Chemically Speaking LLC

Germane

Germane (germanium hydride, CAS#7782-65-2; UN2192)

A. Physical Properties

Pure germane (GeH_4) is a colorless, liquefied gas with a vapor pressure of 569 psig (3.923 MPa) at 70°F (21°C).

- Germane is a liquefied gas that is toxic and flammable
- Germanium Hydride, GeH_4
- CAS# 7782-65-2
- UN# 2192
- Molecular Weight 76.62
- Liquefied Gas with Vapor Pressure of 569 psig (3.923 mPa) @ 70°F (21°C) 625 psig (4.309 mPa) @ 77°F (24°C)
- Gas Density of 0.2 lb/ft^3 (3.19 gm/l) @ 70°F (21°C)
- Liquid Density of 53.76 lb/ft^3 (859 gm/l) @ 70°F (21°C)
- Highly Toxic Gas with PEL of none listed, TLV of 0.2 ppm, LC_{50} of 622 ppm, IDLH none listed
- Boiling Point, 1 atm. -127.3°F (-88.5°C)
- Freezing Point, 1 atm. -266.76°F (-165.98°C)
- Critical Temperature 94.7°F (34.9°C)
- Germane has a vapor density heavier than air. - 2.65
- Gas Specific Volume @ 70°F (21°C) - 5.05 ft^3/lb (315 cc/gm)
- Autoignition - 343°F (173°C) Note Hazard's Research has reported 90°C and 302°F (150°C) and a Russian paper reported 237°C. Adiabatic compression of air lowered it to 20°C
- Flammability (LFL -UFL) - 2.8-98% In a fire Germane will oxidize to Germanium Dioxide
- Thermal Stability - Germane is thermally stable up to 536°F (280°C). Germane has demonstrated the ability to autodecompose given sufficient energy heating the byproduct H_2 to the mp of Germanium 1721 °F (938°C)
- Water Solubility - Germane is slightly soluble in water
- Odor - Germane is reported to have a metallic odor similar to Arsine
- Latent Heat of Vaporization -126.7°F (-88°C) - 81.1 btu/lb (188.5 kJ/kg) at Boiling Point

It is a toxic gas with no personal exposure limit (PEL) listed, a lethal concentration value (LC_{50}) of 622 ppm and no immediately dangerous to life or health (IDLH) value listed. Germane is much heavier than air (specific gravity 2.65) and is insoluble in water. Germane is thermally stable up to 536°F (280°C) Germane has demonstrated the ability to auto decompose given sufficient energy heating the byproduct H_2 to the mp of Germanium 1721 °F (938°C) see Incidents for details. Germane has a auto-ignition temperature 343°F (173°C). It has an extremely wide flammable range of 2.8% – 98% in air. It burns in air

B. Health and Safety

The primary route of entry into the body is through inhalation. Germane is not known to have a dermal route of entry.

The odor of Germane is reported to be similar to arsine which is not unpleasant or irritating, as a result an acute exposure can easily occur. Major effect of acute exposure is believed to be similar to arsine

hemolysis of red blood cells. The key symptom of arsine acute exposure is red urine which is caused by the body trying to eliminate the dead red blood cells. If left untreated, renal (kidney, liver) failure will occur. Based on mouse exposure studies, germane is not as toxic as arsine.
Guidance on proper medical treatment for arsine exposure is available from the US Health Department Agency for Toxic Substances and Disease Registry (ATSDR). Treatment is whole blood transfusion.

Similar to acetylene (C_2H_2), germane (GeH_4)is an unstable gas. Others include nitrogen trifluoride (NF_3), nitrous oxide (N_2O) and nitric oxide (NO). These gases can start to decompose when given sufficient energy input. (thermodynamically unstable).

An unstable gas is defined as the heat (exothermic) given off by the decomposition or polymerization reaction causes other molecules to decompose and accelerates the reaction rate. The reaction wave front can heat and compress the unreacted gas to detonation in a large diameter tube/chamber.

