Diborane

Diborane (B_2H_6) is a pyrophoric and highly toxic gas. It has a permissible exposure limit (PEL) of 100 ppb, a lethal concentration value (LC_{50}) of 80 ppm and an immediately dangerous to life or health (IDLH) value of 15 ppm. It is a liquefied gas with a vapor pressure of 522 psig @ 60°F (15°C). It cannot exist as a liquefied gas at a room temperature of 70°F (21°C) since it has a critical temperature of 62°F (16°C).

Because of the boron, it burns with a green flame

Fig. 1: Green Flame

Diborane is used as a p type dopant for silicon devices but it is used primarily in semiconductors as a raw material to form a metal insulating layer. Silane, diborane and oxygen are used in an Atmospheric Pressure Chemical Vapor Deposition (APCVD) system to grow a borosilicate glass layer. Due to its lower temperature melting point, Borophosphosilicate glass (BPSG) is favored for most Semiconductor insulating processes.[1]

It decomposes slowly into higher boranes and hydrogen at room temperature. At room temperature it slowly decomposes in a series of sequential steps of hydrogen elimination and oligomer formation, i.e. the so-called "higher boranes", tetra-, penta-(s) and deca-. The last (fast) step in this process is the formation of decaborane (and hydrogen) The amount and rate of decomposition is dependent upon temperature, pressure, and other factors.

The decomposition rate in Dr. Flaherty's article is proportional to the partial pressure of diborane raised to the 1.5 power.[2]

The kinetic constant at 20°C is .001 mole to the power -½, liter to the power -½, day to the power -1.

$$-\frac{d[B_2H_6]}{dt} = k(T)(\text{in } mol^{-0.5}L^{0.5}day^{-1})[B_2H_{.6}]^{1.5}$$

For example, a 9.14% mixture of diborane in helium at 1077 psia at 20°C decomposes at a rate of 2.07 x 10^{-4} moles per liter/day.

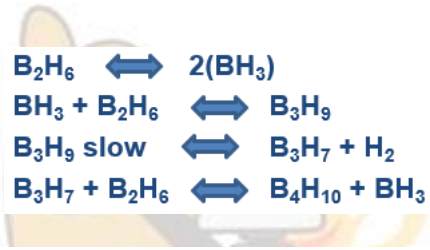
Appendix 1 of SEMI Standard SEMI C3.56-0600, Specification for Diborane Mixtures

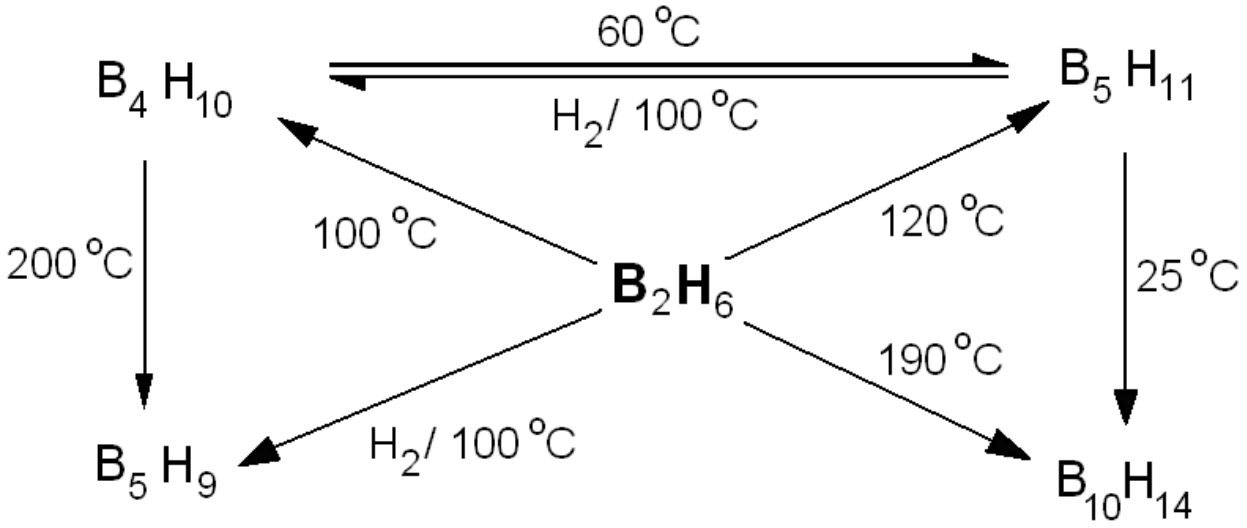
Storage Temperature	*Diborane Concentration (%) in Nitrogen after*				
	2	17	45	100	160 Days
8 °C	0.549	0.547	0.547	0.543	0.542
22 °C	0.549	0.544	0.539	0.530	0.526
8 °C	5.05	4.91	4.87	4.85	4.78
22 °C	5.05	4.92	4.83	4.72	4.49
8 °C	10.51	10.45	10.43	10.19	10.00
22 °C	10.59	10.30	10.08	9.44	8.85

The decomposition can be described as follows:

$$B_2H_6\ (g) \rightarrow B_5H_9\ (l) + B_{10}H_{14}\ (s) + B_xH_y\ (l/s) + H_2 \quad \text{(not balanced)}$$

Due to the ongoing decomposition gas suppliers store the mixtures in a freezer at 14 to 23°F (-5 to -10°C).





