Safety Overview of Semiconductor Process Gases, Part 2

Eugene Y. Ngai
Director of Compound Semiconductor Technology
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Highly Toxic Gases
DOT Poison Gas Hazard Zone A

- Arsine
- Cyanogen
- Cyanogen Chloride
- Fluorine
- Hydrogen Cyanide (Not a Compressed Gas but under 173.195 is treated as such)
- Hydrogen Selenide
- Nitric Oxide
- Nitrogen Dioxide
- Phosgene
- Phosphine

Other Hazards include: Flammability, Corrosivity

DOT special requirements under 49CFR173.40 for packaging
Arsine
Chemical & Physical Properties

- Arsine is a liquefied gas which is highly toxic and flammable
- Arsenic Hydride, AsH₃
- CAS# 7784-42-1
- UN# 2188
- Molecular Weight 77.95
- Liquefied Gas with Vapor Pressure of 205 psig @ 70°F (21°C)
- Gas Density of 0.2025 lb/ft³ (3.24 gm/l) @ 68°F (20°C)
- Liquid Density of 83.55 lb/ft³ (1.335 kg/l) @ 70°F (21°C)
- Specific Gravity of Gas @ 70°F (air = 1) 2.69
- Highly Toxic Gas with PEL of 50 ppb, LC₅₀ of 20 ppm, IDLH of 3 ppm
- Boiling Point, 1 atm. -80.5°F (-62.5°C)
- Freezing Point, 1 atm. -178.4°F (-116.9°C)
- Critical Temperature 211.8°F (99.9°C)
Arsine Poisoning

- Major effect is on Red Blood Cells causing hemolysis, hemoglobinuria or free plasma hemoglobin
- Effects can occur from 20 min. to 36 hours after exposure as a function of concentration and time
- Most significant noticeable affect is red urine due to breakdown of Red Blood Cells which can lead to renal failure. Kidney function can return after a few months with proper treatment
- Is not absorbed through the skin
- Only effective treatment is whole blood transfusion
- US Health Dept Medical Treatment Protocol
Theoretical Mechanism for Arsine Metabolism and Toxicity in Humans

Arsine Acute Exposures

- Exposure of 250 ppm (797 mg/m³) can be lethal after a few minutes, 25-50 ppm for 30 minutes
- Dangerous threshold of 6.25 ppm (20 mg/m³) for 30 minutes and 15.5 ppm (50 mg/m³) for 30 minutes
- No effect reported for 3.1 ppm (10 mg/m³) for a few hours

Effects of Exposure to Toxic Gases, Matheson Gas Products, 1988
Arsine Exposure Estimate

- An individual exposed to a PEL of 50 ppb for 8 hours will receive a dose of 1.28 mg. Estimated by $0.05 \text{ ppm} \times 3.2 \text{ mg/m}^3 \times 8 \text{ m}^3$ (normal breathing)

- Typically an individual breaths as follows:
  - Resting: 7.4 liters/min
  - Light Work: 29 liters/min
  - Heavy Work: 60 liters/min

- Assuming a safe dose of 1 mg and individual would have to be exposed as follows:
  - 30 sec: 21.6 ppm
  - 1 min: 10.8 ppm
  - 5 min: 2.4 ppm

“Report for Trinity Consultants”, Dr. E.T. Wei, Prof of Toxicology, University of California, July 21, 1984
Arsine Fatalities From Arsine Use

- MIT Lincoln Labs Technician on June 14, 1982, suicide
- M/A-Com Technician on June 11, 1984, deliberate exposure
Pyrophoric Gases

- Diborane
- Disilane
- Metal Alkyls e.g. Dimethyl Zinc
- Methyl Silane
- Phosphine
- Silane

Other Hazards include Toxicity
Pyrophoric Gas Characteristics

- Pyrophoric gases are flammable gases which have autoignition temperatures that are below 130°F (54.4°C).
- Pyrophoric gases require oxidizers to burn.
- Of all the Pyrophoric Gases, Silane is the most unpredictable. When released into air, Silane will react in one of the following manner:
  
