



Silane Safety Notes

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Silicon Tetrahydride aka Silane

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

Arsine (AsH_3)

Diborane B_2H_6

Germane (GeH_4)

Hydrogen Selenide (H_2Se)

Phosphine (PH_3)

Silane (SiH_4)

Silane is 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 HSiCl_3

R_3N , R_3P , RCN , Al_2O_3 , $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{SiO}_2/\text{R}_3\text{N}$, $(\text{R}_3\text{P})\text{NX}$ ($\text{X} = \text{Cl}$, CN , BF_4 , RO , etc.), weak base ion exchange resin, etc.

Metal reduction chemistry of SiF_4 , HSiCl_3 , $\text{Si}(\text{OR})_4$ or SiCl_4

DIBAH , MH ($\text{M} = \text{Li}$, K , Na , etc.), MgH_2 , etc.

Magnesium Silicide (Mg_2Si) in NH_4Cl 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)

	Autoignition			Autoignition	
	°F	°C		°F	°C
Silane	<-148	<-100	Acetylene	581	305
Disilane	-100	-73	Diethyl Amine	594	312
Monochlorosilane	-22	-30	Butylene	725	385
Phosphine	<32	<0	Hydrogen	752	400
Nickel Carbonyl	68	20	1,3 Butadiene	788	420
Diborane	44	7	Ethylene Oxide	804	429
Dichlorosilane	136	58	Propane	842	450
Diethyl Ether	320	160	Ethylene	842	450
Germane	343	173	Propylene	851	455
Trichlorosilane	360	182	Vinyl Chloride	882	472
Hydrogen Sulfide	500	260	Ethane	882	472
Arsine	545	285	Ammonia	928	498
Butane	550	288	Methane	999	537

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 $\sim 800^{\circ}\text{F}$

At stoichiometric concentration 9.51% flame temperature $\sim 4,400^{\circ}\text{F}$

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 NF_3 or N_2O 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 Ceodux

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

The Ceodux D388 Pneumatic cylinder valve has a knife edge seat to minimize seat leakage

A 1×10^{-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:

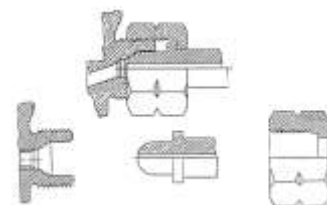
- Don appropriate PPE (fire gloves, nomex suit or firefighter turnout, faceshield, earplugs, safetyglasses, nomex hood)
- Have a “buddy” with the same PPE on visually observing, ready to assist if necessary
- Physically secure cylinder away from other cylinders and other hazards
- Stand to side of valve 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 165⁰F (73.9⁰C) fuse metal with 3360 - 4000 psig metal rupture disk

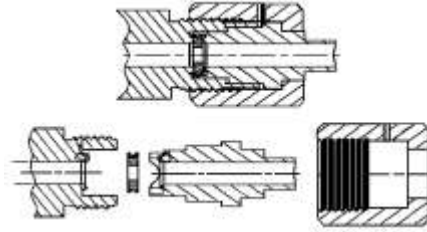
Because of numerous problems PRDs are now optional under CGA S1.1

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