



CRYO-STORAGE AND TECHNOLOGIES (CST)

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SafetyAlert-34

The Toxic Metal Hydrides

Arsine, Diborane, Germane, Hydrogen Selenide, Phosphine

General

These products are members of the compound family called metal hydrides. Hydrides are compounds of hydrogen with a more electropositive element. Arsine, diborane, germane, hydrogen selenide, and phosphine are members of a subset family called toxic metal hydrides because of their significant toxicity. The scope of this SafetyAlert will be limited to these five products, which are all liquefied compressed gases. Liquefied compressed gases are gases that, when compressed in a container, partially liquefy at ordinary temperatures and pressures ranging from 25 to 2500 psig (172 to 17237 kPa). In addition to their extreme toxicity, these products are also highly flammable. Toxic metal hydrides are commonly used in the manufacture of semiconductors, as they are used to deposit the base element into the structures of semiconductor circuits to change the properties or grow crystals.

The highly toxic nature of these products has motivated many regulator and code organizations to develop strict rules for the storage and use of these products. Because of their hazardous properties, the purchase of these products is controlled.

Safety Considerations

Health

As can be determined from the exposure levels for the toxic hydrides, these materials are extremely toxic. Even though odor thresholds are noted, odor should never be depended upon for the detection of these materials. Loss of ability to detect the odor after exposure (olfactory fatigue) may also occur, especially for hydrogen selenide. Also, in most cases the odor threshold is above the TWA/PEL. Monitoring is a requirement under most codes and internal EH&S programs.

Arsine

Arsine is an extremely toxic gas that attacks the central nervous system and the circulatory system. Chronic and acute exposures pose serious health effects. Symptoms can be delayed as much as 24 hours. Acute exposures can result in intravascular hemolysis (red blood cell destruction), hemoglobinuria (hemoglobin in the urine), malaise, dizziness,

headache, vomiting, abdominal pain, diarrhea, fainting, and death. In severe exposures the mucous membranes may take on a bluish appearance and the urine may become dark or blood-stained. Jaundice and anemia may occur after a day or two. Chronic exposures may result in cardiovascular disease, peripheral neuropathy, hyperpigmentation, ketatosis, and anemia. Severe kidney, cardiac, and liver damage may occur.

Diborane

Diborane is an extremely toxic gas that attacks the respiratory and central nervous systems. Exposure to the eye may include irritation, redness, and swelling of the conjunctiva. Diborane is an irritant to the respiratory tract and a central nervous system depressant. Symptoms may include headache, nausea, fatigue, shivering, drowsiness, shortness of breath, coughing, chest tightness, pulmonary edema, convulsions, and death. Symptoms may be delayed for up to 24 hours. Skin contact may result in irritation, redness, and swelling. Repeated exposures to low concentrations may result in nausea, dizziness, vertigo, chills, headache, muscular weakness, fatigue, drowsiness, chest tightness, dyspnea, coughing, and wheezing. Sensitive individuals may develop pneumonitis or asthmatic bronchitis from chronic overexposure to diborane. For sublethal exposures symptoms may be present for several days before resolving. Diborane is not stable at ambient temperatures, decomposing to higher boranes, which are liquids and solids. These compounds are just as toxic as diborane but are toxic by skin absorption as well.

Germane

Germane's primary route of exposure is by inhalation and the symptoms of exposure are similar to arsine. These symptoms may include headache, malaise, nausea, vomiting, anorexia, anemia, numbness or tingling of the extremities, abdominal pain, and abnormal breathing. Pulmonary edema, tachycardia, delirium, coma, and death are possible. The urine will usually become darkened in color and the skin may take on a bronze color. Germane causes red blood cell destruction, anemia, hematuria, oliguria, and coppery bronze jaundice and kidney failure.