  Delayed Ignition (Explosion)
  No Ignition
  Immediate Ignition

Of these the latter is only safe condition. Temperature, humidity, flow rate, will influence the ignition.
## Autoignition Temperature Of Common Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Autoignition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane</td>
<td>&lt;-148°F</td>
</tr>
<tr>
<td>Disilane</td>
<td>&lt;-100°F</td>
</tr>
<tr>
<td>Nickel Carbonyl</td>
<td>68°F</td>
</tr>
<tr>
<td>Phosphine</td>
<td>&lt;32°F</td>
</tr>
<tr>
<td>Diborane</td>
<td>44°F</td>
</tr>
<tr>
<td>Dichlorosilane</td>
<td>111-133°F</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>320°F</td>
</tr>
<tr>
<td>Trichlorosilane</td>
<td>360°F</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>500°F</td>
</tr>
<tr>
<td>Butane</td>
<td>550°F</td>
</tr>
<tr>
<td>Acetylene</td>
<td>581°F</td>
</tr>
<tr>
<td>Diethyl Amine</td>
<td>594°F</td>
</tr>
<tr>
<td>Butylene</td>
<td>725°F</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>752°F</td>
</tr>
<tr>
<td>1,3 Butadiene</td>
<td>788°F</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>804°F</td>
</tr>
<tr>
<td>Propane</td>
<td>842°F</td>
</tr>
<tr>
<td>Ethylene</td>
<td>842°F</td>
</tr>
<tr>
<td>Propylene</td>
<td>851°F</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>882°F</td>
</tr>
<tr>
<td>Ethane</td>
<td>882°F</td>
</tr>
<tr>
<td>Ammonia</td>
<td>928°F</td>
</tr>
<tr>
<td>Methane</td>
<td>999°F</td>
</tr>
<tr>
<td>Hydrogen Cyanide</td>
<td>1000°F</td>
</tr>
</tbody>
</table>
Silane
Chemical & Physical Properties

- Silane is a compressed gas which is pyrophoric (in Japan, Taiwan and Korea it is also classified as a Toxic Gas)
- Silicon Tetrahydride, SiH₄
- CAS# 7803-62-5
- UN# 2203
- Molecular Weight 32.11
- Compressed Gas which is filled by weight due to high compressibility
- Gas Density of 0.083 lb/ft³, 1.33 gm/l @ 70°F (21°C)
- Liquid Density of lb/ft³, ( gm/l) NA at @ 70°F (21°C)
- PEL of 5 ppm, LC₅₀ & IDLH are not reported due to pyrophoricity
- Boiling Point, 1 atm. -169.6°F (-112°C)
- Freezing Point, 1 atm. -299°F (-184°C)
- Critical Temperature 25.8°F (-3.4°C)
For the user, the most common problem occurs when the gastight outlet cap is removed.
Silane Tube Trailer Release Studies
Conducted by CGA at Socorro, NM, 1996

Immediate Ignition

No Ignition

Detonation
Silane Cylinder Release from 1/8” Tube
Conducted by CGA at Socorro, NM, 1996

Immediate Ignition

Reignites

Flame Goes Out

Flame Goes Out
Silane Incidents

A number of major incidents have occurred with Silane use. The following caused fatalities:

- Release and detonation of gas cabinet
  - IBM, Zurich
  - Hitachi

- Contamination of cylinder with Nitrous Oxide
  - Osaka University
  - Gollub Labs

- Solid Byproducts of Reaction exposed to air
OSAKA UNIVERSITY INCIDENT
Oct. 2, 1991

BASED ON JUNE, 1992 MITI REPORT

Eugene Y. Ngai
INCIDENT

● Location

Plasma CVD Laboratory on the 5th floor of Department of Basic Technology at Osaka University, Osaka, Japan

● Event

On the afternoon of Oct. 2, 1991 at 4 PM as a graduate student opened the cylinder valve of a 10 liter silane cylinder it exploded killing him and another graduate student. Another 5 students were seriously injured.

● Aftermath

The explosion also sheared a natural gas line and shattered solvent cabinets which ignited, destroying two Laboratories.
BACKGROUND

- 10 liter cylinder of pure Silane from which only 13 grams was used. Was filled almost 4 years prior.

