## Reducing Gases will React with Inert Gases, even Carbon Dioxide

Many of the metal hydride gases (arsine, phosphine, germane, etc) are strong reducing gases. Reaction with strong oxidizers such as $F_2$, $ClF_3$ and $Cl_2$ are known to be immediate and violent.

An inert gas such as carbon dioxide under certain conditions will react with silane like an oxidizer. While Conrad and others have tested silane/carbon dioxide mixtures for flammability, they were tested only at atmospheric pressure.

To power the Mars lander NASA proposed a silane/carbon dioxide rocket engine. With the fuel and oxidizer being manufactured on Mars.

$$SiH_4 + 2CO_2 \rightarrow SiO_2 + 2C + 2H_2O$$

Diborane reaction with carbon dioxide was also considered.

Silane when mixed with halogenated gases that are normally considered inert become explosive because of their strong reducing behavior.

Larry Britton stated

> Unlike the alkanes, silanes have pronounced reducing properties and reactivity with even mildly oxidizing is much enhanced. The difference is electronegativity. While C-H bonds are polarized giving a positive charge on the hydrogen, the Si-H hydrogen is charged negatively. Hydrogen abstraction by materials such as halogens introduces the potential for hazardous reactions with halocarbons.

Testing has shown the following to be reactive with silane and in many cases explosive.[1]

- Nitrogen Trifluoride ($NF_3$)
- Halon 1301 ($CBrF_3$) Bromotrifluoromethane
- Sulfur Hexafluoride ($SF_6$)
- Sulfur Tetrafluoride ($SF_4$)
- No reaction with $CF_4$, $PF_5$ or $BF_3$

Perfluorocarbons [3]

- Perfluoroethane ($C_2F_6$,Hexafluoroethane)
- Perfluorobutane ($C_4F_{10}$)
- Perfluorohexane($C_6F_{14}$)
- Perfluorooctane ($C_8F_{18}$)

Halocarbons (Freons) [2,3]

- Halocarbon 11($Cl_3FC$, Trichlorofluoromethane)

Halocarbon 12 ($Cl_2F_2C$, Dichlorodifluoromethane)
Halocarbon 22 ($ClF_2HC$, Chlorodifluoromethane)
Halocarbon 13 ($ClF_3C$, Chlorotrifluoromethane)

Halocarbon 22 (Chlorodifluoromethane) has also been found to be explosive with Dichlorosilane (L. Britton). Hydrogen selenide is also a strong reducing gas and should be considered reactive with all the above unless proven otherwise. Diborane reacts violently with halocarbon liquids such as those typically used as vaporizing fire extinguishers.[4]

The higher hydrides (disilane, diphosphine, digermane, etc)can produce explosive conditions with other gases as easily as their monomers, e.g. disilane/$SF_6$.

**Incidents**

1. **Gas Manufacturer, US, 1955**[5]
   Pilot plant exploded. The blast killed two Olin Mathieson employees working inside the facility and resulted in total destruction of the physical plant.
   The explosion was thought to have been caused by using carbon tetrachloride (CCl4 ) rather than kerosene as a cleaning solvent in some 4 process vessels. Subsequent research showed that combination of the two chemicals forms a highly shock-sensitive compound.

2. **Gas Manufacturer, US, 1979**
   During a shutdown of the silane purification unit, silane mixed with the distillation system refrigerant Halocarbon 13 ($ClF_3C$, Chlorotrifluoromethane). The system was vented to 20 psig and a 12 gallon sample cylinder was attached. When the valve was opened to the cylinder there was a detonation that blew out both ends of the cylinder. Black soot covered the immediate area. Minor injuries to 2 operators, hearing loss.

3. **Gas Manufacturer, US, 2014**
   Tetrasilane in a vacuum pump filled with fluorinated oil exploded after some air was sucked in. The air/tetrasilane reaction triggered the decomposition reaction releasing fluorine. Considerable damage to room. The explosion lifted all the roof mount explosion panels that prevented the walls from being blown out. Eight cylinders in a metal rack in front of the metal enclosure were propelled 25 ft. across the room.

Eugene Ngai

**References**

1. Horiguchi, S. “Explosion Hazards of Fluorinated Gases Mixed with Silane”, Fifth International Symposium on Semiconductor Manufacturing”, Oct 2-4, 1996, Tokyo, Japan

2. Britton, L. G., “Combustion Hazards of Silane and Its Chlorides”, Paper 12b, Loss Prevention Symposium, AIChE Spring National Meeting and Petrochemical EXPO’89, Houston, TX April 6, 1989
3. Horiguchi, S. “Explosion Hazards of Fluorinated Gases Mixed with Silane”, Fifth International Symposium on Semiconductor Manufacturing”, Oct 2-4, 1996, Tokyo, Japan
4. Urano, Y., Horiguchi, S., Tokuhashi, K., Ohtani, H., Iwasaka, M., Kondo, S. and Tokuhashi, M., “Explosion Hazard of Diborane”, Koatsu Gasu, Vol 255, No. 11, pp 37-43, 1988
5. Dequasie, A., “The Green Flame”, Chapter 7, American Chemical Society, 1991