C. Production

Germane was originally manufactured by Matheson Gas Products in the early 1970's at the Gloucester, MA facility. The primary use was for the production of germanium based rectifiers and diodes. It was also used to make photocopy drums.
Germane (GeH_4) was prepared from $NaBH_4$ reduction of $GeCl_4$ that was dissolved in ether.

$$GeCl_4 + 4NaBH_4 \Rightarrow GeH_4 + 4NaCl + 2B_2H_6$$

The disadvantage to this method was the formation of diborane which is an electrically active contaminant and had to be reduced to very low levels.

1. Germanium Dioxide

Voltaix (1987, US Patent 4,668,502) and Mitsui (1998, Japanese Patent 10,291,804) both have patents describing the conversion of GeO_2 to GeH_4 with high yields. The process works by dissolving GeO_2 and $NaBH_4$ in a KOH or NaOH solution, and then acidifying with aqueous acid at 25°C

$$GeO_2 \ + \ NaBH_4 \ \ KOH\ (aq) \Rightarrow \ HGeO- \ + \ BH_4- \quad H- \quad GeHb + \ H_3BO_3$$

This process was developed at Energy Conversion Devices (ECD) where J. De Neufville, founder of Voltaix was working. When ECD closed their North Branch, NJ location, Voltaix was founded a short distance away to manufacture germane and other specialty gases. Voltaix opened a germane manufacturing facility in Korea in 2012.

2. Germanium Tetrachloride

The reaction of $GeCl_4$ with hydride to generate GeH_4 does not proceed smoothly. The problem lies in the production of Ge(II) species, such as GeCl2, along with the production of polymeric (GeH2)x and (GeH)x (both of which could be explosive). The reaction shown in Eq.2 in THF solvent is described by Macklen (J. Chem. Soc. (1959), 1984.) to give only 20-40% yields. Decomposition products included polymeric GeH_2 compounds, H_2, and HCl. It was also shown that germane is significantly soluble in THF, making it difficult to recover.

$$GeCl_4 + LiAlH_4 \text{ in THF} \Rightarrow GeH_4 + LiCl + AlCl_3$$

3. Electrochemical

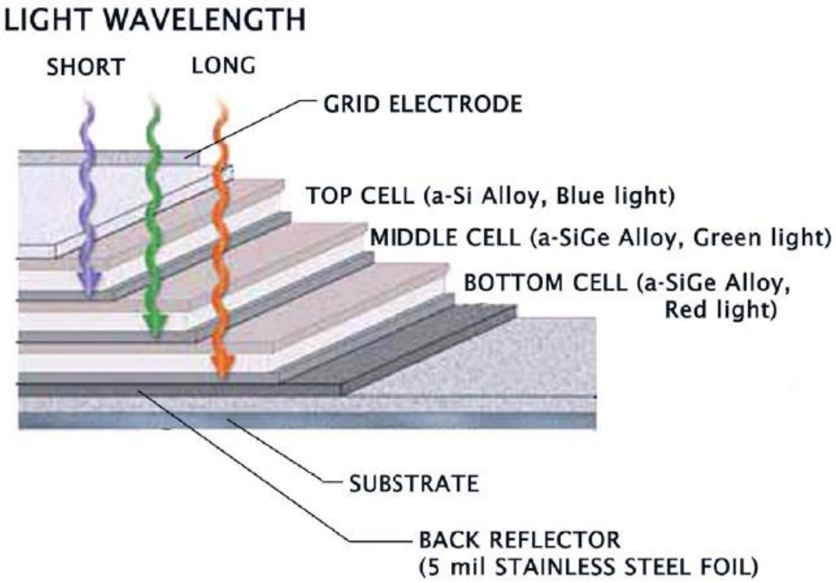
There are two patents by Electron Transfer Technologies (ETT) describing the electrochemical production and delivery of GeH_4 (2000: US 6,080,297, 1992: US 5,158,656). A solid Ge cathode is immersed into a NaOH electrolyte solution. GeH_4 and H_2 evolve off the cathode at room temperature with 30% efficiency of GeH_4, the balance being H_2. The germane is generated, purified, mixed with dilutant gas (H_2), and delivered as needed directly to the semiconductor processing tool as needed.

