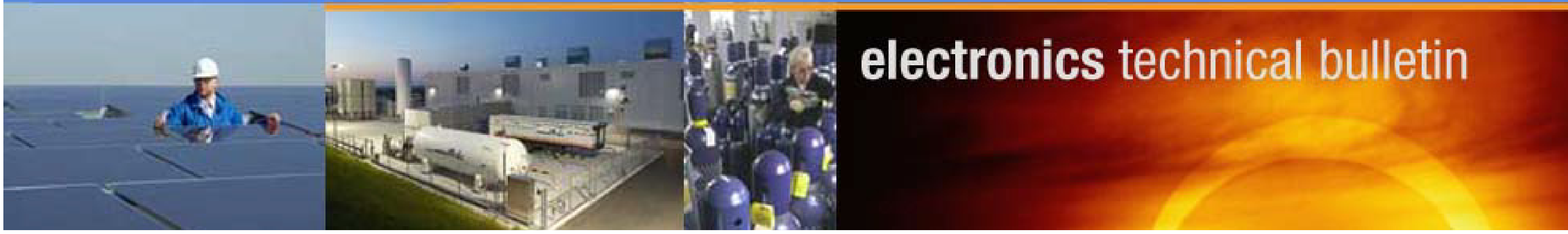
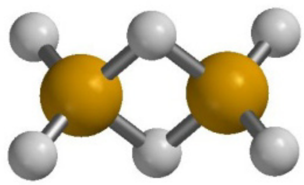


Diborane (B_2H_6)
Storage and Delivery

Air Products supplies a wide range of gases and chemicals that are used for integrated circuit, flat panel display and photovoltaic device manufacturing. Understanding the proper storage and handling requirements of these specialty materials is essential to obtain consistent results and to ensure the highest level of process safety. In this technical bulletin, we will provide the user with some of the knowledge required for its effective storage and use.



Diborane (formula B2H6) is a colorless, spontaneously flammable (pyrophoric) gas. It burns rapidly in air and reacts vigorously with water with the evolution of heat. The gas has a distinct, noxious odor and is extremely toxic by inhalation or by skin exposure. Because of these hazards, it is essential that all gas handling systems used for diborane be tightly sealed and carefully leak checked. Furthermore, additional controls such as localized exhaust, operator training and personal protective equipment should be used to minimize the risk of personnel exposures.

The extreme chemical reactivity of diborane also provides numerous challenges in order to maintain its integrity and purity sufficient for its intended uses. Since B2H6 reacts rapidly with oxygen (Equation 1) or with trace moisture (Equation 2) as found in air, all delivery lines must be thoroughly dried and purged with inert gas prior to charging with diborane to avoid the possibility of contamination with boron oxides.

$$2\ B_2H_6 + 3\ O_2 = 2\ B_2O_3 + 6\ H_2 \text{ (Eq. 1)}$$
$$B_2H_6 + 3\ H_2O = B_2O_3 + 6\ H_2 \text{ (Eq. 2)}$$

Even in the absence of contamination, diborane is so reactive that it will slowly decompose by itself, forming H_2 gas and heavier boron hydrides in the form of volatile liquids such as B_5H_9 and sublimable solids such as $B_{10}H_{14}$. These heavier hydrides are delivered with the gas and can cause contamination of the process and fouling of the delivery system components. Figure 1 shows the internals of the first stage of a two-stage gas regulator that was fouled by $B_{10}H_{14}$ deposits.

Figure 1: Picture of the first stage of diborane mixture regulator fouled with solid decomposition products.

The gas-phase decomposition rate of diborane was shown to increase with concentration and with temperature. Pure diborane is so reactive in its pure state that it may only be stored or transported if surrounded with dry ice to prevent rapid degradation that could lead to hazardous overpressurization.

For convenience, dilute mixtures of diborane in an unreactive matrix gas can be prepared to enhance the storage life of this material and make dry ice storage unnecessary. Typically, concentrations of $<5\%$ by volume are used in either H_2 or N_2 as the base gas. There is some evidence that H_2 further enhances the stability of the mixture and thus is the preferred base gas.

Figure 2 shows the expected degradation rate of diborane mixtures of varying concentration based on the rate law developed by Flaherty, et al. [1] This model shows how a 10% diborane could decompose sufficiently

[1] Flaherty, E.T.; Marshall, J.; Albert, P.; Brzychcy, A.M.; Forbes, D. *J. Electrochem. Soc*. **1993**, *140,* 1709.

for its concentration to fall out of tolerance within several months, whereas a more dilute mixture might be expected to remain relatively stable if stored at room temperature for up to a year. Typically, a 6 month (180 day) certification validity period, or shelf life, is assigned to mixtures containing ≤5% by volume diborane.