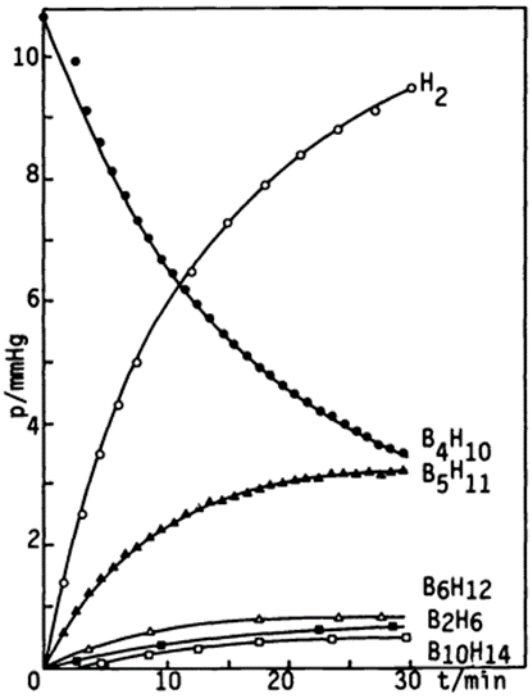


Fig. 1. Reaction profile for thermolysis of B_4H_{10} at 10.7 mmHg and 78 °C

These higher boranes accumulate over time as a liquid or solid in the cylinders and must be removed. Although many higher boranes are formed, the primary decomposition products are Pentaborane and Decaborane with hydrogen as a byproduct.

> Pentaborane is a volatile, pyrophoric colorless liquid. ACGIH has established a TLV-TWA of 0.005 ppm and TLV-STEL of 0.015 ppm.
>
> Decaborane is a white, needle-like crystal that may appear pale yellow in an impure state. Decaborane is an extremely toxic dermal poison

Due to the decomposition, DOT requires a cylinder filled with diborane or its mixture to limit the fill amount assuming byproduct hydrogen if it fully decomposed will not exceed the working pressure of the cylinder. (49CFR§173.302a Additional requirements for shipment of nonliquefied (permanent) compressed gases in specification cylinders. (d) Diborane and diborane mixtures). This severely limits the amount of pure diborane that can be shipped to 0.070 kg/l (2707 psia). To increase this amount (0.280 kg/l (10,832 psia H_2)., pure diborane is shipped to gas suppliers in the US in an insulated container packed with dry ice under a DOT Special Permit 970 and it must reach the destination in 10 days. otherwise the supplier would have to conduct an immediate search for the cylinder since the amount of diborane in the cylinder if fully decomposed would over pressurize the cylinder with hydrogen.

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Fig 2: Insulated Shipping Drum

Most users take mixtures. As the mixture concentration is important, gas suppliers typically store the mixture cylinders in a refrigerated room and use chilling jackets during gas delivery to mitigate decomposition during use. Refrigeration or chilling of diborane mixtures with hydrogen as the balance gas is not typically required, as the mixture is generally stable if used within one year. For inert balance gases, decomposition of diborane even by small fractions of a percent and generation of higher boranes can have significant process impact

As a result, only mixtures are sold to users. Most gas suppliers in Europe and Asia would order diborane in a hydrogen mixture. Once received they would freeze out the diborane in an aluminum or stainless steel cylinder. They would then use the pure diborane to male mixtures.

Diborane will also readily react with any moisture or oxygen in the piping system, forming solids which can plug the system or cause regulators to no longer control. These solids can be toxic and flammable, Decaborane 14.

Fig. 3: Regulator with Solids

Removal of the higher borane compounds from the cylinders is a significant problem. Some of the compounds are only water soluble while others require an organic solvent. Some are violently reactive with water.

Companies in the US, Europe and Asia have all experienced severe incidents when they attempted to clean these cylinders. In some cases, the cylinders have ruptured due to the violent reactions with the neutralization liquids.