- 4 cylinders for reactor were stored in same Gas Cabinet and used the same purge Nitrogen
  - 10% Silane/Hydrogen
  - 100% Nitrous Oxide
  - 100% Sulfur Hexafluoride
  - 100% Silane

- System installed and used since 1987
CAUSES

- Common Nitrogen purge system allowed the interchange of incompatible gases
- Degradation of check valve elastomer seat in Nitrous Oxide service
- Opening of purge valves for Silane and Nitrous Oxide cylinders at the same time
- Vapor pressure of Nitrous Oxide is 745 psig @ 70°F which is higher than the Silane cylinder pressure of 600 psig
SYSTEM FLOW SCHEMATIC

GAS CABINET

Backflow of Nitrous Oxide

100% Purge Nitrogen

10% Silane/Hydrogen

100% Nitrous Oxide

100% Sulfur Hexafluoride

100% Silane

To Reactor

To Reactor

To Reactor

To Reactor
HITACHI INCIDENT
SILANE EXPLOSION, Dec. 13, 1990

A VALID REASON FOR THE RECENT INCIDENT AT THE MUSASHI PLANT OF HITACHI, IS A MAJOR LEAKAGE OF MONOSILANE

On 13. December of last year, an explosion occurred at the Musashi Plant of Hitachi (Kodaira City, Tokyo, Mr. Sadao Yoneyama, Factory Superintendent). According to the investigation held afterwards, the most plausible explanation at this time would seem to be that monosilane, which had reached a very high degree of density, exploded at the operations section which is located alongside of the cylinder cabinet.

This theory is based on the on-the-spot inspection carried out shortly after the explosion by a high pressure gas expert. A new fact is that, “Compared to the damage done to the cylinder cabinet and the gas control board themselves, the damage done to the operations section was far greater.” “Powders of such items as silica found to have accumulated nearby seem to back up the theory of the explosion being caused by a leak of monosilane.” These statements seem to make the cause of the explosion rather clear.

Based on all of the above, a line of reasoning is gathering strength which seems to be able to refute the theories in the papers blaming the incident on “an explosion of a vacuum pump” or “Monosilane and nitrogen trifluoride mixed in the piping and reacted, causing the explosion.”

On an official level, the Kodaira Police Station confiscated the cylinder cabinet and the vacuum pump, and conducted a thorough investigation as to the cause of the explosion. Up to now, however, they have not released the results of their investigation.

Also, the NHK, or High Pressure Gas Safety Institute in Japan, in January of this year, based on the intentions of MITI, formed a Committee for Adopting Safety Measures for Specialty Gases, appointing Prof. Keiho Namba, an honorary professor of Tokyo University as chairman. This committee, along with the piping diagram submitted by Hitachi, is conducting an investigation at the site of the explosion and will submit a preliminary report to MITI by the end of March.

Silane Explosion At Hitachi Fab
Sets Off Regulatory Furo In Japan
An explosion Dec. 13 in Hitachi’s Musashi chip fab, across the bay from Tokyo, has rocked the Japanese electronic chemicals industry and could create severe regulatory aftershocks.

One worker died, one was heavily injured and two were lightly injured when monosilane gas leaked from a gas cabinet and exploded on contact with air, according to reports in Japanese newspapers the following day. The explosion reportedly occurred just after the ringing of an alarm bell signaled the leak.

The precise cause of the explosion is still under investigation, according to Hitachi officials, but it has alarmed local governments across Japan. “It’s still too early to say whether this event will be enough to trigger the institution of new regulatory measures, but this remains a strong possibility,” said Robert Stevenson, an electronic chemicals industry analyst at Kline & Co.’s Tokyo office.
Silane Incidents

- Technician forgot washer in connection- Dec. 21, 1997, Shizuoka Prefecture
- During routine maintenance to a gas panel it was removed. Technician did not cap the vent line. Technician was purging Silane gas cabinet and a few minutes later the Silane exploded. Technician was hit on back of head with cabinet door
Hazards of Silane Combustion and Reaction Byproducts

- Burning in open Air is ineffective in oxidizing Silane to Silicon Dioxide. A dull Orange flame and Brown solids will indicate formation of $\text{SiO}_x\text{H}_y$ which is flammable.

- Exhaust from Silicon Nitride CVD can create unstable solids which are air reactive $\text{SiO}_x\text{N}_y\text{H}_z$ which has been involved in a number of incidents:
  - 1997 - Worker Fatality - Japan
  - 1998 - UMC Fire $1$ Billion Loss
Electronics Division

Flammable Gases

- Acetylene
- Carbon Monoxide
- Ethylene
- Hydrogen
- Hydrogen Sulfide
- Propane
- Methane
- MAPP Gas (Methyl Acetylene and Propadiene)

COMMON HAZARDS: Flammability, Toxicity

For additional information see References in Chapter 10
Flammable Gases

- Wide Flammability Range
  - Acetylene
  - Diborane
  - Dichlorosilane
  - Hydrogen
  - Phosphine
  - Silane

- Low Ignition Energy
  - Acetylene
  - Hydrogen
Flammable Gases Definition

- **DOT**
  Is Flammable in concentrations of <13% in air or has a flammability range wider than 12% regardless of lower flammability concentration. Will not identify some gases which are flammable under certain conditions e.g..