Bill Ayers the owner of ETT worked at Energy Conversion Devices and was involved in the development of the GeH_4 process

D. Application and Use:

Germane is not used in compound semiconductor applications. A key use for germane was for tandem junction solar cells made by Unisolar (an Energy Conversion Device company). These were thin films deposited onto a flexible stainless steel sheet to form a high efficiency solar cell.

United Solar Ovonic Triple Junction Solar Cells

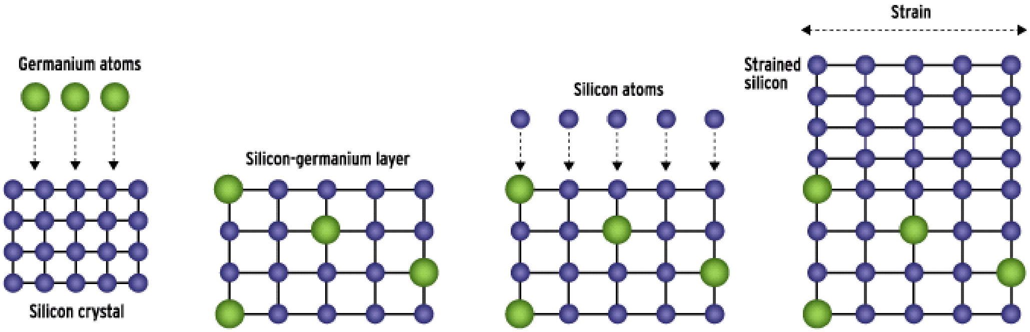


Due to the downturn in the solar cell business, Unisolar and ECD filed for bankruptcy in May 2012. It is not known what will happen to the technology.

Low concentration germane/hydrogen mixtures are used in the epitaxial growth of silicon germanium (SiGe). SiGe ICs compete directly with both Si-based CMOS ICs and GaAs-based ICs. SiGe applications have grown significantly because:

Provides faster chip speeds
Lower power consumption
Lower production costs

Band gap engineering through substitution of Si with Ge atoms creates tensile or compressive strain that increases carrier mobility



Major IC companies such as Samsung, IBM, Intel have increased their usage of germane

History

Matheson manufactured and filled pure germane cylinders for many years to a density of 0.227 kg/liter. On Nov. 26, 1984, a 44 liter cylinder filled to 10 kg (5% liquid) ruptured violently as a worker at the Nippon Sanso Kawasaki Japan facility was removing it from the delivery truck. He and a second worker were seriously injured. This cylinder was shipped from the Matheson, Gloucester, MA facility. MITI could not establish the source of ignition. The decomposition reaction heated the byproducts of the reaction Germanium & Hydrogen to 1719°F (937°C)

$$GeH_4 \Rightarrow Ge + 2H_2 + \text{Heat}$$

The decomposition reaction was a rapid deflagration that occurred in 100 milliseconds creating a final pressure of over 9000 psig rupturing the high pressure seamless cylinder.

