

## 1: PRODUCT AND COMPANY IDENTIFICATION

Product Name: **Germane (GeH<sub>4</sub>) & Hydrogen (H<sub>2</sub>) Mixtures**  
(0.00002% and higher concentrations of GeH<sub>4</sub> in hydrogen or deuterium).

IUPAC Name of Main Process Gas: Germanium tetrahydride

Other Names: Germanium hydride, monogermane, germanomethane, tetrahydridogermanium, gerylene

Shipping Description: **UN1953, Compressed gas, toxic, flammable, n.o.s. ( x mol% germane, 100-x mol% hydrogen), Class 2.3 (2.1), Toxic-Inhalation Hazard Zone B**

Manufacturer: **Metaloid Precursors, Inc.**  
226 Metro Drive, Metrocrest Business Park  
Terrell, TX 75160-9169  
United States of America  
<http://www.metaloids.com>

Telephone Number: 1-972-563-2010

Facsimile: 1-972-692-5486

Hazard Class: 2.3 (toxic – poisonous by inhalation)  
Subsidiary Risks: 2.1 (flammable)  
Code Number: UN 1953  
Chemical Family: Gas, flammable, toxic.  
Product Class: Compressed chemical gas.  
D.O.T. Label: Poison gas, flammable gas.  
NFPA 704: Health 4, Fire 4, Reactivity 3, Other unspecified.  
HMIS code: Health 4, Fire 4, Physical Hazard 3

Product Use: Germane is a precursor for germanium in thin films and amorphous silicon-germanium (SiGe) alloy hetero-structures in electronic device manufacturing.

## 2: COMPOSITION/INFORMATION ON INGREDIENTS

INGREDIENTS	CAS Registry	Molar Concentration	PEL – OSHA †
Germanium tetrahydride, GeH <sub>4</sub>	7782-65-2	0.00002% and higher	0.2ppm
Deuterium, D <sub>2</sub>	7782-39-0	Balance	Simple asphyxiant
Hydrogen, H <sub>2</sub>	1333-74-0	Balance	Simple asphyxiant

† As stated in 29 CFR 1910, Subpart Z (revised July 1, 1993)

## 3: HAZARDS IDENTIFICATION

### 3.1 Emergency overview

Color None	Flammable Yes	Toxic/Poison Gas Yes	Odor Pungent	Heavier than air Yes, 2.7 times at stp
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Germane mixtures are toxic and flammable if released into the atmosphere. Avoid inhalation by all means. Strictly, there should be NO sparks, NO smoking and NO flames.

### 3.2 Health effects

Inhalation Hazard Yes	Respiratory Irritant Yes	Exposure Limits Yes	Eye Irritant Not known	Skin Irritant Not known
Teratogen Not known	Mutagen Not known	Carcinogen Not known	Ingestion Hazard Not known	Asphyxiant Yes

Health hazards resulting from germane poisoning include, but are not limited to, hemolysis (breaking open of red blood cells and the release of hemoglobin into the surrounding fluid), and renal or kidney tissue damage.

Primary route of entry:	Inhalation of germane contaminated air.
Effects of acute exposure:	General malaise, including headache, breathing problems, nausea, tightness in the chest and abdominal pain. Depending on dosage of inhaled gas, acute exposure can result in unconsciousness and possible death.
Effects of chronic exposure:	Kidney damage, possible death

### 3.3 Flammability

<b>Flammability Classification</b>	<b>Flammable</b>
Flash Point	Not available.
Auto ignition temperature	Not available.
Flammable Limits in Air	None established. Assume 100% at upper limit

## 4. First Aid Measures

<b>Inhalation</b>	<p>This is the primary route of exposure to poisonous gases. Do not enter a confined space containing germane-contaminated air unless you are equipped with a portable and self-contained breathing apparatus.</p> <p>(a) If safe, immediately remove the casualty from contaminated area into fresh air.</p> <p>(b) If casualty is unresponsive, open his/her airway by tilting head and lifting chin at the same time.</p> <p>(c) Look, listen and feel for signs of breathing and pulse. If breathing is compromised, administer cardiopulmonary resuscitation (CPR) with two initial breaths. Each breath should make the chest rise.</p> <p>(d) If there is no pulse, administer 15 chest compressions for every CPR breath.</p> <p>(e) Place casualty in recovery position to prevent tongue from blocking the</p>
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For emergency assistance (accident, fire, exposure, or leak), contact CHEMTREC 1-800-424-9300