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Table 1: Physical and Chemical Properties

Property	Arsine	Diborane	Germane	Hydrogen Selenide	Phosphine
Molecular Formula	AsH ₃	B ₂ H ₆	GeH ₄	H ₂ Se	PH ₃
Molecular Weight	77.95	27.67	76.62	80.98	34.0
Specific Gravity (air=1)	2.691	0.96	2.66	2.12	1.174
Vapor Pressure @ 70°F psia	217.9	536.55*	640	137.78	493.2
Vapor Pressure @ 21.1°C kPa, abs	1502	3699*	4413	950	3400
Boiling Point °F	-79.9	-134.8	-127.3	-42	-126
Boiling Point °C	-62	-93	-88.5	-41	-88
Specific Volume (scf/lb)	4.91	13.86	5.05	4.8	11.3
Specific Volume (m ³ /kg)	0.306	0.865	0.315	0.299	0.705
Gas Density (lb/scf)	0.204	0.072	0.2	0.209	0.088
Gas Density (kg/m ³)	3.268	1.153	3.204	3.348	1.41
*vapor pressure is at 60°F (15.6°C)					
Warning: Improper storage, handling, or use of toxic metal hydrides can result in serious injury and/or property damage. Use these products in accordance with the CST Material Safety Data Sheets.					

Table 2: Toxicity

Property	Arsine	Diborane	Germane	Hydrogen Selenide	Phosphine
TLV (TWA)	0.005 ppm	0.1 ppm	0.2 ppm	0.05 ppm	0.3 ppm
PEL (TWA)	0.05 ppm	0.1 ppm	NA	0.05 ppm	0.3 ppm
IDLH	3 ppm	15 ppm	NA	1 ppm	50 ppm
AEGL-1 (30 min)	NA	NA	NA	NA	NA
AEGL-2 (30 min)	0.24 ppm	2.0*	NA	NA	0.36 ppm
AEGL-3 (30 min)	0.7 ppm	7.3*	NA	NA	2.1 ppm
ERPG-1	NA	NA	NA	NA	NA
ERPG-2	0.5 ppm	1 ppm	NA	0.2 ppm	0.5 ppm
ERPG-3	1.5 ppm	3 ppm	NA	2 ppm	5 ppm
LC(50) (1 hr, rat)	178 ppm	80 ppm (TA)	620 ppm	51 ppm	20 ppm (TA)
Odor	Garlic-like	Sickly sweet	Pungent	Penetrating	Decaying fish
Odor Threshold**	<1.0 ppm	1.8-3.5 ppm	Unknown	0.3 ppm	0.14 ppm
TWA: time-weighted average TA: time adjusted * proposed values ** data taken from the 3M 2002 Respirator Selection Guide					

Hydrogen Selenide

Hydrogen selenide is not only toxic by inhalation but also forms selenous acid on contact with the moisture in human tissue, which can lead to chemical burns. Symptoms of inhalation of low concentrations may include coughing, sneezing, and difficulty in breathing. Levels of 0.2 ppm may cause nausea, vomiting, a metallic taste in the mouth, and garlic breath. Levels of 1.5 ppm cause intolerable irritation of the mouth and nose. Higher levels

may cause pulmonary edema; onset may be delayed several hours. Hydrogen selenide is also known to have a hemolytic effect. Hydrogen selenide is metabolized to the relatively nontoxic demethyl selenide. People overexposed to hydrogen selenide can develop a garlic odor to the breath, perspiration, and urine.

Phosphine

Phosphine is an irritant and a general systemic poison. Symptoms may include lacrimation, pulmonary irritation, shortness of breath, cough,

pulmonary edema, cyanosis, headache, dizziness, fatigue, nausea, vomiting, severe epigastric pain, dyspepsia, numbness, paresthesia, ataxia, double vision, tremors, toxic convulsions, agitated psychotic behavior, cardiac abnormalities, liver dysfunction, jaundice, kidney inflammation, and death. The highly toxic nature of these materials makes monitoring an essential part of any process using these products.

The United States Health Department has generated treatment protocols for these products; they are available from their web site or from CST.

In addition to the above toxicity, exposure to the liquid phase of any of these products may cause irritation and frostbite.