  *Ammonia (16-25%)*
  *HCFC’s e.g. 134b*

- **Internationally (ISO 10156)**
  Same, however a second definition which covers gases that are flammable in any concentration in air for storage
Flammable versus Explosive

![Graph showing flame temperature versus mole fraction for different gases]
### Ignition Energy Of Gases In Millijoules @1 Atm, 25°C Stochiometric Conc.

<table>
<thead>
<tr>
<th></th>
<th>AIR</th>
<th>OXYGEN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>0.017-0.018</td>
<td>0.0002</td>
</tr>
<tr>
<td>1,3 Butadiene</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>0.24</td>
<td>0.002</td>
</tr>
<tr>
<td>Ethylene</td>
<td>0.07-0.08</td>
<td>0.001</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.017-0.018</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>0.28</td>
<td>0.003</td>
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<tr>
<td>Methyl Acetylene</td>
<td>0.11</td>
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<tr>
<td>Propylene</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Vinyl Acetylene</td>
<td>0.082</td>
<td></td>
</tr>
</tbody>
</table>

**NOTE:** A spark generated from a person shuffling across a rug is 200 mj
Hydrogen
Chemical & Physical Properties

- Hydrogen is a compressed gas which is flammable
- Pure element, H₂
- CAS# 1333-74-0
- UN# 1049 for gas and 1966 for liquid
- Molecular Weight 2.02
- Compressed gas filled in cylinders to pressures >2000 psig
- Gas Density of 0.005 lb/ft³ (0.083 gm/l) @ 70°F (21°C)
- Liquid Density of 4.43 lb/ft³ (71 g/l) @ boiling point
- Specific Gravity of Gas @ 70°F (air = 1) 0.07
- Flammable Range in air @ 1 atm 4% – 76%
- Boiling Point, 1 atm. -423°F (-253°C)
- Freezing Point, 1 atm. -435°F (-259°C)
- Critical Temperature -400°F (-240°C)
Acetylene Plant Fire
Oxidizer Gases

- Chlorine
- Chlorine Trifluoride
- Fluorine
- Nitrogen Dioxide
- Nitrous Oxide
- Nitric Oxide
- Oxygen

Some are also highly toxic and/or corrosive

For additional information on Oxygen see References in Chapter 10
Oxidizer Gas Characteristics

- Oxidizer gases will promote and accelerate combustion
- Is reactive with all fuels
- Some Oxidizer Gases require some energy to cause it to react
  - Nitrogen Trifluoride
  - Nitrous Oxide
Oxygen Adiabatic Compression & Explosion From Quick Opening Valve

Quick Opening Valve Closed

Quick Opening Valve Opened

High Velocity Oxygen Impacting Closed Regulator
Oxygen Regulator Fire, During Pressure Check, June 12, 1998
How not to handle Liquid Oxygen
Nitrous Oxide
Chemical & Physical Properties

- Nitrous Oxide is a liquefied gas which is an Oxidizer
- Nitrous Oxide, N₂O
- CAS# 10024-97-2
- UN# 1070
- Molecular Weight 44.01
- Liquefied Gas with Vapor Pressure of 739 psig @ 70°F (21°C)
- Gas Density of 0.115 lb/ft³ (1.947 gm/l) @ 70°F (21°C)
- Liquid Density of 48.25 lb/ft³ (773 gm/l) @ 70°F (21°C)
- Nonflammable Gas with TLV of 50 ppm, LC₅₀ none established, IDLH none established
- DOT Nonflammable Gas
- Boiling Point, 1 atm. -127.4°F (-88.5°C)
- Freezing Point, 1 atm. -131.5°F (-90.8°C)
- Critical Temperature 97.6°F (36.4°C)
Corrosive Gases – Acid

- Boron Trifluoride
- Boron Trichloride
- Chlorine
- Hydrogen Bromide
- Hydrogen Chloride
- Hydrogen Fluoride (Not a compressed gas)