Diborane Cylinders

As noted earlier, diborane cylinders have to be cleaned of the liquid and solid boranes that accumulates. Gas companies would weigh returned cylinder to determine the amount of residue in the cylinder. At a predetermined a mount the cylinders would be cleaned of residue. This has been a significant challenge as well as a safety problem. Incidents that have occurred during this

Gas Supplier, US, Jan 2007

Operator cleaning diborane cylinders accidentally touched the boranes residue without his gloves. The next day he developed myoclonic symptoms in feet and hands. Myoclonic (MY-o-KLON-ik) seizures are brief, shock-like jerks of a muscle or a group of muscles. Drooling, headaches, dizziness, slurred speech, muscle contraction. Given 2 rounds of Antivan intravenously with marked improvement
Hospital for 1 week, induced coma. Neurological problems afterward

Gas Supplier, Korea, Oct 15, 1997

10 l stainless steel collector, 2130 psig working pressure that was used to condense B_2H_6 from 30% mixture cylinders. After 15 cycles it was being cleaned of residue. NaOH sol was added and valve closed. 2-3 sec later cyl ruptured. One operator was burned on face and hair. Hearing loss. Burning residue shredded pants of second operator and burned his leg. A 11”x 8”x ¼” fragment flew 500-600 yards and damaged a car.

Fig 4: Cylinder Ruptured Minutes after Sodium Hydroxide Addition

Numerous cylinder cleaning incidents and as a result CGA published P-73 Safety Alert, Hazards Associated with the Decontamination, Disposal, or Requalification of Cylinders in Diborane, Diborane Mixtures, and Pentaborane Service

These cylinders are now cleaned using special procedures and systems or by waste disposal companies.

Pentaborane a byproduct of the decomposition is a severe dermal toxin At least 2 cases of temporary paralysis have been reported. It has a dermal route of entry.

After WW2 there was great interest in using the boranes (diborane, pentaborane) as a rocket fuel. Both have much higher heating values than any hydrocarbon fuel giving it more thrust. These were projects Hermes and Zip

A number of companies were involved in the development of manufacturing processes from the late 1940's to early 1960's. During this time numerous incidents occurred some fatal:[3]

1. **Borane Manufacturer, New York, early 1950's**
   First recorded accident occurred in New York Test Facility. An employee was killed while vacuum distilling pentaborane. Details are sketchy.
2. **Borane Manufacturer, New York, June 21, 1955**
   Another company took over the Test Facility after the above incident. There was an explosion, killing 2 employees and totally destroying the facility. This was as a reaction of carbon tetrachloride with the boranes forming an explosive byproduct.
3. **Borane Manufacturer, New York, Dec 5, 1956**
   The Pilot Plant was relocated to another part of New York where an accident occurred on when air entered a process vessel containing diborane. The resulting explosion and fire killed one employee and injured 4 others.
4. **Borane Manufacturer, New York, 1959**
   A third accident occurred at the same pilot plant in early 1959. An employee was killed as a result of a vent line explosion. It was suspected that the vent line contained sublimed residues of both pentaborane and decaborane.

A study at another Boranes Manufacturer beginning in 1961 recorded 21 serious exposures to toxic borane chemicals and 46 minor exposures over a three year period.

They also reported only one accident during production of pentaborane but this was unrelated to plant operations. Several employees decided to build a model rocket fueled with the experimental high energy rocket fuel being developed. During the process of loading fuel into the model rocket, it exploded killing 3 employees and injuring 3 others.[3]

Warning label on pentaborane cylinder!

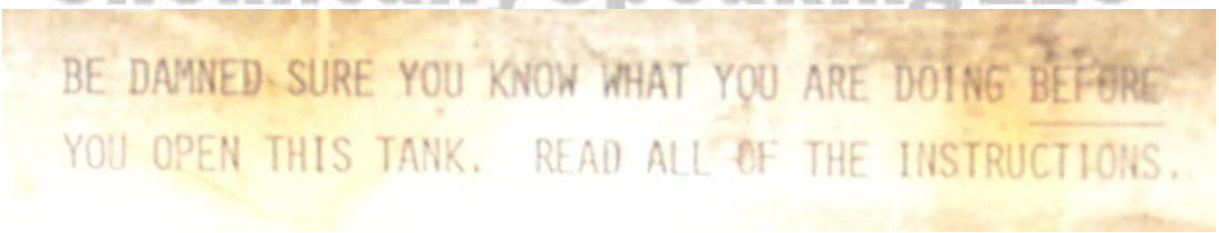

Fig. 5: Pentaborane Warning Label

Pentaborane was gifted to numerous research centers around the world by the US Navy for further fuels and medical testing in the 1960's. Disposal of these cylinders have proven to be a significant safety problem. One US disposal company quoted $80,000 to dispose of 2 cylinders in the UK.

