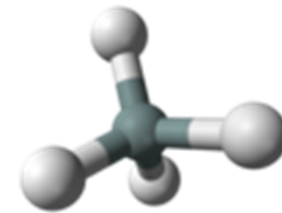

Silane

and Other Pyrophoric Gases

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UGIM 2024
6/26/2024

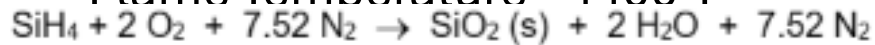
Silane Properties

- Silicon Tetrahydride - SiH_4
- CAS # 7803-62-5
- Autoignition Temperature - 64°F
- Molecular Weight 32.11
- Gas Density - 0.084 lb/ft^3
- Boiling Point - -169.6°F
- Vapor Density - 1.11
- Specific Gravity in Air at 1 ATM & 70°F - 1.12
- Colorless, Odorless Gas



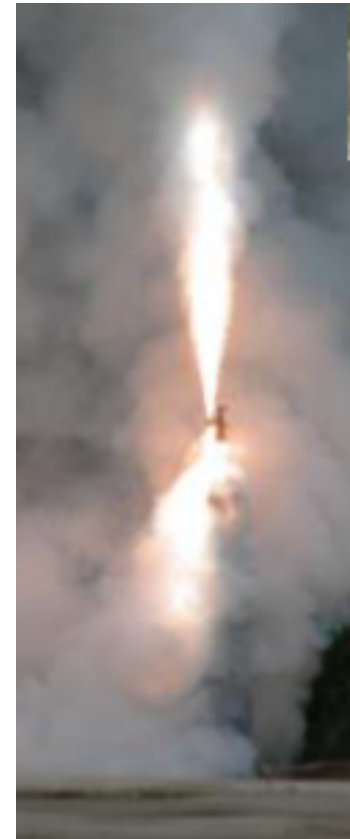
Silane Flame Temperature

- Flammability Limits $\geq 1.4\%$ - $\leq 96\%$
 - Flame Temperature $\sim 800^\circ\text{F}$
- Metastable at $> 4.5\%$
- Stoichiometric Mixture in Air
(9.51% Silane)
 - Flame and Smoke is White
 - Flame Temperature $\sim 4400^\circ\text{F}$



1 lb Silane Gas \longrightarrow 1.87 lb Amorphous Silicon

Source: 2023 CGA G-13, 4.3.2



100% Silane Gas

Hazard Categories

- **Pyrophoric:**

*Auto-ignition Temperature <130°F
(2012 IFC Chapter 64)*

- **Unstable Reactive
Class 1**

Unstable reactive materials may react spontaneously with themselves, other chemicals or when exposed to light, heat, cold, moisture, air or physical shock (2012 IFC Chapter 66)

The HME Assistant Chemical Classification					
	G.A.S. No. 7803-62-5	Concentration 100%	State Gas	RTECS VV1400000	
Boiling Point	-168.5 F	LD 50	NA	Molecular Weight	32.12
Melting Point	-301 F	LC 50	19,000P	Specific Gravity	0.71
Flash Point	ND	LFL/LEL	1.37	Vapor Density	1.11
Autoignition Temp.	-58 F	UFL/UEL	96.00	Vapor Pressure	ND
IUPAC Name					
silane					
Synonyms					
silicon tetrahydride silicane monosilane silicon hydride					
IFC Physical Hazards			IFC Health Hazards		
Pyrophoric Unstable Reactive Class 1					
DOT			SARA		
Shipping Name Silane					
Labels Required FLAMMABLE GAS					
Hazard Class or Division 2.1			GA Section 112 Threshold Quantity 10,000		
ID # UN2203					
Notes Air mixtures can detonate if released into confinement Specific Gravity (liquid) at -185 degrees Centigrade LC50 inh-rat LC50: 9600 ppm/4H					

Silane > 1.37%%

- International Fire Code, Chapter 64, Pyrophoric Materials Governs the Storage and Dispense of Silane above the Maximum Allowable Quantities and with concentrations above 1.37% by Volume.
- Chapter 6404.1, Indoor Storage and Chapter 6404.2, Outdoor Storage both indicate in part “... The storage of silane gas and gas mixtures with silane concentrations of 1.37 percent or more by volume, shall be in accordance with ANSI/CGA G- 13.”