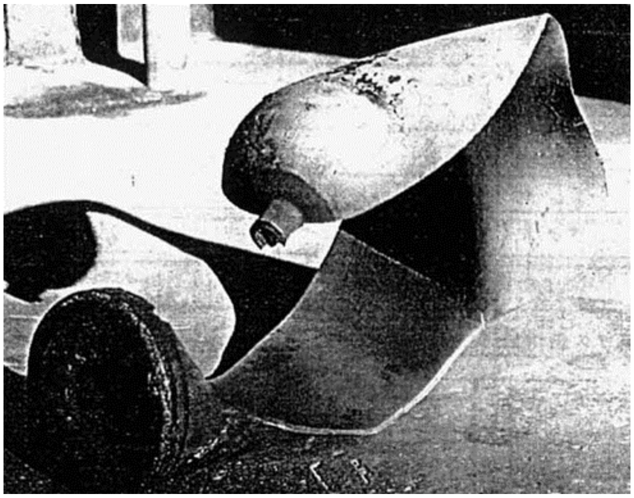


Fig. 1: Germane Cylinder Explosion

Hazards Research Corporation was contracted by Matheson to test pure Germane. They determined that pure germane can deflagrate when ignited with a spark in the absence of air, decomposing to Ge metal and hydrogen, exothermically.[1,2] It is estimated that the cylinder reached a pressure >9000 psig in

100 milliseconds. Immediately after this report, Matheson changed the fill density from 0.227 kg/liter to 0.062 kg/liter based on theoretical calculations assuming full adiabatic decomposition and the test pressure of the cylinder.

Additional testing by Hazards Research in 1986 for Voltaix Inc and Horiguchi, Urano and Kondo confirmed that pure Germane will deflagrate.[2]

One test by Horiguchi at a fill density of 0.225 kg/liter resulted in a pressure increase to 9775 psig confirming the earlier theoretical calculations.

Based on this testing Voltaix Inc. established a maximum fill density of 0.045 kg/liter assuming the working pressure of the cylinder could not be exceeded during an event causing full decoposition.

T. Hirano in his article "Accidental explosions of semiconductor manufacturing gases in Japan", Journal of Loss Prevention in the Process Industries, 17, pg 29-34, 2004 reported a second Germane explosion in a process collector in Japan believed to be Honjo Chemical. The company and date of the incident was not given.

Numerous tests were conducted on germane, autoignition, impact, etc which confirmed its instability.[1,2,3]

There was concern that the other metal hydride gases would exhibit the same behavior so the Compressed Gas Association funded the study of the other metal hydride gases for stability'

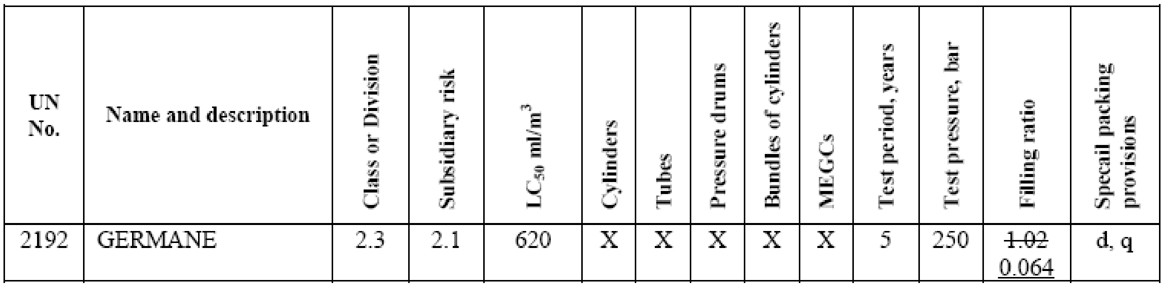
Arsine
Diborane Mixtures
Disilane
Hydrogen Selenide
Phosphine

Silane was not included as it had been studied numerous times and proven to be ok. and they all were proven not to undergo the same self sustaining decomposition of germane. [7]

