Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501
Telephone (610) 706-2269
Fax (610) 706-7029
ngaiey@airproducts.com

Mr. Mark M. Toughiry, P.E.
NDE Specialist
Office of Hazardous Materials Technology
U.S. Dept. of Transportation
Room 8430N, Nassif Building
400 Seventh St, SW
Washington, DC 20590-0001

Sept. 25, 2005

Subject: Information for Germane, Stibine and Dichlorosilane Cylinder Fill Calculations

Dear Mark

As discussed at the recent meeting at CGA, the following letter summarizes the additional information for Germane, Stibine and Dichlorosilane.

As I indicated in my letter to CGA on July 7, 2005, "**Fill Density for Germane and Nitric Oxide",** Germane (UN2192) can autodecompose to its elements if enough energy is applied to the gas. This reaction once initiated will propagate throughout the material. There have been two reported cases where the cylinders have ruptured. [1, 2]

$$GeH4 \rightarrow Ge(s) + 2H_2 \quad 91\ kj/mole$$

One mole of Germane will produce 2 moles of superheated Hydrogen. Assuming adiadatic conditions the reaction will heat the byproduct Hydrogen to 1719^0F (937^0C) This was confirmed in testing done by Hazards Research Corporation in April 1986 on a cylinder of pure Germane.[3] The pressure calculation should ignore the volume of the Germanium solids which will be negligible. Is the maximum allowable pressure the working or test pressure of the cylinder?

Stibine (Antimony Hydride, SbH_3, UN2676) is chemically similar to Diborane in that it is thermodynamcially unstable at room temperature. The decomposition is reported to occur even at temperatures of -60^0C which is well below its boilimg point of -18^0C.[4]. At room temperature, Stibine is less stable than Diborane, in a test conducted in a vacuum (5 torr) the Stibine fully decomposed in 3 days.[5] At higher pressures, the decomposition is more rapid. The decomposition byproducts are Antimony solids and Hydrogen gas.

$$SbH_3 \rightarrow Sb\ (s) + 1½H_2$$

The Antimony will have a negligible volume while the Hydrogen will be 1½ times the gaseous volume of the Stibine. The process is slow enough that the reaction heat is absorbed by the surroundings (non adiabatic) and is not considered in the final pressure estimate. This is similar to that of the Diborane decomposition reaction. Since the maxmimum fill ratio for Diborane took into consideration the decomposition byproducts, Stibine should have the same consideration.

Attached are also data and references for Dichlorosilane liquid density and vapor pressure

Should you have any questions regarding these, please do not hesitate to contact me.

Sincerely,

Eugene Y. Ngai
Director of ER & Disposal Technology

1. Horiguchi, S Urano, Y and Kondo, S. **"Decomposition explosion hazards of semiconductor manufacturing gases"**, *Journal of High Pressure Gas Safety Institute of Japan*, 28(3), pg 270-284, 1991
2. Horiguchi, S Urano, Y and Kondo, S. **"Decomposition explosion hazards of semiconductor manufacturing gases"**, *Journal of High Pressure Gas Safety Institute of Japan*, 28(5), pg 351-363, 1991
3. Hazards Research Corp. Report #6023, ***"Germane Deflagration Study",*** for Energy Conversion Devices, Inc, North Branch, NJ, April 11, 1986
4. Todd, M A , Bandari, G. and Buam, T H, ***"Synthesis and Stabilization of Stibine for Low Temperature Chemcial Vapor Deposition of Carbon Free Antimony Films"***, Chem. Mater., 02/02/99, 11, 547-551
5. Knczkowski, A., SAchulz, S. and Assenmacher, W., ***"Growth of GaSb whiskers by thermal decomposition of a single source precursor"***, J. Mater. Chem., The Royal Society of Chemistry, 2001, 11, 3241-3248

Vapor Pressure of Dichlorosilane

T K	P Pa

I Wintgen, R. Dampfdrucke und Verdampfungswarmen von Siliciumwasserstoffen und Deren Einfachen Abkommlingen. Ber. Dtsch. Chem. Ges., 52, (1919) 724.

193.15	599.95
222.65	5692.8
257.95	37930
268.05	58995
273.15	73194
281.35	100800

II Stock, A., Somieski, C. Siliciumwasserstoffe VI Chlorierung und Methylierung des monosilane. Chem. Ber., 52B, (1919) 695.

199.15	999.92
203.05	1399.9
207.65	1999.8
212.55	2799.8
218.65	4399.6
222.65	5732.9
227.65	7732.7
232.65	10466
237.65	13966
242.65	18132
247.85	23731
252.95	30264
258.05	37864
263.05	47329
268.05	58929
273.15	73194
278.15	88526
281.35	100790

III Glemser, Lohman. Neues Verfahren zur Darstellung von SiH3Cl und SiH2Cl2. (in German) Z. Anorg. Allg. Chem., 275, (1954) 260.

206.65	1733.2
226.15	7066.1
236.15	12132
237.15	12799

IV Stock, A., Somieski, C. Siliciumwasserstoffe VI Chlorierung und Methylierung des monosilane. Chem. Ber., 52B, (1919) 695.

163.05	26.664
172.65	66.665
177.65	133.33
182.85	226.65
188.55	399.98
193.15	599.96

Liquid Density of Dichlorosilane

T	P	Density
K	Pa	kmol/m3

Washburn, E.W., ed. International Critical Tables of Numerical Data, Physics, Chemistry, and Technology. McGraw-Hill, New York, 1926-1933 7 Vols + Index.

151.15	101325	14.058

Britton, L.G. Combustion Hazards of Silane and its Chlorides. Plant/Oper. Prog., 9, (1), (1990) 16.

253.15	101325	12.653