transportation must be designed to meet the Department of Transportation (DOT) code.

Gaseous hydrogen may be supplied in tube trailers and cylinders. Hydrogen is usually compressed into gas cylinders by oil-lubricated compressors. The amount of gas in a cylinder is determined by the pressure, temperature, cylinder size, and cylinder pressure rating.

Flammability

The wide flammability range, 4% to 74% in air, and the small amount of energy required for ignition necessitate special handling to prevent the inadvertent mixing of hydrogen with air. Care should be taken to eliminate sources of ignition such as sparks from electrical equipment, static electricity sparks, open flames, or any extremely hot objects.

Hydrogen and air mixtures, within the flammable range, can explode and may burn with a pale blue, almost invisible flame.

Manufacture

Hydrogen is produced by the steam reforming of natural gas, the electrolysis of water, the dissociation of ammonia, and as a by-product of petroleum distillation and chlorine manufacture, with the primary method for on-purpose generation being the steam reforming of natural gas. Other feedstocks can include ethane, propane, butane, and light and heavy naphtha but are not commonly used. The steam reforming process produces syngas, which is a mixture of hydrogen and carbon monoxide. Regardless of the method of production, the product steam is then separated into its components and the hydrogen dried, purified, and compressed into cylinders or tubes for transportation.

Uses

Hydrogen is used in the chemical industry to synthesize ammonia and in the hydrogenation of vegetable and animal oils and fats.

In the metallurgical industry, hydrogen is used to reduce metal oxides and prevent oxidation in heat-treating certain metals and alloys. Some use of hydrogen is made in the welding and cutting of metals. Hydrogen is also used by semiconductor manufacturers, primarily to form reducing atmospheres.

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.

Caution: 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

Cylinders

Cylinders are intended to be secured and stored upright. They are tapered to a small opening on the top. The open end is threaded to receive a cylinder valve or other suitable outlet connection. A threaded neckring is secured to the tapered end of the cylinder to allow a protective cap to be installed. Cylinders may be used individually or can be manifolded together to allow for larger gas storage volume.

Tubes

Tubes are generally mounted on truck-trailer chassis, referred to as tube trailers. Stationary tube or hydril tube modules store larger quantities of hydrogen at customer locations. The tubes are tapered on both ends. Each end has threaded openings to which connections, valves, or safety devices can be attached. The amount of hydrogen contained in each tube depends on tube diameter, length, and pressure rating.

Figure 1 depicts a typical tube trailer for transporting large volumes of gaseous hydrogen. Tube trailers are available in capacities up to 126,000 standard cubic feet and 2,640 psig pressure.

A typical module bulk gaseous hydrogen system is depicted in Figure 2. Modules are available in 3 to 18 tube configurations with capacities to 150,000 standard cubic feet of hydrogen. Mobile and stationary tubes have individual valves and safety devices but are manifolded together so that the customer can withdraw product from a single tube or several tubes at a time. Tube modules can be filled to 2,400 psig.

Specifications

Cylinders and mobile tubes are manufactured according to 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, periodical hydrostatic testing is not required.

Table 1

Properties

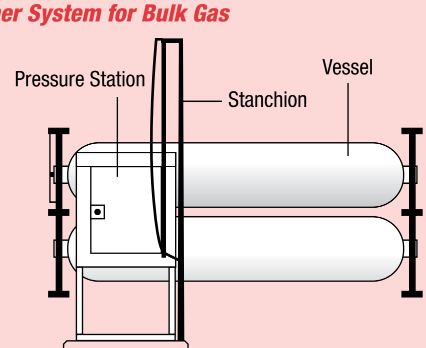
Chemical Formula	H_2
Molecular Weight	2.016
Boiling Point @ 1 atm	–423.2°F (–252.9°C)
Freezing Point @ 1 atm	–434.8°F (–259.3°C)
Critical Temperature	–400.4°F (–240.2°C)
Critical Pressure	186 psia (12.7 atm)
Density, Liquid @ B.P., 1 atm	4.42 lb./cu.ft.
Density, Gas @ 68°F (20°C), 1 atm	0.005229 lb./cu.ft.
Specific Gravity, Gas (air=1) @ 68°F (20°C), 1 atm	0.0696
Specific Gravity, Liquid @ B.P., [water=1 @ 68°F (20°C)]	0.0710
Specific Volume @ 68°F (20°C), 1 atm	191 cu. ft./lb.
Latent Heat of Vaporization	389 Btu/lb. mole
Flammable Limits @ 1 atm in air	4.00%–74.2% (by Volume)
Flammable Limits @ 1 atm in oxygen	3.90%–95.8% (by Volume)
Detonable Limits @ 1 atm in air	18.2%–58.9% (by Volume)
Detonable Limits @ 1 atm in oxygen	15%–90% (by Volume)
Autoignition Temperature @ 1 atm	1060°F (571°C)
Expansion Ratio, Liquid to Gas, B.P. to 68°F (20°C)	1 to 845