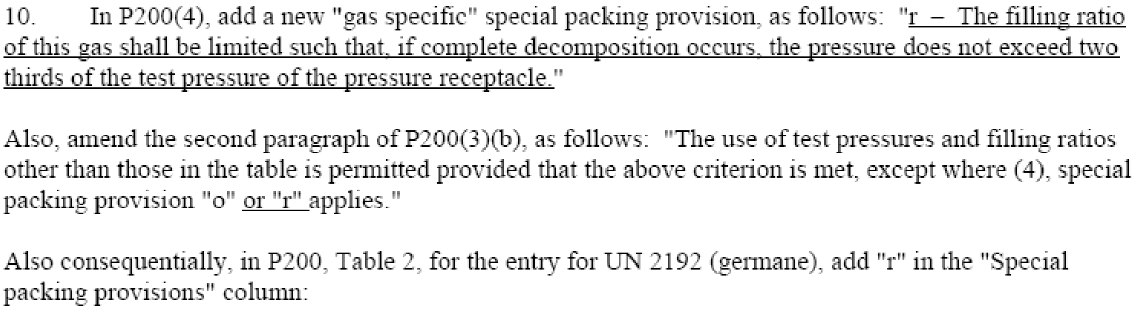
The reduction in fill density has prevented at least 3 incidents from becoming significant events in the last 10 years. The reasons for the decompositions have not been determined. However all 3 cylinders were found to have only H_2. In one incident the operator reported that the cylinder jumped up and felt hot while he was preparing for shipment.

This lesson was forgotten in 2004 when the US DOT and the UN Transport of Dangerous Goods Committee proposed an increased fill density. (See CGA Letter Germane Nitric Oxide Maximum Fill) On Nov. 22, 2005 E. Ngai's letter to Bob Richards of the U.S. Dept. of Transportation, Subject: Recommended Fill Density for Germane summarized the history and reasons for the reduced fill density. This included a letter to CGA on July 7, 2005, "Fill Density for Germane and Nitric Oxide" and to M.

Toughiry, Sept 25, 2005, “Information for Germane, Stibine and Dichlorosilane Cylinder Fill Calculations” and the lower fill density was kept in place. (See DOT Letter Re Germane, Stibine, and Dichlorosilane Cylinder Fill Calculations)



UN No.	Name and description	Class or Division	Subsidiary risk	LC_{50} ml/m^3	Cylinders	Tubes	Pressure drums	Bundles of cylinders	MEGCs	Test period, years	Test pressure, bar	Filling ratio	Specail packing provisions
2192	GERMANE	2.3	2.1	620	X	X	X	X	X	5	250	~~1.02~~ 0.064	d, q

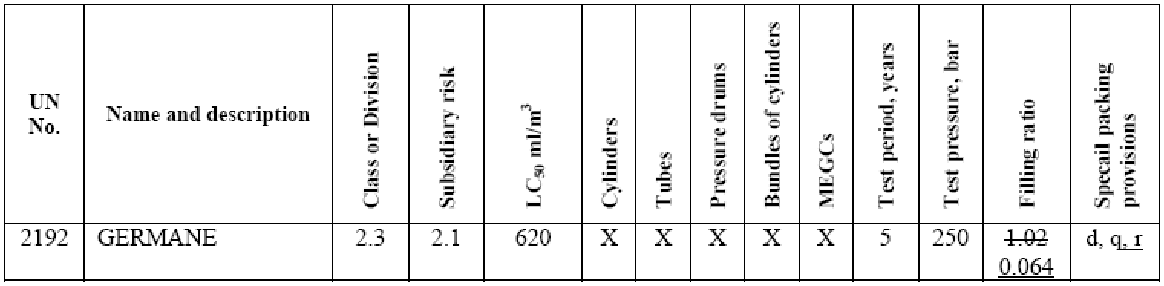


10. In P200(4), add a new "gas specific" special packing provision, as follows: "r – The filling ratio of this gas shall be limited such that, if complete decomposition occurs, the pressure does not exceed two thirds of the test pressure of the pressure receptacle."

Also, amend the second paragraph of P200(3)(b), as follows: "The use of test pressures and filling ratios other than those in the table is permitted provided that the above criterion is met, except where (4), special packing provision "o" or "r" applies."

