Silane is one of the key metal hydride gases used in the semiconductor industry

- Arsine (AsH₃)
- Diborane B₂H₆
- Germane (GeH₄)
- Hydrogen Selenide (H₂Se)
- Phosphine (PH₃)
- Silane (SiH₄)

Silane is the only metal hydride gas in common use that is not toxic

Major hazard is pyrophoric and high pressure

Silane can be released without immediate ignition

Silane has caused more fatalities than all of the metal hydride gases put together

Silane is Used

- Integrated circuits
  - Memory
  - CPU
  - Logic
- TFT-Liquid Crystal Displays
- Silicon Photovoltaic Cells
  - Crystalline
  - Thin Film
- Compound Semiconductor Dopant
- Glass coating

Silane is made

Catalytic redistribution chemistry of HSiCl₃
  - R₃N, R₃P, RCN, Al₂O₃, Al₂O₃/SiO₂, SiO₂/R₃N, (R₃P)NX (X= Cl, CN, BF₄, RO, etc.), weak base ion exchange resin, etc.

Metal reduction chemistry of SiF₄, HSiCl₃, Si(OR)₄ or SiCl₄
  - DIBAH, MH (M=Li, K, Na, etc.), MgH₂, etc.

Magnesium Silicide (Mg₂Si) in NH₄Cl or HCl
Silane Properties
CAS#  7803-62-5
UN# 2203
Molecular Weight  32.11
Compressed Gas which is filled by weight due to high compressibility
Gas Density of 0.083 lb/ft³, 1.33 gm/l @ 70°F (21°C)
Boiling Point, 1 atm.  -169.6°F (-112°C)
Freezing Point, 1 atm.  -299°F (-184°C)
Critical Temperature 19.9°F (-7°C)
Critical Pressure 632 psia (43 atm)
Liquid Density @ 10°F (-12°C)  21.1 lbs/ft³ (338 gm/l)

Pyrophoric gases are flammable gases which have autoignition temperatures that are below 130°F (54.4°C)

<table>
<thead>
<tr>
<th>Autoignition</th>
<th>Autoignition</th>
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<tbody>
<tr>
<td>°F</td>
<td>°C</td>
</tr>
<tr>
<td>Silane</td>
<td>&lt;-148</td>
</tr>
<tr>
<td>Disilane</td>
<td>-100</td>
</tr>
<tr>
<td>Monochlorosilane</td>
<td>-22</td>
</tr>
<tr>
<td>Phosphine</td>
<td>&lt;32</td>
</tr>
<tr>
<td>Nickel Carbonyl</td>
<td>68</td>
</tr>
<tr>
<td>Diborane</td>
<td>44</td>
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<tr>
<td>Dichlorosilane</td>
<td>136</td>
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<tr>
<td>Diethyl Ether</td>
<td>320</td>
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<tr>
<td>Germane</td>
<td>343</td>
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<tr>
<td>Trichlorosilane</td>
<td>360</td>
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<tr>
<td>Hydrogen Sulfide</td>
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<tr>
<td>Arsine</td>
<td>545</td>
</tr>
<tr>
<td>Butane</td>
<td>550</td>
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Dichlorosilane does not meet the definition 136°F (58°C) however it is a self ignitor. It reacts with the moisture in the air which can self heat the release above the autoignition temperature

Pyrophoric gases require oxidizers to burn.

Silane is not toxic LC₅₀ - 19,200 ppm

Forms silicon dioxide particles which are irritants

No odor
Complete combustion forms white silicon dioxide while partial forms brown.

At low concentrations the flame temperature is cold ~800°F.

At stoichiometric concentration 9.51% flame temperature ~4,400°F.

The flammable and pyrophoric limits vary based on dilution gas.

Brown silicon oxides can still be reactive.

A fire cannot backflash into cylinder since there is no oxidizer inside.

Silane is a very compressible gas. It does not behave like an ideal gas. Cylinders must be weighed to determine contents.

Current maximum fill pressure = 1,500 psig (103 barg)

Silane is thermally stable. In a fire it will not violently decompose.

Silane is a strong reducing gas. Reactive with the perfluorocarbons and Halocarbons.

Silane will react with carbon dioxide.

The oxidizer gas will determine how quickly it will react. Some like NF₃ or N₂O can remain stable.

Silane has significant thermal expansion properties. Small change in temperatures can cause large pressure increases.

Silane has a high coefficient of expansion, a high pressure release into the atmosphere will cool and condense some gas.

The cooling has caused leakage at VCR connections and regulators.

Silicon dioxide particles can cause leakage.
Packages

A variety of cylinders and valves are used to package silane. As a best practice cylinders used are high pressure seamless stainless steel valves connections are replaceable metal washer (DISS)

Spun cylinders can leak from bottom due to a bad weld. They can also be 30 lbs lighter

Cylinder bundles are cylinders manifolded together and housed in a rigid metal frame.