Figure 1

Hydrogen Tube Trailer

Figure 2

A Typical Tube Container System for Bulk Gas



Valves

The Compressed Gas Association and the American National Standards Institute have recommended a thread size of 0.825 inch–14 external left-hand threads per inch, designated as valve connection No. 350. Further information on valves is provided in Air Products' Safetygram-23, "Cylinder Valves," and Safetygram-31, "Cylinder Valve Outlet Connections."

Pressure Relief Devices

Pressure relief devices provide protection against excessive pressure in the container. Pressure relief devices are integral parts of the cylinder valves. They are also recommended for use on pressurized systems. These devices take the form of frangible disks or pressure relief valves. Further information on pressure relief devices is provided in Safetygram-15.

Identification: Cylinders and Mobile Tubes

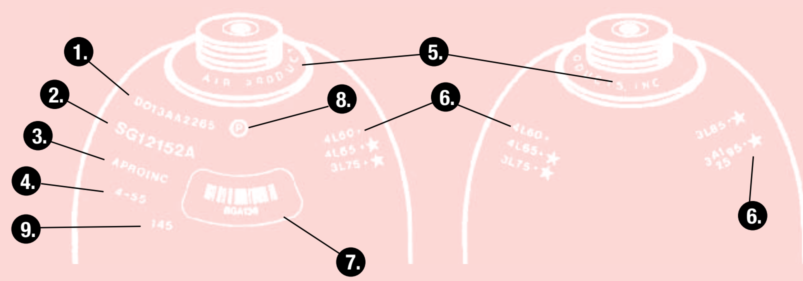
Each cylinder or mobile tube is identified by stampings in the metal of the cylinder shoulder. Figure 3 depicts an example of these markings and what they mean.

Shipment: Hydrogen Cylinders

The shipment of hydrogen cylinders by surface transportation must conform to DOT regulations as set forth in the Code of Federal Regulations, Title 49, which describes the marking, labeling, placarding, and shipping papers required. A DOT 4" x 4" red, flammable label, as illustrated in Figure 4, is required for common carrier shipments. For emergency response, refer to UN Number 1049 in the Department of Transportation's "Emergency Response Guide." Shipments by air must conform with Title 49 in the Code of Federal Regulations. Final acceptance for air transport is at the discretion of the airline.

Figure 3

Key to Cylinder Stampings



1. Cylinder Specification

- DOT–Department of Transportation, which is the regulatory body that governs the use of cylinders.
- Specification of the cylinder type of material of construction (e.g., 3AA).
- Service or working pressure in pounds per square inch (e.g., 2,265 psi).

2. Cylinder Serial Number

3. Registered Owner Symbol

- Symbol used to indicate the original owner of the cylinders.
- APROINC is a Registered Owner Symbol for Air Products.

4. Date of Manufacture

- This date (month-year) also indicates the original hydrostatic test.

5. Neck Ring Identification

- The cylinder neck ring displays the name of the current owner of the cylinder.

6. Retest Markings

- The format for a retest marking is: Month–Facility–Year–Plus Rating–Star Stamp.
- The + symbol (Plus Rating) indicates that the cylinder qualifies for 10% overfill.
- The ★ symbol (Star Stamp) indicates that the cylinder meets the requirements for 10-year retest.

7. Bar Code Label

- The bar code label provides a unique cylinder identifier and is used by computer systems to track cylinders throughout the fill process.

8. Cylinder Manufacturer's Inspection Marking

9. Cylinder Tare (Empty) Weight

Safety Considerations

The hazards associated with handling hydrogen are fire, explosion, and asphyxiation. Although hydrogen tends to dissipate quickly, the potential for forming and igniting flammable mixtures containing hydrogen may be higher than for other flammable gases because:

1. Hydrogen migrates quickly through small openings.

2. The minimum ignition energy for flammable mixtures containing hydrogen is extremely low.

Hydrogen burns with an almost invisable flame and severeburns may result from unknowingly walking into a hydrogen fire. The fire and explosion hazards can be controlled by appropriate design and operating procedures. Preventing the formation of combustible fuel-oxidant mixtures and removing or otherwise inerting potential sources of ignition (electric spark, static electricity, open flames, etc.) in areas where the hydrogen will be used are essential. Careful evacuation and purge operations should be used to prevent the formation of flammable or explosive mixtures. Adequate ventilation will help reduce the possible formation of flammable mixtures in the event of a hydrogen leak and will also eliminate the potential hazard of asphyxiation.