	<p>throat and allow liquids to drain easily from the mouth. In the recovery position, the head, neck and back should be kept aligned, while the bent limbs keep the body propped comfortably and securely.</p> <p>(f) Call an emergency ambulance (911 in US/Canada, 999 in UK).</p> <p>(g) Keep casualty warm, comfortable, and at rest while awaiting professional medical care. <i>Monitor breathing and pulse every 10 minutes while waiting for medical assistance to arrive.</i> Administer CPR and chest compressions if needed.</p>
<b>Skin Contact</b>	<p>Germane is gaseous at room conditions. Although intimate skin contact is unlikely under safe operating conditions, a defective valve can throw a gaseous plume onto personnel, in which case, clothing can become saturated in germane leading to prolonged skin contact. First aid measures include:-</p> <p>(a) Quickly move away from source of contamination to fresh air</p> <p>(b) Immediately remove contaminated clothing.</p> <p>(c) Assume gas has been inhaled and summon assistance. Call an emergency ambulance (911 in US/Canada, 999 in UK).</p>
<b>Eye Contact</b>	<p>(a) Flush eye several times with clean cold water ensuring the water drains away from the eye.</p> <p>(b) Do not touch or rub the eye.</p> <p>(c) Refrain from looking around to avoid moving eye-ball.</p> <p>(d) Place sterile dressing or clean pad over eye and keep uninjured eye closed.</p> <p>(e) Call an emergency ambulance (911 in US/Canada, 999 in UK).</p>
<b>Ingestion</b>	<p>Although exposure by ingestion is not common, however under such circumstances immediately call an emergency ambulance.</p>

## 5. Fire Fighting Measures

Conditions of flammability	Ignition source and oxidant present.
Exinction	<p>Immediately evacuate all personnel and isolate scene as a hazard area. If safe to do so shut off germane gas supply, otherwise allow fire to consume the gas completely.</p> <p>Allowing gas to burn avoids the formation of a toxic and explosive mixture in air. If fire is proximal to gas cylinder, spray cylinder and surrounding area with cold water to dissipate heat of combustion and prevent dangerous pressure buildup and possible mechanical weakening of cylinder and its valve.</p>

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	Use a positive pressure, self contained breathing apparatus with a full face-piece that meets industry standards in all fire fighting involving germane gas.
Upper flammable limit	Assume 100%
Lower flammable limit	Not established.
Hazardous combustion products	Germanium hydride burns to form germanium oxide particulates which present an inhalation (dust) hazard.
Explosion data	None established.

## 6. Accidental Release Measures

In a germane gas release in an unconfined space (e.g. outside storage area), immediately evacuate all personnel to a location up-wind of leakage source. Because germane gas is 2.7 times heavier than air at room conditions, gas leakage can diffuse at ground level for hundreds of feet. The footprint depends on quantity of germane gas released, ambient wind speed, temperature and nature of terrain. Evacuated personnel should avoid ignition sources, e.g. lit cigarettes.

Where a leak occurs in a confined space such as in a laboratory setting, or in a fume hood or gas cabinet, the user should purge the contaminated space thoroughly with a non-reactive gas such as nitrogen. Air in the contaminated space should be tested for residual germane gas. The affected space should not be considered safe until the air has been tested and demonstrated to contain at least 19.5% oxygen. Personnel should strictly observe safety procedures which include wearing a full body suit and breathing equipment with a full-face mask attached to a portable air pack or airline.

### Containment

Germane gas should be stored at room temperature in a sealed cylinder in compliance with CGA P-1, *Safe Handling of Compressed Gases in Containers*, local ordinances and applicable regulations. If gas cylinder is connected to a piping system fed by other fluids from high pressure sources, the piping design and operation should prevent possible back flow of process or non-process fluids into the germane gas cylinder. Should back-flow occur and the germane cylinder becomes contaminated, user should immediately contact vendor.

## 7. Handling and Storage

Health hazard from germane gas inhalation can occur at 0.2ppm. Small germane gas leaks can spread rapidly in air currents generated by room fans and vehicle motion. Any small leak presents a potential health risk and must be appropriately managed (see Section 6).

### Handling Procedures and Safety Considerations

Facilities using germane gas are advised to install emergency oxygen equipment, safety showers and eyewash fountains. Additionally, an emergency response plan and personnel trained on emergency procedures are recommended. Strictly, there should be NO open flames, NO sparks and NO smoking.