What is a Pyrophoric??

- International Fire Code, Chapter 2, Definitions:

“Pyrophoric. *A chemical with an autoignition temperature in air, at or below a temperature of 130°F (54°C).”*

100% Pyrophoric Gases / Autoignition Temperature:

- Silane 64°F Pyrophoric, UR1
- Disilane 130°F Pyrophoric
- Phosphine 100°F Pyrophoric, Highly Toxic
- Diborane 40 – 50°F Pyrophoric, Highly Toxic, UR3D, WR1

Hazard Classifications Concentration Dependent

Pyrophorics' with other Hazard Categories

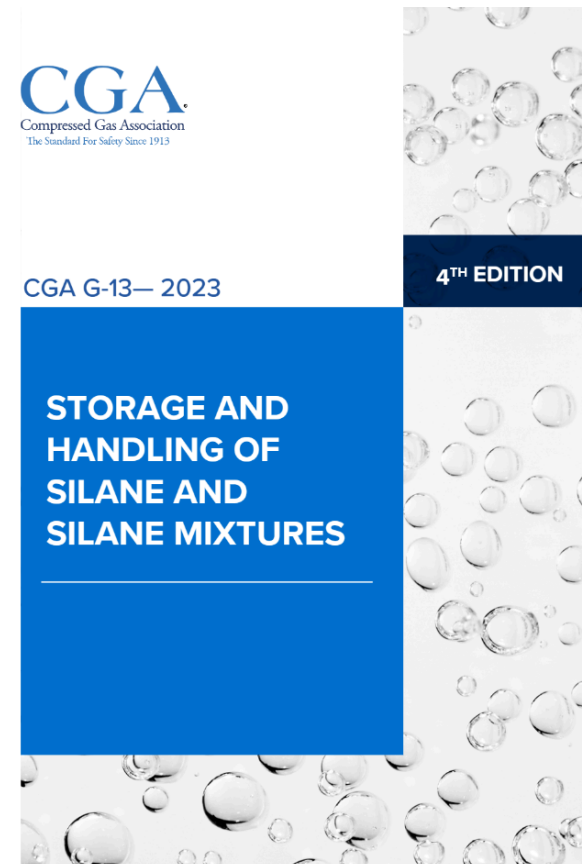
- International Fire Code:
 - Chapter 53 - Compressed Gases
 - Chapter 58 - Flammable Gases*
 - Chapter 60 - Highly Toxic and Toxic Materials*
 - Chapter 63 - Oxidizers, Oxidizing Gases and Oxidizing Cryogenic Fluids
 - Chapter 66 - Unstable (Reactive) Materials*
 - Chapter 67 - Water Reactive Solids and Liquids

*Gas Cabinets with exhaust treatment (where required)

CGA G-13

- Issues
 - 1st Edition - 2000
 - 2nd Edition - 2006
 - 3rd Edition - 2015
 - 4th Edition - 2023
- Available at: <https://www.cganet.com>)
- Purpose:

The purpose of this standard is to prescribe the controls for the installation of silane systems and the recommended methods for storage or transfer of silane or its mixtures from a source of supply to a point of use to provide protection against injury, loss of life, and property damage.



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Other Design Standards

- **NFPA 318:** “*Standard for the Protection of Semiconductor Fabrication Facilities*”
- **NFPA 69:** “*Standard on Explosion Prevention Systems*”
- **NFPA 495:** “*Explosive Materials Code*”
- **FM Global Data Sheet 7-108:** “*Silane*”
- **FM Global Data Sheet 1-44:** “*Damage Limiting Construction*”

To Name a Few!