Figure 4

Flammable Gas Shipping Label

Purging

Gaseous hydrogen systems must be purged of air, oxygen, or other oxidizers prior to admitting hydrogen to the systems, and purged of hydrogen before opening the system to the atmosphere. Purging should be done to prevent the formation of flammable mixtures and can be accomplished in several ways.

Piping systems and vessels intended for gaseous hydrogen service should be inerted by suitable purging or evacuation procedures. If the piping systems are extensive or complicated, successive evacuations broken first by an inert gas and finally with hydrogen are most reliable.

Evacuating and purging of equipment in gaseous hydrogen service should include the following considerations:

1. Evacuate the equipment and break vacuum with an inert gas, such as nitrogen. If equipment design does not permit evacuation, pressure and pruge the system with inert gas.

2. Repeat step 1 at least three times. If analytical equipment is available, purge system until oxygen content of residual gas is either less than or meets the process specification impurity level.

   Evacuate or reduce the inert gas pressure in the system to as low pressure as possible

3. Hydrogen may now be introduced to the equipment.

4. Flush system with hydrogen until required purity is reached. Vent all waste hydrogen through a flue or flare stack.

Any purge method should be repeated as often as required to be certain a flammable mixture cannot be formed upon introducing hydrogen or air to the system.

Buildings

1. Provide adequate ventilation, particularly in roof areas where hydrogen might collect. Forced ventilation may be necessary in some applications.

2. The atmosphere in areas in which hydrogen gas may be vented and might collect should be tested with a portable or continuous flammable gas analyzer.

3. 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.

4. Buildings should be electrically grounded.

5. Electrical equipment must conform to the existing National Electrical Codes. Electrical equipment not conforming must be located outside the electrical area classified as hazardous. All electrical equipment must be grounded.

6. Building materials should be noncombustible.

7. Post “No Smoking” and “No Open Flames” signs.

Storage

1. Cylinders should be stored upright in a well ventilated, dry, cool, secure area that is protected from the weather and preferable fire-resistant.

2. No part of a cylinder should ever be allowed to exceed 125º F (52º C) and areas should be free of combustible materials. Never deliberately over-heat a cylinder to increase the pressure or discharge rate.

3. Cylinders should be stored away from heavily traveled areas and emergency exits.

4. Avoid areas where salt and other corrosive materials are present.

5. The valve outlet seal and valve protective cap should be left in place until the cylinder has been secured against a wall or bench, or placed in a cylinder stand and is ready for use.

6. When returning empty cylinders, insure the valve is closed and that some positive pressure remains in the cylinder. Replace any valve outlet and protective caps originally shipped with the container and label the cylinder as "Empty." Do not store full and empty containers together.

7. Post "No Smoking" and "No Open Flames" signs in storage and use areas. Copies of signs may be downloaded from the Air Products' Product Safety website at www.airproducts.com/productsafety.

8. Total storage capacity of an indoor hydrogen system should be limited to 3000 cubic feet.

9. Hydrogen storage inside a building should not be near oxidants or other combustible storage

Handling

1. Know and understand the properties, proper uses and safety precautions of hydrogen before using the gas and associated equipment. Consult the Air Products Material Safety Data Sheet (MSDS) for safety information.

2. Never crack open a hydrogen cylinder to clear the valve of dust as the escaping hydrogen may ignite.

3. Never drop, drag, roll or slide cylinders. Use a specifically designed hand-truck for cylinder movement.

4. Never attempt to lift a cylinder by its cap.

5. Wrenches should never be used to open or close a valve equipped with a handwheel. If the valve is faulty, contact the gas supplier.

6. If difficulty is experienced operating the container valve or using the container connections, discontinue use and contact the gas supplier. Use only the proper connections on the container. **DO NOT USE ADAPTERS!**

7. Always open a compressed gas cylinder valve slowly to avoid rapid system pressurization.

8. **NEVER** insert an object (e.g. wrench, screw driver, pry bar, etc.) into the opening of the cylinder cap. Doing so may damage or inadvertently open the valve. Use only a specially designed strap-wrench to remove over-tightened or rusted caps.

9. Never tamper with the safety devices on valves or cylinders.

10. Use piping and equipment designed to withstand the maximum pressures encountered.

11. Use a pressure reducing regulator or separate control valve along with properly designed pressure relief devices to safety discharge gas to working systems.