Operations should be conducted in facilities suitably designed to handle hazardous gases safely and should comply with industry guidelines (see CGA P-1, *Safe Handling of Compressed Gases in Containers*), local ordinances and applicable regulations. Users are hereby recommended to consult



specialists on hazardous gaseous material for the design and operation of gas handling systems. Key safety components include:-

### **Codes and Standards**

ATEX, NEC and other national/regional codes. Non-sparking equipment and earth bonding of equipment are recommended. Electrical equipment should be explosion proof or rendered safe by appropriate shrouding and continuous purging of shrouds with non reactive gases such as nitrogen.

### **Enclosed Spaces**

Should be provided with inert purge gases such as helium or nitrogen. Enclosures should advantageously have vent line sensors and aerial detectors in adjacent work areas, all hard wired to facility alarms. Use of Hydrogen deflagration Nomograph for venting is recommended (see NFPA document 68 "Venting of Deflagrations").

### **Removing Valve Dust Caps**

A bubble of germane gas can buildup behind the outlet dust cap during transportation, after prolonged storage, due to defective cylinder valve or if dust cap is inserted without adequate evacuation of germane gas from line. When loosening dust cap, preferably stand cylinder in a suitable enclosure under negative pressure (relative to atmospheric pressure) and take off cap slowly. Never face the dust cap directly when removing it and point cap away from any personnel or any object that may pose a hazard.

### **Connecting and Disconnecting Germane Gas Cylinders**

The tubing network design connecting germane gas cylinders to your system should include appropriate pressure indicators, inert gas supply and vacuum or suction lines. Fully-welded types of pressure gauges where the bourdon tube sensing element is welded to gage body are recommended. Before connecting germane gas cylinder, ensure the manifold is mechanically secure and does not contain an oxidizing gas. Before disconnecting germane gas cylinder, isolate supply line segment proximal to cylinder, remove trapped germane gas in supply line with the aid of a vacuum pump and back-fill it with helium or nitrogen. Never introduce any substance into a germane gas cylinder. If your gas cylinder is contaminated then notify gas manufacturer or vendor immediately.

### **Storage Cylinder Handling**

Germane gas cylinders should be stored and maintained in accordance with CGA P-1, *Safe Handling of Compressed Gases in Containers*, and in compliance with State and Federal Laws, including building and fire codes. Germane cylinders should be stored upright, firmly secured in a cool, dry, well-ventilated area and away from heavily used access routes and emergency exits. Storage room temperatures should not exceed 50°C (122°F). All cylinders, full or empty, should be fitted with dust caps. Do not store close to oxidizers and halogens.

### **Cylinder Handling**

Use a suitable hand truck to move cylinders. Do not drag, roll, slide or drop. Never attempt to lift a cylinder by its cap. Cylinder cap is intended to protect valve. Never insert pointed objects (e.g., hooks) into cylinder cap openings as a means to open cap or move cylinder. Such action can inadvertently turn the valve and cause a toxic gas leak. Use an adjustable strap instead of a wrench to free an over-tight or rusted cap. Open valve slowly. If valve is resistant to opening then contact your supervisor.

## **8. Exposure Controls/Personal Protection**

### **Specific engineering controls to be used**

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Also see Section 7. To minimize the risk of personnel exposure to germane gas, the cylinders should be kept in a hazard gas cabinet or dedicated storage area fitted with leak detectors. When carrying out routine work, such as changing germane gas cylinders, operator should stand outside enclosure where possible, carry a portable leak detector or wear a respiratory protection system to go inside enclosure.

**Personal protective equipment to be used**

<b>Inhalation hazard</b>	Use full face positive-pressure mask on an air line or a portable self-contained breathing apparatus equipped with an escape air capsule in response to a leak.
<b>Eye/Face Protection</b>	Use safety goggles or glasses to guard against accidental gas jet-impact.
<b>Skin Protection</b>	Use industry standard gloves for fire protection.
<b>Slip</b>	Use industry standard non-slip and anti-static shoes.

## 9. Physical and Chemical Properties

Property data tabulated at 0°C and 1.0 atmosphere unless stated otherwise.