FM Global
Property Loss Prevention Data Sheets **1-44**
September 2000
Interim Revision January 2023
Page 1 of 26

DAMAGE-LIMITING CONSTRUCTION

FM Global
Property Loss Prevention Data Sheets **7-108**
April 2014
Page 1 of 22



Silane Hazards

- Concentration of Silane
 - <1.4% - Non-Flammable, Non-Hazardous Gas
 - 1.4% - 4.5% - Flammable Gas
 - >4.5% - Pyrophoric Gas (Metastable and is capable of autoignition)

Note: CGA G-13, 2023 changed LFL from 1.37% to 1.4%



Silane and the International Fire Code

Silane concentration in compressed gas mixture	Minimum engineering controls	Maximum allowable quantity (MAQ)	Applicable fire code chapter (IFC 2012) and referenced standards [13]
<1.4%	Standard controls for non-flammable gases	No MAQ limit	Chapter 53: Compressed gases
1.4 – 4.5%	Standard controls for flammable gases	MAQ for flammable gases (dependent on occupancy class, Control Zone and floor level)	Chapter 58: Flammable Gases
>4.5%	All prescribed controls for pyrophoric gases as described in this document	MAQ for pyrophoric gases (dependent on occupancy class, Control Zone and floor level)	Chapter 64: Pyrophoric Materials, FM Global Property Loss Prevention Data Sheet: Silane

Source: 2023 CGA G-13 Appendix C

Pyrophoric Hazard

Metastable

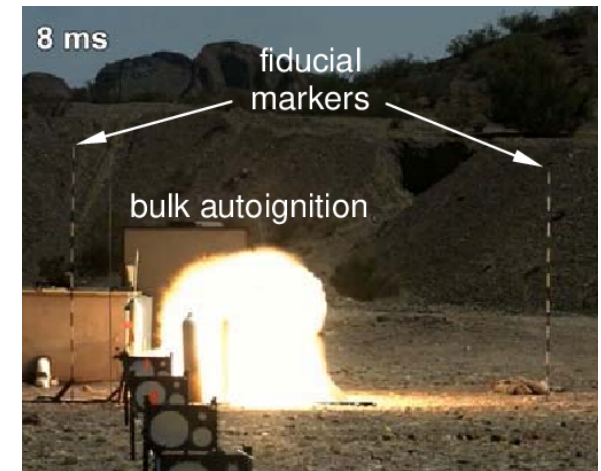
Silane is a unique hazardous material in that it is also metastable, meaning that it can have delayed ignition. This metastable characteristic is dangerous because it allows a volume of gas to accumulate inside of an enclosure. In such cases, a deflagration or detonation can occur, which can cause structural damage to the facility and seriously injure or kill individuals located close to the release.

G.A.S. No.		Concentration	State	RTECS	
7803-62-5		100%	Gas	VV1400000	
Boiling Point	-168.5 F	LD 50	NA	Molecular Weight	32.12
Melting Point	-301 F	LC 50	19,000P	Specific Gravity	0.71
Flash Point	ND	LR/LEL	1.37	Vapor Density	1.11
Autoignition Temp.	-58 F	UL/UEL	96.00	Vapor Pressure	ND
IUPAC Name					
silane					
Synonyms					
silicon tetrahydride silicane monosilane silicon hydride					
IFC Physical Hazards			IFC Health Hazards		
Pyrophoric Unstable Reactive Class 1					
DOT			SARA		
Shipping Name Silane					
Labels Required FLAMMABLE GAS					
Hazard Class or Division 2.1					
ID # UN2203			CAA Section 112 Threshold Quantity 10,000		
Notes Air mixtures can detonate if released into confinement Specific Gravity (liquid) at -185 degrees Centigrade LC50 ihl-rat LC50: 9600 ppm/4H					