Also consequentially, in P200, Table 2, for the entry for UN 2192 (germane), add "r" in the "Special packing provisions" column:

Horiguchi and co-workers have done definitive research on the properties of germane mixtures. They have shown that mixtures in helium containing up to 30% germane and mixtures in hydrogen containing up to 40% germane will not deflagrate in the presence of a source of ignition (including experiments using nitrocellulose on the ignition wire as an additional source of energy input into the mixture).4 The thermal conductivity of the balance gas quenches the decomposition reaction and prevents the propagation. As a result, a greater quantity of germane can be shipped in a mixture than as a pure gas.



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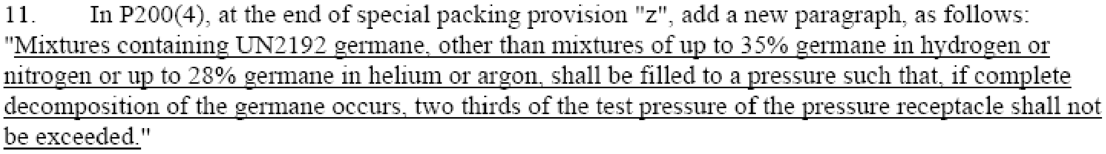

11. In P200(4), at the end of special packing provision "z", add a new paragraph, as follows: "Mixtures containing UN2192 germane, other than mixtures of up to 35% germane in hydrogen or nitrogen or up to 28% germane in helium or argon, shall be filled to a pressure such that, if complete decomposition of the germane occurs, two thirds of the test pressure of the pressure receptacle shall not be exceeded."

Autoignition temperature reported varied considerably. 343°F (173°C) Note Hazard's Research has reported 194°F (90°C) and 302°F (150°C) and a Russian paper reported 459°F (237°C).

What is significant is the influence of very small quantities of air. The oxidation reaction can provide sufficient energy to initiate the decomposition reaction. A forseeable event is an operator not purging the pigtail of air. Opening a full germane cylinder can create enough adiabatic compression heat to ignite the germane/oxygen mixture. This is sufficient energy to trigger the decomposition reaction which will propagate in the pigtail back into the cylinder, causing the contents to decompose.

Pure Germane decomposition is initiated at a temperature of 240-280°C or higher. The introduction of a small quantity of air greatly decreases this temperature. Increasing pressure also lowers it dramatically. For example, at a pressure of 0 psig with the addition of air ignition occurred at 150°C. At 250 psig this drops to 65°C and at 500 psig it is ambient temperatures 20°C

The second item of significance is the influence of pressure. At 0 psig the autoignition temperature of germane in air was 145-150 C. Pressurizing it to 500 psig dropped it to less than 20 C.

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References:

1. "Hazardous Properties of Germane Mixtures", HRC Report 5879A to Matheson Gas Products, Hazards Research Inc., Oct 28, 1985
2. "Hazardous Properties of Germane Mixtures", HRC Report 5879B to Matheson Gas Products, Hazards Research Inc., April 10, 1986
3. Hazards Research Report 6023, "Germane Deflagration Study", to Energy Conversion Devices, North Branch, NJ, April 11, 1986
4. Horiguchi, S., Kondo, S., Urano, Y. and Gasu, K., "Explosive Decomposition of Germane-Propagating Flame and Minimum Explosive Pressure", Journal of the High Pressure Gas Safety Institute of Japan, Vol 30, No. 11 799-809, 1993
5. "Decomposition Explosion Hazards of Semiconductor Manufacturing Gases", Journal of High Pressure Gas Safety Institute of Japan, 28(3), pp 270-284, 1991
6. "Decomposition Explosion Hazards of Semiconductor Manufacturing Gases", Journal of High Pressure Gas Safety Institute of Japan, 28(5), pp 351-363, 1991
7. Report on the Thermal Stability and Self Flammability of Five Metal Hydride Gases. Hazards Testing Company, Blue Springs, MO for the Compressed Gas Association, May 2, 1988

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