AIR PRODUCTS

Safetygram #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 Safetygram 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 regulatory 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.

Table 1

Physical and Chemical Properties

Property		Arsine	Diborane	Germane	Hydrogen Selenide	Phosphine
Molecular Formula		AsH_3	B_2H_6	GeH_4	H_2Se	PH_3
Molecular Weight		77.95	27.67	76.62	80.98	34.0
Specific Gravity (air=1)		2.691	0.955	2.66	2.12	1.174
Vapor Pressure						
@ 70ºF psia		217.9	536.55*	640	120.7	493.2
@ 21.1ºC kPa, abs		1502	3699*	4413	832	3400
Boiling Point	ºF	-79.9	-134.8	-127.3	-42	-126
	ºC	-62	-93	-88.5	-41	-88
Specific Volume	(scf/lb)	4.91	13.86	5.05	4.8	11.3
	(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
	(kg/m^3)	3.268	1.153	3.204	3.348	1.41

*vapor pressure is at 60ºF (15.6ºC)

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 Air Products Material Safety Data Sheets.

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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 bloodstained. Jaundice and anemia may occur after a day or two. Chronic exposures may result in cardiovascular disease, peripheral neuropathy, hyperpigmentation, keratosis, 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.

Table 2

Toxicity

Property	Arsine	Diborane	Germane	Hydrogen Selenide	Phosphine
TWA	0.05 ppm	0.1 ppm	0.2 ppm	0.05 ppm	0.3 ppm
PEL	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 (30min)	NA	NA	NA	NA	NA
AEGL-2 (30min)	0.24 ppm	2.0*	NA	NA	0.36 ppm
AEGL-3 (30min)	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) (1hr,rat)	178 ppm (TA)	80 ppm (TA)	622 ppm (TA)	51-73 ppm	22 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

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 dimethyl 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, parethesia, 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 Air Products.

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 nontoxic, 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.

Table 3

Flammability

Property	Arsine	Diborane	Germane	Hydrogen Selenide	Phosphine
Flammable Range Volume % in air	4.5–64%	0.8–98%	8–30%	4.5–67.5%	1.6–95%
Autoignition Temp	NE	-44 ºF	190 ºF	NE	< 32 ºF

NE = none established

Diborane and phosphine are pyrophoric, which means they may ignite on contact with air.

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 nonperforated 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 Air Products Safetygram-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.

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)	—	—	—

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 Air Products Safetygram-31, "Cylinder Valve Outlet Connections." Pressure relief devices are prohibited on arsine, diborane, hydrogen selenide, and phosphine. The device is optional on germane; however, Air Products 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 Air Products Safetygram-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 should not exceed 125ºF (52ºC) 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