Aluminum cylinders are lightweight but are temperature sensitive, in a fire they can rupture due to heat embrittlement

Gas suppliers use a variety of methods to detect high temperature exposures

ISO Modules of silane are horizontal cylinders fixed in a rigid 20’ or 40’ frame

A 40’ ISO of Silane is equal to 600 cylinders

The most common cylinder valve for silane is a high flow rate tied diaphragm valve from Ceoduex

The Ceoduex pneumatically operated cylinder valves must be manually locked for shipment

The Ceoduex D388 Penumatic cylinder valve has a knife edge seat to minimize seat leakage

A $1 \times 10^6$ seat leaker will pressurize the vaportight outlet cap to 110 psig in 3 months

The silane will be released when the cap is loosen. It will flare or pop
The most likely point for a leak in preparing a silane cylinder for use is when the vaportight outlet cap is removed. So that the operator is not surprised or injured, they must be properly trained and fully clothed in proper PPE. The following are the minimum guidelines that should be followed:

- Don appropriate PPE (fire gloves, nomex suit or firefighter turnout, faceshield, earplugs, safetyglasses, nomex hood)
- Have a “buddy” with the same PPE on visually observing, ready to assist if necessary
- Physically secure cylinder away from other cylinders and other hazards
- Stand to side of valve outlet, remove plastic bag and holddown wire
- Confirm that the valve is closed tightly
- Position cylinder to pull down with wrench (boxwrench preferred) when loosening vaportight outlet cap
- Be aware that flames can come out of the leakcheck hole in the DISS vaportight outlet cap
- Pull down slowly anticipating a leak, be ready to push up to reseal
- If Silane is behind vaportight outlet cap, one of the following will occur
  - Ignite immediately (Flamer)
  - Explode (Popper)
  - Release and not ignite

Because of this problem, Silane ISO’s have a second shutoff valve for each tube on the manifold

Silane Pressure Relief Device (PRD) is a CG-4, combination 165°F (73.9°C) fuse metal with 3360 - 4000 psig metal rupture disk

Because of numerous problems PRDs are now optional under CGA S1.1

Older cylinder outlet connection is CGA 350 which seals by deforming the nipple
Diameter Index Safety System (DISS) To provide high integrity connection via use of replaceable metal gasket between two polished beaded surfaces, $10^{-9}$ cc/sec

Requires a larger cylinder valve protection cap

Right handed connection

Requires torque wrench to properly tighten seal

Leak check hole

Requires a torque wrench to properly seal

**Restrictive Flow Orifice (RFO)** To reduce the hazard of Silane and the Highly Toxic Gases, the US Fire Codes and Insurance standards are requiring the use of a Restrictive Flow Orifice (RFO) to limit the gas flow from a cylinder

The typical RFO for silane is 0.010” dia. This reduces the flame from a full cylinder from 0.5 m vs 3 m 2.5 cfm (70.8 lpm) vs 333 cfm (9430 lpm) silane flow

A 15 kg cylinder with RFO will take over 10 hours to empty while without, it will be 6-7 minutes RFO’s are inserted into the cylinder valve after the cylinder has been filled.

Never look directly into cylinder valve outlet for the presence of an RFO, use mirror or boroscope

**Vaportight cylinder valve outlet cap** provides a secondary seal for the cylinder valve. Required for highly toxic and pyrophoric gas cylinders

**Cylinder Cap** protects the cylinder valve from damage. Must always be in place except when the cylinder is connected and in use

For highly toxic gas cylinders the cap must pass a performance test

Cylinder cap collars are installed on a cylinder after fabrication. They are peened into place. It is not safe to lift a cylinder by the cap.

DISS Caps are much larger. The collar is threaded onto the cylinder collar and secured with a setscrew
Never stick a screwdriver or a wrench into the cylinder cap vent hole to remove it. Use a strap wrench or other suitably designed tool.

To prevent insects from nesting in cylinder caps, some gas suppliers use plastic screens.

2 cylinder gas cabinets for silane are different than typical 2 cylinder cabinet. There is a metal wall between the cylinders.

Many users use an open cabinet to allow natural ventilation.

A variety of **codes and standards** apply to silane use, handling and storage in the US:
- NFPA 318 & 55 (National Fire Protection Association)
- IFC Chapters 18, 27, 30 & 41 (International Fire Code)
- FM Global 7-7 (Factory Mutual)
- ANSI/CGA-G-13 (American National Standards Institute / Compressed Gas Association)
- SEMI S-18

CGA G13 has become the key standard that is now referenced by the other codes and standards.

CGA G-13 is an international standard for silane.

**Silane storage and Handling**
- Both cylinder cap and outlet seal are tightly installed all the time the cylinder is not connected (including storage, handling, return shipment).
- Secure cylinder during storage and handling.
- Use a proper cart when moving cylinders.
- Protect storage area from the elements.
- Proper segregation of product hazard classes and full / empty cylinders.
- Limit silane storage quantity in same area (“nest”).
- Easy access and egress for personnel and emergency responders.
- Proper security.
- Good housekeeping.

Use good inventory control (first in, first out).

A number of incidents have been reported when the wrong cylinder was removed or tubing cut.

Always expect a leak
- Be prepared to seal off
- Stand to the side
- PPE
- Buddy
Personal Protective Equipment (PPE) is critical to protect user.

Silane flames from a DISS leakcheck hole can be long

Nomex is the most common PPE for silane
  Designed for flashover
  Direct flame impingement will burn through
  No synthetic material undergarments, natural fibers (wool, cotton)

PPE if worn improperly may not protect the user