Reactivity

Arsine and phosphine are thermally stable.

Diborane is thermally unstable. It decomposes at ambient temperatures to produce hydrogen and higher boranes. Decomposition rate increases with temperature and concentration, producing nonvolatile boranes such as tetraborane and pentaborane. Higher borane decomposition products may be shock-sensitive in air. Some of these higher boranes have high vapor pressures for solids and are as toxic or more toxic than diborane. They are toxic not only by inhalation but also through skin absorption. Diborane also reacts with moisture to form boric acid, a solid. These solids may cause plugging or flow problems in systems. The boric acid is non-toxic, but it is always contaminated with the higher boranes. Extreme care must be taken when working on diborane systems to avoid contact with any solids because they may be highly toxic. Do not blow out systems with a purge since this may spread the solids contaminating the area. Supplied air and body protection is recommended when working on diborane systems even after purging to protect from exposure to the higher boranes.

Germane can decompose instantaneously under certain conditions. The decomposition requires an energy source to initiate, similar to nitrous oxide. Fill volumes of cylinders are adjusted so that if complete decomposition occurs, the cylinder can contain the pressure rise.

Hydrogen selenide reacts with moisture to form selenous acid, which is corrosive to human tissue.

Flammability

The toxic metal hydrides are extremely flammable. They have very low autoignition temperatures and wide flammability ranges. See Table 3 for details.

Containers

The toxic metal hydrides are shipped and stored in high-pressure cylinders. Arsine, germane, hydrogen selenide, and phosphine are sold as pure products and are shipped as liquefied compressed gases under their own vapor pressure (see Table 1, Properties). Diborane is not sold as pure product because of its instability at ambient temperatures. The toxic hydrides are commonly available in mixtures with nitrogen, argon, helium, and hydrogen as the diluent. These mixtures are packaged at pressures up to 2100 psig (14479 kPa). Containers are designed and manufactured to applicable codes and specifications for the pressures and temperatures involved. These include regulations by the Department of Transportation in the United States and the ADR in the European Union. These regulations define the materials of construction, method of manufacture, testing, and what products are permitted to be packaged in cylinders, as well as other details.

Cylinders

A cylinder is a hollow metal tube, typically with a closed concave base that permits the cylinder to stand upright. The opposite end is tapered to a small opening that is threaded to accommodate the installation of a valve. A threaded neck ring is attached to the tapered end to allow a protective cylinder cap to be installed.

Valves and Connections

Valves

Cylinders used to contain the toxic metal hydrides are equipped with diaphragm valves. Diaphragm valves come in two different designs: the spring-loaded diaphragm and the tied diaphragm. The two designs come in manual or pneumatic versions. In the United States, the Department of Transportation requires additional safeguards under CFR49, 173.40.

This includes non-perforated metal diaphragm valves, gas-tight valve outlet seals, performance-tested valve protection, and National Gas Thread connection between valve and cylinder. For more information on these and other types of cylinder valves, refer to CST SafetyAlert-23, "Cylinder Valves." Many regulatory agencies and local code officers require the valves of these products to be equipped with restrictive flow orifices (RFOs). The RFO is a small plug that screws into the valve outlet. It has a hole in the middle that can range in size from 0.006 to 0.16 inches (0.5-4 mm) in diameter. The purpose of the RFO is to restrict the amount of flow that can come from the cylinder in the event of a system failure downstream. There are recommended sizes for most products, but customers can specify their requirements.

Connections

Valve connections for these products may vary from country to country. Table 4 lists the various connections.

For more information on cylinder valve connections, refer to CST SafetyAlert-31, "Cylinder Valve Outlet Connections." Pressure relief devices are prohibited on arsine, diborane, hydrogen selenide, and phosphine. The device is optional on germane; however, CST does not use a pressure relief device because it eliminates possible leak paths.

Storage and Handling

Always store and handle cylinders containing toxic hydrides and other compressed gas cylinders in accordance with Compressed Gas Association Pamphlet P-1, "Safe Handling of Compressed Gases in Containers." For more information, refer to CST SafetyAlert-10, "Handling, Storage, and Use of Compressed Gas Cylinders."