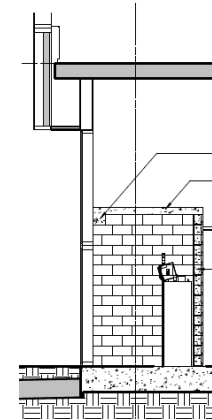
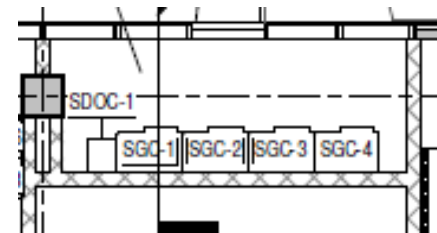
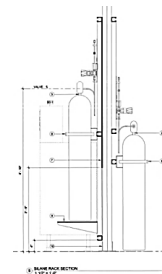
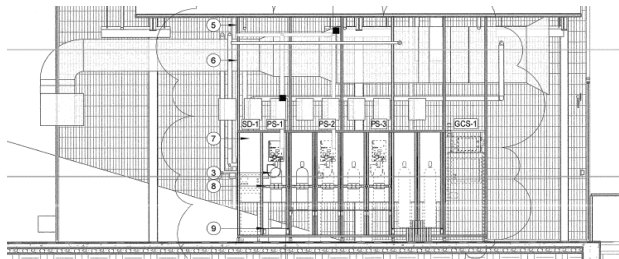
Silane Release Reactions

- **Prompt ignition**
- **Ignition during flow decay:** Gradual reduction of flow such as that with no supply connected to line with the leak.
- **Ignition at shutoff (delayed ignition):** Abrupt stop of RFO controlled flow.
- **Bulk auto-ignition:** Large amount of silane released unreacted.
Reaching concentration of $\pm 4.5\%$, mixture becomes metastable and will auto-ignite (No ignition source needed) after a delay



Silane Storage

- Two Storage Options
 - Outdoor Storage (CGA G-13 Chapter 6)
 - Indoor Storage (CGA G-13 Chapter 7)



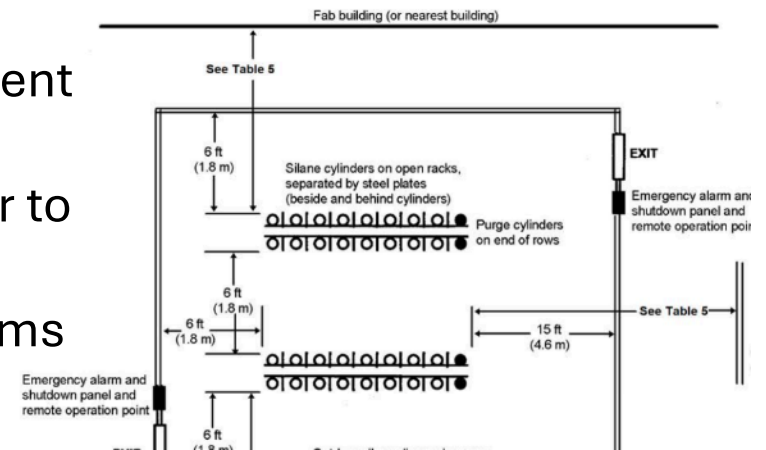
Outdoor Storage

- Less Prescriptive Design Requirements
 - No Over Pressure Containment, Risk of Deflagration or Detonation Mitigated
 - Open Gas Racks
 - Blast Relief and Calculations NOT required
 - Open to the Surrounding Environment (Per CGA G-13, 6.2.1.1)
 - Fenced Area with weather protection Roof (Per CGA G-13, 6.2.1.2)
 - Exposure Distances up to 50L (Per CGA G-13, Table 5)



Outdoor Design Requirements

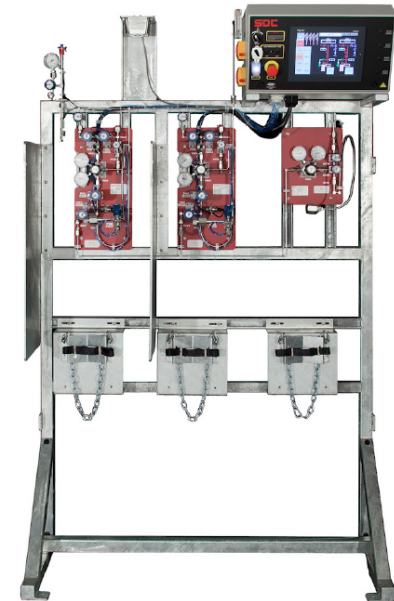
- Over Pressure (Blast) Calculations NOT Required
 - Rated Wall Construction required if Adjacent to Building
 - Three Sides of Enclosure MUST be exterior to Building
 - Fenced Exclusion required, Intrusion Alarms Recommended
 - Weather Protection Roof Required
 - .006” RFO w/ Pneumatic Shut-off at cylinder Highly Recommended