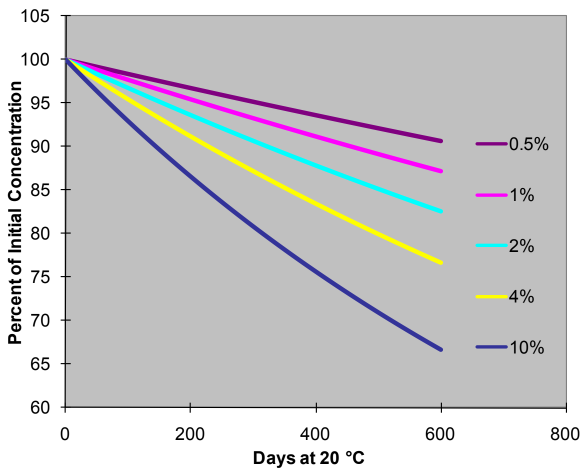


Figure 2: Role of concentration on gas-phase decomposition rate of diborane at 20ºC.

Temperature also affects the stability of diborane mixes, with an exponential increase in degradation with elevated temperature. Conversely, lower temperatures can be used to significantly retard the decomposition of diborane mixtures. While temperature controlled transportation and temperature controlled storage are possible; these options are very costly and logistically difficult to manage. Simpler means of enhancing diborane stability are therefore preferable. Such measures include storing cylinders out of direct sunlight under roof or even in air-conditioned hazardous materials storage areas.

Figure 3 shows the expected decomposition rate at several different temperatures. Based on an estimated activation energy of 100 kj/mol, the decomposition rate should double for each increase in temperature of about 6ºC.

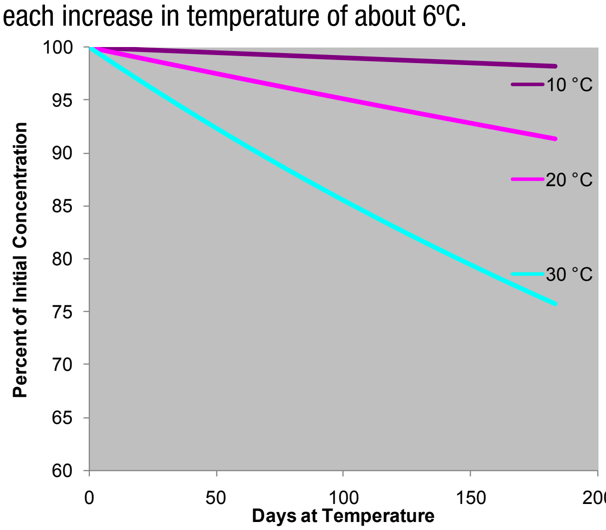


Figure 3: Role of temperature on gas-phase decomposition of diborane

In addition to concentration and temperature, diborane decomposition can be dramatically affected by contact with reactive surfaces. Certain metals and metal oxides can catalyze and thereby speed up the decomposition rate of diborane. Nickel and nickel-rich alloys are particularly noteworthy in this detrimental ability. Although 300-series stainless steels (e.g. UNS31600) contain significant quantities of nickel, diborane stability is not significantly impacted by clean stainless steel delivery systems. Higher nickel alloys (e.g. UNS N02200, N04400, N06022) should be avoided, especially in high surface area forms such as found in filter elements.

In recognition of the challenges unavoidably associated with the chemical properties of diborane, some best practices have been developed over the years to enable its application. These practices cover system design, system operation, system maintenance as well as container handling recommendation.

The solid decomposition product, decaborane ($B_{10}H1_{4}$) can transport in the gas phase, particularly when the gas is at high pressure. When the pressure is dropped by using a regulator, these solids may precipitate and cause serious regulator creep, causing the delivery pressure to rise over time. One design feature that can delay the onset of regulator creep is the use of two-stage regulators in diborane systems (standard in Air Products GASGUARD® delivery systems). The use of disposable stainless steel filter elements upstream of the regulator, which can be regularly replaced, has also been reported to be effective. Decaborane deposits may also be removed by extended purging with inert gas.

To deal with the potential variability of the diborane concentrating over time, especially in critical doping applications, it may be prudent to qualify each new source container of diborane and adjust the flow rate accordingly to achieve the desired boron incorporation level.

To learn more about diborane mixtures and GASGUARD® delivery systems, contact your Air Products representative. For more detailed technical questions, you may contact Ronald Pearlstein from our technology department at pearlsrm@airproducts.com; tel. +1(610)481-8594.

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