International or local regulations may require additional safeguards for storage or use. Personnel must know and understand the properties, proper uses, and safety precautions for the specific product before using the product or associated equipment.

Storage

Cylinders should be secured in an upright position and stored in a well-ventilated area protected from the weather. The storage area should be secure with limited access. The toxicity of these materials requires area monitoring where these materials are stored and used. Storage area temperatures

Table 3: Flammability

Property	Arsine	Diborane	Germane	Hydrogen Selenide	Phosphine
Flammable Range	3.9-77.8%	0.8-98%	8-30%	4.5-67.5%	1.6-95%
Volume % in air					
Autoignition Temp	NE	-44°F	190°F	NE	< 32°F
NE = none established					
Diborane and phosphine are pyrophoric, which means they may ignite on contact with air.					

Table 4: Valves and Connections

Country	Arsine	Diborane	Germane	Hydrogen Selenide	Phosphine
United States					
Std (CGA)	350/660	350	350/660	350/660	350/660
High Integrity (DISS)	632	632	632	632	632
United Kingdom (BS)	4 or DIN 1	4 or DIN 1	2 or DIN 1	15 or DIN 1	4 or DIN 1
Germany (DIN)	DIN 1	DIN 1	DIN 1	DIN 1	DIN 1
France (NF-E)	E	E	E	E	E
Japan (JIS)	A(W22L)	A(W22L)	--	--	--

should not exceed 125°F (52°C) and should be free from combustible materials and ignition sources. Storage should be away from heavily traveled areas and emergency exits. Avoid areas where salt or other corrosive materials are present. Valve protection caps and valve outlet seals must remain on cylinders not connected. When returning a cylinder to storage, the valve outlet seal must be installed leak-tight. Separate full and empty cylinders. Avoid excess inventory and storage time. Visually inspect stored cylinders on a routine basis, at least weekly, for any indication of leakage or other problems. Use a first-in, first-out inventory system and keep up-to-date inventory records. The use of "FULL," "IN USE," and "EMPTY" tags is highly recommended. Some locales require special planning when storage of these materials exceeds a specific amount. CST has developed overviews for arsine, phosphine, and hydrogen selenide to assist customers with this planning. Before purchasing any of the toxic hydrides, contact the local

authorities to determine the requirements for the storage of these materials. They are typically stored in Hazardous Process Materials rooms, or HPMS. These rooms are designed to meet code requirements for these materials. Storage areas must be posted with the proper signage, such as "No Smoking or Open Flames" and NFPA 704 ratings.

Handling and Use

Use only in well-ventilated areas, preferably in a gas cabinet. Use a suitable handcart designed for cylinder movement. Do not drag, roll, or slide cylinders. Never attempt to lift a cylinder by its cap. Secure cylinders at all times during storage, transport, and use. Use a pressure-reducing regulator or separate control valve to discharge gas from the cylinder. Never apply flame or local heat to any part of a cylinder. Do not allow any part of the cylinder to exceed 125°F (52°C). High temperature may cause damage to the cylinder. If a user experiences any difficulty operating the cylinder valve, discontinue use and contact the supplier. Use an adjustable strap wrench to remove overly tight cylinder caps. Never insert anything into the cap holes to assist in cap removal.

Rapid withdrawal of product (vapor phase) from a cylinder will cause the temperature of the remaining liquid to drop, which may cause sweating or frosting on the outside of the cylinder at the liquid level. The cold temperature of the liquid will decrease the vapor pressure in the cylinder. This may reduce product withdrawal below the requirements of the process or may reverse the flow and allow other process products to backflow into the cylinder. This is an extremely dangerous situation and must be prevented. Extreme care must also be used in compensating for temperature and flow drops. For more detailed information on the use of liquefied compressed gases, refer to CST SafetyAlert-30, "Handling Liquefied Compressed Gas."