12. Use a check valve to prevent reverse gas flow into the containers.

13. When finished with the cylinder, always close the valve. For lengthy work interruptions, the valve should be closed and all residual gas vented from the system to a safe location.

14. If a cylinder or valve is defective or leaking, remove the cylinder to a remote outdoor location away from possible sources of ignition and post the as to the hazard involved. Notify the gas supplier.

15. It is recommended that all vents be piped to the exterior of the building and are in accor dance with local regulations.

16. **Refilling or shipping a compressed gas cylinder without consent of the owner is a violation of federal law**

Bulk Gaseous Storage

Location – General Requirements

A. The system should be located so that is readily accessible to delivery equipment and to authorized personnel.

B. Systems must be located above ground.

C. Systems should not be located beneath electric power lines.

D. Systems should not be located close to flammable liquid piping or piping of other flammable gases.

E. 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 taken.

F. The hydrogen storage location should be permanently placarded: "Hydrogen – Flammable Gas – No Smoking – No Open Flames," or equivalent.

G. The area within 15 feet of any hydrogen container should be kept free of dry vegetation and combustible material.

Table 2

Minimum Distance (ft) from Gaseous Hydrogen Systems to Exposures*

Type of Outdoor Exposure	Size of Hydrogen System		
	Less than 3,500 SCF (99 m^3)	3,500 SCF (99 m^3) to 15,000 SCF (425 m^3)	In Excess of 15,000 SCF (425 m^3)
1. Building/Structure			
a) Wall(s) adjacent to system constructed of noncombustible or limited-combustible materials			
1) Sprinklered building/structure or contents noncombustible.	0[1]	5[1]	5[1]
2) Unsprinklered building/structure with combustible contents.			
Adjacent wall(s) with fire-resistance rating less than 2 hours.[2]	0[3]	10	25[4]
Adjacent wall(s) with fire-resistance rating of 2 hours or greater.[2]	0	5	5
b) Wall(s) adjacent to system constructed of other than noncombustible or limited-combustible materials	10	25	50[4]
2. Wall Openings			
a) Not above any part of a system	10 ft (3.1 m)	10 ft (3.1 m)	10 ft (3.1 m)
b) Above any part of a system	25 ft (7.6 m)	25 ft (7.6 m)	25 ft (7.6 m)
3. All Classes of Flammable and Combustible Liquids Above Ground*			
a) 0–1,000 gallons	10 ft (3.1 m)	25 ft (7.6 m)	25 ft (7.6 m)
b) In excess of 1,000 gallons	25 ft (7.6 m)	50 ft (15.2 m)	50 ft (15.2 m)
4. All Classes of Flammable and Combustible Liquids Below Ground—0–1,000 gallons**			
a) Tank	10 ft (3.1 m)	10 ft (3.1 m)	10 ft (3.1 m)
b) Vent or fill opening of tank	25 ft (7.6 m)	25 ft (7.6 m)	25 ft (7.6 m)
5. All Classes of Flammable and Combustible Liquids Below Ground—In Excess of 1,000 Gallons**			
a) Tank	20 ft (6.1 m)	20 ft (6.1 m)	20 ft (6.1 m)
b) Vent or fill opening of tank	25 ft (7.6 m)	25 ft (7.6 m)	25 ft (7.6 m)
6. Flammable Gas Storage (Other than Hydrogen), Either High Pressure or Low Pressure			
a) 0–15,000 CF (255 m^3) capacity	10 ft (3.1 m)	25 ft (7.6 m)	25 ft (7.6 m)
b) In excess of 15,000 CF (255 m^3) capacity	25 ft (7.6 m)	50 ft (15.2 m)	50 ft (15.2 m)
7. Oxygen Storage			
a) 20,000 CF (566 m^3) or less	Refer to NFPA 51, Gas Systems for Welding and Cutting		
b) More than 20,000 CF (566 m^3)	Refer to NFPA 55 Storage, Use and Handling of Compressed Gases and Cryogenic Fluids		
8. Fast-Burning Solids Such as Ordinary Lumber, Excelsior, or Paper	50 ft (15.2 m)	50 ft (15.2 m)	50 ft (15.2 m)
9. Slow-Burning Solids Such as Heavy Timber or Coal	25 ft (7.6 m)	25 ft (7.6 m)	25 ft (7.6 m)
10. Open Flames and Welding	25 ft (7.6 m)	25 ft (7.6 m)	25 ft (7.6 m)
11. Air Compressor Intakes or Inlets to Ventilating or Air Conditioning Equipment	50 ft (15.2 m)	50 ft (15.2 m)	50 ft (15.2 m)
12. Places of Public Assembly	25 ft (7.6 m)	50 ft (15.2 m)	50 ft (15.2 m)
13. Public Sidewalks	15 ft (4.6 m)	15 ft (4.6 m)	15 ft (4.6 m)
14. Line of Adjoining Property Which May Be Built Upon	5 ft (1.5 m)	5 ft (1.5 m)	5 ft (1.5 m)