CGA G-13 Figure 3 - Typical end user outdoor cylinder layout

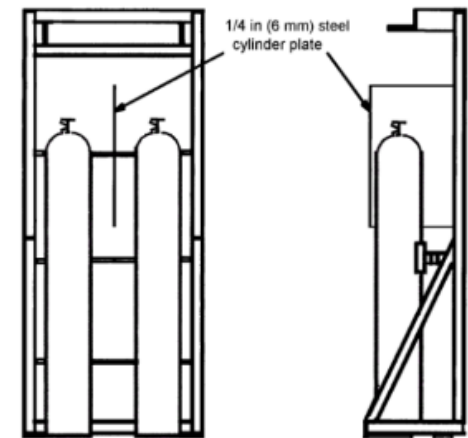
Outdoor Design Requirements

- Dedicated Air System Requirements
 - Exhaust Requirements:
 - None (except as a Mitigation, CGA G-13 Section 6.2.1.1)
 - Ventilation Air (Where Required)
 - 100% outside Air
 - Temperature Minimum - 40°F
 - Air Flow Rate (CGA G-13 Section 13.1.1)



Outdoor Design Requirements

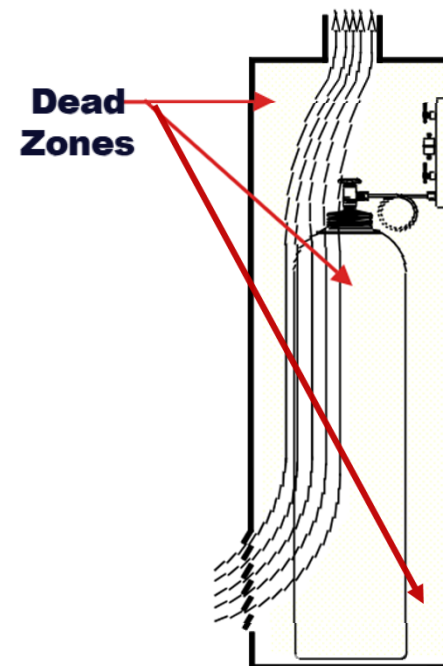
- Dispense Silane from CGA G-13 Compliant Gas Racks Per CGA G-13 Section 6.4.2
 - ¼” Steel Plate Separation above and Below Mechanical Joints
 - Fill Complement of Cylinder Life Safety and Process Controls
 - UVIR Detection for each Cylinders (CGA G-13, 11.2.1)
 - Gas Leak Detection - NOT Required (CGA G-13, 11.1.1)
 - Area Shall have Deluge Sprinklers, Extra Hazard Group 2 (CGA G-13, 12.2.2)



Source: CGA G-13 - 6.4.2

Indoor Storage

- Prescriptive Design Requirements
 - Barricade Construction Required (CGA G-13, 7.4)
 - Silane Specific Gas Cabinets Meeting the Requirements c CGA-G-13, 8.2.2.
 - Requires Blast Relief (Explosion Control) (CGA G-13, 7.6)
 - Ventilation Requirements (CGA G-13, 13.2)
 - Gas Detection / Monitoring / Shutdown (CGA G-13, 11.1.2 through 11.1.5)
 - Fire Suppression (CGA G013, 12.3)
 - Flame Detection (CGA-G-13, 11.2.2)



Indoor Design Requirements

- Requires Over Pressure (Blast) Calculations on Room with Relief Panels (if Silane Quantity $>0.50\text{SCF}$)
 - Wall Construction 100 – 150PSF (Determined by Blast Calc)
 - 25% of room walls MUST be on perimeter of Building
 - Keep Room Volume as Small as Possible
 - Blast Relief Panels Required
 - Blast Resistant Doors / Hardware (2 Exits required if room is $>200\text{sf}$)
 - Exclusion zone required at relief panels
 - .006” RFO w/ Pneumatic Shut-off at cylinder Recommended