Ensure that the cylinder valve is properly closed, the valve outlet seal has been reinstalled leak-tight, and the valve protection cap is installed before returning to storage, moving, or shipping the cylinder.

Disposal

Return unused product to the supplier. Disposal by incineration followed by scrubbing is the most commonly used method for these products. Low concentrations of these materials may be treated through the use of liquid scrubbers containing oxidizing solutions, such as sodium hypochlorite or potassium

permanganate, or with dry scrubbers containing oxidizing or absorbing agents. Disposal of these products by incineration, scrubbing, neutralization, or any other means must be done in an environmentally acceptable manner in compliance with all applicable national and local codes.

System Design and Maintenance

CST strongly suggests that these materials be used in a gas cabinet. This is required by many codes and industry standard practices. The gas cabinets should be ventilated, monitored, and equipped with a sprinkler system. CST gas cabinets designed for these products are equipped with excess flow devices, pressure control valves, process vent, and vacuum and inert purge capability. Recommended options include an automatic shut-off valve as close to the cylinder valve as possible, cylinder connection isolation valve, restricted flow orifice (RFO) preferably located in the cylinder valve, redundant panel isolation valves, various types of monitoring including flame detection, temperature detection, and hydride detection. Some codes may require coaxial tubing; CST recommends the use of coaxial tubing for any tubing runs passing through areas where a corrosive attack may be possible. Automated operation is highly recommended for cylinder changeout. A remote emergency shutdown device is recommended to shut off the product at the source.

The preferred piping for gas lines is seamless 316 or 316L stainless steel and should be of welded construction, rated for at least 1.5 times the maximum operating pressure and leak-tested with helium to at least three times the normal delivery pressure up to the maximum pressure rating of the cylinder. The ideal system would be all welded; however, because of the

necessity of maintenance and replacement of portions of the system, properly installed mechanical fittings can be used. The number of mechanical fittings should be kept to a minimum and located so that they will not be subject to vibration or rotational forces. These fittings should be leak-checked regularly. All possible interconnecting piping between toxic hydrides and oxidizers should be eliminated. All valves used in toxic hydride systems should be of the packless diaphragm or bellows type. Toxic hydride systems should undergo a thorough leak check at every cylinder change as a minimum.

Leak-testing methods may include an outboard helium leak test using a helium mix as a purge source.

Dedicated inert purge gas cylinders should be used for each dispensing system and should be contained in the same gas cabinet or exhausted enclosure. The purge cylinder should be equipped with a pressure-reducing regulator with pressure relief protection and a low-pressure alarm. The purge system should be equipped with back-flow protection and isolation valves. A houseline nitrogen system should never be used for a purge source.

All operators must be trained in system operation as well as the hazards of the gas and only authorized personnel should have access to the system. The system must be regularly inspected. Safe work procedures, including lockout and tagout procedures, should be followed anytime the system is opened.

Personal Protective Equipment (minimum requirements)

General Cylinder Handling

Safety glasses with side shields, leather gloves, and safety shoes.

System Operations

Chemical goggles or safety glasses with side shields as a minimum, leather gloves (except for hydrogen selenide—use nitrile or neoprene).

Emergency Operations

Self-contained breathing apparatus, total body covering with flame-resistant material such as Nomex.

First Aid

Skin and Eye Contact

Frostbite (contact with liquid)—Remove contaminated clothing, warm with lukewarm water, do not rub.

Irritation—Flush with water for 15 minutes, remove contaminated clothing

Seek medical assistance immediately.

Inhalation

Move exposed personnel to uncontaminated area; if victim is not breathing, perform artificial respiration. If breathing is difficult, give oxygen. Seek immediate medical assistance while continuing to administer oxygen.

Thermal Burns

Cool burns with water or clean cloths soaked in cold water. Do not clean wound or remove embedded clothing. Cover burn with clean dry sterile dressing. Seek immediate medical assistance.