[1] Portions of wall less than 10 ft (3 m) (measured horizontally) from any part of a system shall have a fire-resistance rating of at least 1/2 hour.
[2] Exclusive of windows and doors (see item 2).
[3] Portions of wall less than 10 ft (3 m) (measured horizontally) from any part of a system shall have a fire-resistance rating of at least 1 hour.
[4] But not less than one-half the height of adjacent wall of building or structure.
* Distances listed are from NFPA 55.
** Distances may be reduced to 15 ft (4.5 m) for Class IIIB combustible liquids.

Location – Specific Requirements

A. Bulk gaseous hydrogen systems in excess of 15,000 standard cubic feet storage capacity must be located in a separate building or outdoors. It is preferable to locate all bulk gaseous hydrogen systems outdoors, even when the storage capacity is less than 15,000 standard cubic feet.

B. For requirements on storage of hydrogen at less than 15,000 standard cubic feet other than outdoors, see the latest edition of NFPA 55 *Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids*.

C. The minimum distance in feet from a bulk gaseous hydrogen system of indicated capacity located outdoors to any specified outdoor exposure shall be in accordance with the minimum distances as given in Table 2.

D. If protective walls or roofs are provided, they should be constructed of noncombustible materials.

E. If the enclosing sides adjoin each other, the area should be properly vented.

F. Electrical equipment within 15 feet shall be in accordance with Article 501 or the National Electrical Code for Class 1, Division 2, Group B locations.

G. The gaseous hydrogen storage vessels and associated piping shall be electrically bonded and grounded.

H. Adequate lighting shall be provided for nighttime transfer operation.

Personnel Equipment

1. Personnel must be thoroughly familiar with the properties and safety precautions before being allowed to handle hydrogen and/or associated equipment.
2. Safety glasses, safety shoes, and leather gloves are recommended when handling cylinders.
3. In the event of emergency situations, a fire-resistant suit and gloves should be worn. SCBA is also recommended, however, atmospheres that are oxygen-deficient are within the flammable range and should not be entered.

First Aid

Persons suffering from lack of oxygen should be moved to areas with normal atmosphere. Self-contained breathing apparatus may be required to prevent asphyxiation of rescue workers. Assisted respiration and supplemental oxygen should be given if the victim is not breathing.

Fire Fighting

Hydrogen is easily ignited by heat, open flames, electrical sparks, and static electricity. It will burn with a pale blue, almost invisible flame. Most hydrogen fires will have the flame characteristic of a torch or jet and will 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 it is necessary to extinguish the flame in order to get to a place where the flow of hydrogen can be shut off, a dry powder extinguisher is recommended. However, 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 from the hot surfaces or other sources.

The usual fire fighting practice is to prevent the fire from spreading and let it burn until the hydrogen is consumed. Dry powder fire extinguishers should be available in the area. A fire blanket should be conveniently located. An adequate water supply should be available to keep surrounding equipment cool in the event of a hydrogen fire. The local fire department should be advised of the nature of the products handled and made aware of the best known methods for combating hydrogen fires.

Pipeline fires, where shutoff is possible and with flame characteristics of a jet or torch, can be effectively controlled as follows:

1. Slowly reduce the flow of hydrogen feeding the fire. Do not completely stop the flow.
2. When the jet is small enough to be approached, put out the flame with a carbon dioxide or dry powder extinguisher.
3. Close off the supply of hydrogen completely.
4. Ventilate the area thoroughly.

Emergency Response System

- Call: +1-800-523-9374 (Continental U.S. and Puerto Rico)
- Call: +1-610-481-7711 (other locations)
- 24 hours a day, 7 days a week
- For assistance involving Air Products and Chemicals, Inc. products

Product Safety Information

- For MSDS, Safetygrams, and Product Safety Information www.airproducts.com/productsafety

Technical Information Center

- Call: +1-800-752-1597 (U.S.)
- Call: +1-610-481-8565 (other locations)
- Monday–Friday, 8:00 a.m.–5:00 p.m. EST
- Fax: +1-610-481-8690
- E-mail: gastech@airproducts.com

Information Sources

- Compressed Gas Association (CGA) www.cganet.com
- American Chemistry Council www.americanchemistry.com

For More Information

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