Indoor Design Requirements

- Dedicated Exhaust and Make-up Air Systems Required
 - Exhaust Requirements:
 - 1 CFM / SF of floor area ($\frac{1}{2}$ High & $\frac{1}{2}$ Low) ++
 - Exhaust for each Cabinet Based on RO Size (per CGA G-13 Table 5)
 - Additional Exhaust based on one Open Gas Cabinet Window
 - Room to be maintained Negative to surrounding Building
 - Make-Up Air Requirements
 - 100% outside Air (all cabinets + room Ventilation)
 - Suggested Minimum Room Temperature - 40°F
 - Suggested Temperature Max Room Temperature – 90°F

Indoor Design Requirements

- Dispense Silane from CGA G-13 Compliant Gas Cabinets Per CGA G-13 Section 8.2.2
 - ¼” Plate Separation above and Below Mechanical Joints
 - Fill Complement of Cylinder Life Safety and Process Controls
 - UVIR Detection for each Cylinders in Cabinets and in room
 - Gas Leak Detection
 - NO Pocketing (Dead Zones) (Per CGA G-13 Section 13.2.3.2)
 - Each Cabinet to have Fire Sprinklers (Quick Response Heads)
 - Room shall have fire sprinklers with not less than Extra Hazard Group 1 coverage

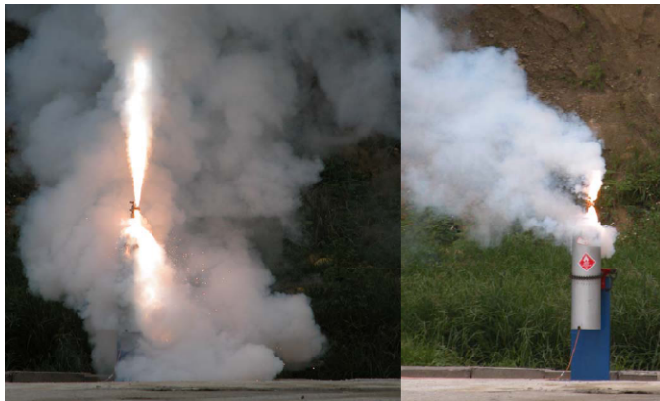
Outdoor / Indoor Design Requirements

- Silane Distribution Tubing:
 - Installed per ASME B31.3, Process Piping
 - Minimum Requirements, Single Wall Tube
- Destruction of Vent Purge (S-DOC or Equivalent) or contained open flare (CGA G-13, Chapter 14)



Ebara S-DOC

Impacts of Restrictive Flow Orifice



No RFO

0.10" RFO

Excerpt from CGA G-13, Table 5
Impacts of RFO

Source pressure (psig)	Typical gas cabinet RFO 0.006 in diameter (0.15 mm diameter)		Typical gas cabinet RFO 0.010 in diameter (0.25 mm diameter)	
	Silane flow (scfm)	Ventilation flow (scfm)	Silane flow (scfm)	Ventilation flow (scfm)
50	0.025	8	0.069	21
100	0.045	14	0.124	37
200	0.085	26	0.237	71
400	0.173	52	0.480	144
600	0.275	83	0.755	227
800	0.395	119	1.08	324
1000	0.555	167	1.51	453
1200	0.724	217	1.97	591
1500	0.913	274	2.50	750
1650	0.987	296	2.70	810

Conclusion

CGA G 10, Paragraph 6.2.1, Location

... “Silane sources and delivery systems shall be located outdoors. Although indoor locations are allowed, it is preferred that areas for the storage and use of silane be located outdoors to lessen risk to users and facilities in the event of a fire or explosion. By locating silane installations in an unconfined space, the surrounding environment is able to absorb unlimited amounts of heat, and the surrounding environment is free to infinitely expand allowing overpressures to quickly attenuate.”

Key Points

- Fire Code Implications of Silane
- What is a Pyrophoric Gas
- Why is Silane a Danger in your facility
- How to Mitigate the Dangers Posed by Silane

Discussion

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