In 1997 Edwards Air Force Base disposed of 100,000 lbs of pentaborane contained in 200 cylinders with 500 lbs each

1. **Waste Disposal Company, US, February 25, 1982**[4,5]
   The first incident resulting from the decommissioning of borane cylinders was reported in Hanover County, Virginia. Twenty one cylinders had been removed from a construction site for decommissioning and one of the workers opened a cylinder valve to see if it was empty. His bare hand was splashed with pentaborane. Within 4 minutes the worker went into convulsions. In another 4 minutes he slid into a coma. He died 8 days later from acute liver, kidney and brain damage.
   A second worker who rushed to aid the first worker, inhaled vapors of pertaborane. He experienced convulsions on the way to the hospital and went into full cardiac arrest at the hospital. Although he survived, he was a quadriplegic and had severe brain damage. A third worker was also exposed at the site; he experienced seizures on the way to the hospital but was later released with no apparent physical problems.

   During the incident, 15 other people were exposed and needed treatment. Ten of the people did not experience the symptoms until the next day. Two bystanders and an environmental protection worker were among the injured

2. **Waste Disposal Company, US, Sept. 6,1993**
   Company president is killed during disposal of cylinder
3. **Waste Disposal Company, US, mid 1994**
   During disposal of 8 large Pentaborane cylinders over 6 fires and explosions with 2 severely injured
4. **Gas Manufacturer, US, Jan 18, 1996**
   Explosion during disposal of 20 lb Pentaborane cylinder when a Sodium Hydroxide/Methanol solution is injected into the cylinder. The explosion ruptured the 200 gallon 200 psig rated containment vessel.

Fig. 6: Reaction of Boranes During Cleaning

5. **Military Base, US, 1997**
   400 cylinders of Pentaborane stored for 30+ years. 100 had walls that were too thin
   Each had 500 lbs
   Disposal only when wind is 5-15 mph and blowing across the desert
   5 placed in 2500 ft^2 pad
   Explosives rupture the cylinders and ignite the Pentaborane
   Burns at 4,300°F

Diborane Incidents

Diborane is the most hazardous pyrophoric gas because of the following

- It is lighter than air
- Quickly hydrolyzes with moisture in the air to form 3 moles of hydrogen.
- Very wide flammable range, 0.8-98%
- Since it is pyrophoric, it can also be the ignition source.

1. **Gas Supplier, US, Sept. 16, 1988**
   On a shipment of 4 cylinders to the gas supplier the driver noted a odd smell in the truck. Prior to delivering at the gas supplier they stopped to offload at a major retail box store. The truck was segregated in the yard when it arrived. ERT found a leaking cylinder in the truck. The big box store was notified and 5 potentially exposed employees were evaluated at the hospital. No acute exposures were detected.
   ER Team found a cylinder valve handle was loose and the vaportight valve outlet cap was also loose leaking diborane into the truck.
2. **Gas Supplier, Korea, Oct. 27, 2001**
   On a cylinder roller a pure diborane cylinder opened releasing diborane. Since it is lighter than air it accumulated in the ceiling. The diborane also hydrolyzes to from 3 moles of hydrogen. This ignited and the explosion blew out the walls in the room and roof. The blast blew out windows 100 ft away.

Figs. 7 & 8: Damaged Ceiling and Windows Blown Out 100 ft Away

3. **Gas Supplier, Korea, July 8, 2006**
   Transfilling diborane mixture

4. **Gas Supplier, US, May 2011**
   During transfill of pure diborane a leak and fire occurred at the cylinder valve outlet connection. The fire triggered the sprinkler head in the hood but the diborane continued burning for 30 minutes melting the valve handwheel. Sprinkler cooled the other cylinders in the hood.
   The cylinder lost 3 kgs of diborane a leak rate of 87.7 liters/min!

   No injuries and damage only to the cylinder valve.

Fig 9: Melted Cylinder valve Handwheel

Lessons Learned

1. The leak was caused by the operator not cleaning the outlet connection of solid borane deposits. While it passed a leak test, full pressurization with loosened the solids and the fire then loosened the connection further.
2. Like a silane leak and fire, the sprinkler water did not extinguish the diborane fire.
3. The melted handwheel and large fire prevented the operator from closing the valve. There have been other incidents like this with pyrophoric gases. In one case the only option was to tighten the outlet connection. This is why the use of a pneumatic cylinder valve is a Best Practice.

5. **Gas Supplier, Korea, April 2022**

   Korean gas supplier had a gas manufacturer had a diborane leak on April 1, 2022 in their cylinder storage room. The fire caused 4 aluminum cylinders to rupture over a period of 30 minutes.

Figs. 10 & 11 : Diborane explosion Korea (KBS News)

The boranes are dermal toxins that can be readily absorbed through the skin. They can cause temporary paralysis. Acute exposure and medical treatment information can be found in *Tox and Hound – Fellow Friday – Metal Hydrides III – Boron Hydrides* [7] and the US Health Dept ATSDR Medical Management Guidelines for Diborane.[8]

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