Property	Germane	Hydrogen	Deuterium
Physical state	Gas	Gas	Gas
Vap. pressure at 21°C	640 psia	Superheated gas	Superheated gas
Auto-ignition temp.	87.8°C	560°C	560°C
Boiling point	-88.4°C	-252.8°C	-249.7°C
Critical temperature	34.8°C	-240 °C	-234.8 °C
Critical pressure	805 psia	188.26 psia	241.49 psia
Vapor density	3.42 g/L	.0897g/ L	0.177 g/L
Melting/freezing point	-165.98°C	-259 °C	-254.6°C
Molar mass, g/mol	76.62	2.016	4.029
Solubility in water, v/v	insoluble	.0214	.02
Spec. gravity of liquid	1.36 at bpt	.071 at bpt	0.1624 at bpt.
Odor	Pungent	None	None
Appearance	Colorless	Colorless	Colorless

## 10. Stability and Reactivity

<b>Chemical stability</b>	Stable at room temperature Thermally decomposes around 300°C into germanium metal and hydrogen gas
<b>Incompatibility</b>	With halogens and oxidizers
<b>Decomposition in air</b>	Produces hydrogen and germanium oxide
<b>Hazardous polymerization</b>	Not known

## 11. Toxicological Information

The respiratory LC<sub>50</sub> in mice is 1380 mg/m<sup>3</sup> for pure germane. In this reported study, clinical signs were dyspnea, convulsion and coma. Autopsy revealed congested internal organs, hemorrhages, nerve cell

vacuolization and degenerative changes in the cells of parenchymal organs. Guinea pigs exposed to 80 – 480ppm presented similar pathological changes.

## 12. Ecological Information

None known.

## 13. Disposal Considerations

Disposal of unused quantities in air is strongly discouraged. Non-direct contact heat exchangers using liquid nitrogen as cooling medium can freeze out germane gas in vent flows. The design of cryogenic vent scrubbers should be undertaken with expert consultation. Recovered concentrations of waste gas can be burned in an approved incinerator equipped with an afterburner and wet scrubber. Users can, with written approval, return in the original shipping cylinder any unused quantities with labels, valve dust cap, cylinder cap and a post-sale certificate of analysis to Metaloid Precursors, Inc. for disposal.

**Classification under RCRA, 40 CFR 261:** Material meets criteria for an "acute hazardous waste".

## 14. Transport Information

**U.S. DOT 49 CFR 172.101 (Hazardous Materials Table):**

SHIPPING NAME: Compressed gas, toxic, flammable, n.o.s. (x% Germane in (1-x%) Hydrogen or Deuterium);	ID NUMBER: UN 1953
HAZARD CLASS: 2.1, 2.3;	LABELING REQUIREMENTS: 2.1; 2.3
PASSENGER AIRCRAFT: Forbidden;	CARGO AIRCRAFT ONLY: Forbidden
RAILCAR: Forbidden	CAR TRUNK/CAR TRUCK/STATION WAGON: Forbidden
ADDITIONAL SHIPPING DESCRIPTION: Toxic-Inhalation Hazard Zone B	

## 15. Regulatory Information

**CERCLA (40 CFR 302.40), the Comprehensive Environmental Response, Compensation & Liability Act (CERCLA) also known as the Super Fund Act:** Germanium hydrides are not listed. The baseline reportable 100lbs (45.4kg) for unlisted hazardous wastes such as germanium hydrides applies.

**Superfund Amendments and Reauthorization Act (SARA) Title III Status (40 CFR 355 §302, 40 CFR 372 §311-313):** Neither threshold planning quantity (TPQ) nor reportable quantity (RQ) for germanium hydride is listed.

**SARA Title III Hazard Classes:** Acute health hazard (poison gas), chronic health hazard, fire hazard, sudden release of pressure hazard.

**Other:** Obtain written permission from owner before refilling a compressed gas cylinder. It is a violation of transportation regulations to transport a compressed gas cylinder that has not been filled by the owner or without the owner's written permission.

## 16. Other Information

### REFERENCES

ANSI Standard Z400.1-1993

§ 29 CFR 1910, Subpart Z, revised July 1993

† *American Conference of Government Industrial Hygienists*, 2006 Threshold Limit Values and Biological Exposure Indices.

Karen Craig and Loraine Hopkins-Pepe, American Heart Association Guidelines, part 1; Nursing 2006, Vol. 36, Number 4, p53.

‡ Health Council of the Netherlands, Report No. 2000/150SH/006, The Hague, 14 December 2000.

Saul Patai, *The Chemistry of Organic Germanium, Tin and Lead Compounds*, John Wiley & Sons, Ltd., 1995

Richard A. Bolmen, *Semiconductor Safety Handbook: Chapter 4 on Industrial Hygiene*, Noyes, 1998.

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Lou Hall, The thermal decomposition of germane, *J. Electrochem. Soc.*, Volume 119, Issue 11, pp. 1593-1596 (1972)

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