Fire Fighting

The toxic hydrides are extremely flammable, with diborane and phosphine being pyrophoric. Only trained personnel should attempt to extinguish fires. Evacuate all personnel from danger area. Do not approach area without self-contained breathing apparatus and protective clothing. Immediately cool cylinders with a water spray from maximum distance, taking care not to extinguish flames. Solid streams of water may be ineffective. Remove ignition sources if without risk. If flames are accidentally extinguished, explosive re-ignition may occur. Appropriate measures must be taken to protect persons from cylinder fragments and toxic fumes should a rupture occur. Re-approach with extreme caution. Combustion products are toxic. Reduce toxic vapors with water spray or fog. If possible, shut off source of gas and let fire burn itself out.

Training

All personnel involved with the handling of these products must be trained in the proper procedures for handling cylinders. Operators must also be trained in the correct operating procedures for the cylinder valves and dispensing and process systems. A thorough knowledge of the product and its associated hazards is required. This would include but not be limited to physical properties, toxicological

properties, and any unusual characteristic of the product. All personnel should have access to the MSDS and training in the proper use of the MSDSs and other reference material.

In the event of a leak only qualified emergency responders, thoroughly familiar with the product and package should respond to the incident. The leaking cylinder should be isolated, and the supplier should be contacted for technical assistance or emergency response.

Information Sources
<ul style="list-style-type: none"> • Compressed Gas Association 1725 Jefferson Davis Highway, Suite 1004 Arlington, VA 22202-4102 Phone: 1-703-412-0900 • National Fire Protection Association 1 Batterymarch Park, P.O. Box 9101 Quincy, MA 02269-9101 Phone: 1-800-344-3555

Table 5: Transportation Information

	Arsine	Germane	Hydrogen Selenide	Phosphine	Diborane Mixtures
Hazard Class	2.3 (toxic gas)	2.3 (toxic gas)	2.3 (toxic gas)	2.3 (toxic gas)	See note
UN Number	UN2188	UN2192	UN2202	UN2199	See note
Shipping Labels	[-----Poison Gas, Flammable Gas-----]				See note
Placard	[-----Poison Gas-----]				See note
Shipping Names	Arsine, 2.3, UN2188, Poison-Inhalation Hazard, Zone A Germane, 2.3, UN2192, Poison-Inhalation Hazard, Zone B Hydrogen Selenide, Anhydrous, 2.3, UN2202, Poison-Inhalation Hazard, Zone A Phosphine, 2.3, UN2199, Poison-Inhalation Hazard, Zone A				
Note: Diborane is shipped in mixtures of various concentrations. These mixtures' shipping categories can range from Compressed Gas Toxic, Flammable, N.O.S. to Compressed Gas, N.O.S. Contact your supplier for details on shipping information for diborane mixtures.					

Emergency Response Telephone Numbers

USA

CHEMTRAC

1-800-424-9300 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
703-527-3887 for calls originating elsewhere (Collect calls are accepted)

CHEM-TEL, INC.

1-800-255-3924 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
813-248-0585 for calls originating elsewhere (Collect calls are accepted)

INFOTRAC

1-800-535-5053 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
352-323-3500 for calls originating elsewhere (Collect calls are accepted)

3E COMPANY

1-800-451-8346 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
760-602-8703 for calls originating elsewhere (Collect calls are accepted)

NATIONAL RESPONSE CENTER (NRC)

Call NRC (24 Hours)

1-800-424-8802 (Toll Free in the U.S., Canada, and U.S. Virgin Islands)
202-267-2675 in the District of Columbia

MILITARY SHIPMENTS

703-697-0218 Explosives/Ammunition Incidents (Collect calls accepted)
1-800-851-8061 All other dangerous goods incidents

NATIONWIDE POISON CONTROL CENTER (United States Only)

1-800-222-1222 (Toll Free in the U.S.)

CANADA

CANUTEC

613-996-6666 (Collect calls are accepted)
*666 Cellular (In Canada only)

Visit Web Site: www.cstusa.biz for further information

or

Call 410-982-6585

or

Ask your local sales representative