HAZARDS: Material Corrosion, Tissue Destruction, Irritation, Toxicity
Corrosive Gas, Acid

The acidic gases are noncorrosive in their anhydrous forms but upon contact with water or moist air become strongly corrosive. Operations performed at elevated temperatures also increase the severity of corrosive reactions. Cylinders can be seriously weakened by corrosive reactions over a long period of time with some reactions forming gaseous products that may increase cylinder pressures to unsafe levels. For example, cylinders contaminated with water containing Hydrogen Chloride or Hydrogen Bromide can form Hydrogen while corroding away the cylinder wall. Cylinder failures have been known to occur due to this action. Cylinder valves and regulators can malfunction because of corrosion. For example, solid corrosion products can build up in a regulator and produce creep, a gradual increase in the delivery pressure when flow is terminated. Uncorrected creep can cause hazardous pressures on the delivery side of the regulator under prolonged no-flow conditions. Similarly, cylinder valves exposed to moist air for long lengths of time will have a build up of corrosive products in the stem.
Hydrogen Chloride Chemical & Physical Properties

- Hydrogen Chloride is a liquefied gas which fumes white
- HCl, Halogen Acid
- CAS# 7647-01-0
- UN# 1050
- Molecular Weight 36.46
- Liquefied Gas with Vapor Pressure of 613 psig @ 70°F (21°C)
- Gas Density of 0.095 lb/ft³, (1.522 gm/l) @ 70°F (21°C)
- Liquid Density of 52.7 lb/ft³, (842 gm/l) @ 70°F (21°C)
- Poison Gas with TLV of 2 ppm, LC₅₀ 3120 ppm, IDLH 50 ppm
- DOT Poison Gas and Corrosive
- Boiling Point, 1 atm. -121°F (-85°C)
- Freezing Point, 1 atm. -173.6°F (-114.2°C)
- Critical Temperature 124.5°F (51.4°C)
Tied Diaphragm Corrosion
Hydrogen Chloride, Leaked for 18 Months
Hydrofluoric Acid Exposure

- < 50% conc. Can be painless with symptoms delayed 2-24 hrs.
- > 50% immediate pain
- 25 in² exposure of skin is critical if left untreated
- As a weak acid it will move undissociated into deep tissue where it will react with calcium or magnesium cations forming insoluble salts which increases cell membrane permeability to potassium causing intense pain.
- Immediate flushing with water for 20 minutes (AP is 5 minutes) followed by topical application of 2.5% Calcium Gluconate gel. (note not FDA approved)
- Wet soaks of Zephiran (benzalkonium chloride), Hyamine (benzethonium chloride) and Magnesium Sulfate have also been used
- If severe pain continues for 45 minutes after topical treatment, injections of 5% Calcium Gluconate solution have been used.

Air Products Guidance On HF Exposures

- Planning for Hydrofluoric Acid (HF) Medical Emergencies, GEG EHS SOP
- APCI Safetygram 29, Treatment Protocol for Hydrofluoric Acid Burns, 9/99
- Hydrogen Fluoride Product Safety Training-GEG Product Safety Group
Bad Gloves
Fluoride Gases

- Some Fluoride Gases can react with the moisture (Hydrolysis) in the air to form HF. These include:
  - Arsenic Pentafluoride
  - Chlorine Trifluoride
  - Fluorine
  - Germanium Tetrafluoride
  - Silicon Tetrafluoride
  - Tungsten Hexafluoride
Corrosive Gases – Base

- AMMONIA
- MONO, DI and TRI METHYLAMINES
- MONOETHYLAMINE

HAZARDS;

Material Corrosion, Tissue Destruction, Irritation, Toxicity
Corrosive Gas, Base

Ammonia and the Amines, such as Methyl and Ethylamine, will react with moisture or water to form basic materials which are corrosive to certain metals, particularly copper and copper alloys. These materials are extremely irritating to human tissue, and low concentrations will create severe eye irritation. Spills of liquid on the skin will cause immediate burns. These materials are also flammable, particularly the amines, which are shipped as flammable gases. In handling these gases, not only should they be treated as regular flammable gases, but protective equipment should be worn to protect against eye and skin injury if spillage should occur. Face shields, and rubber or plastic coated full aprons, and gloves are recommended when handling these materials, particularly when handling them in the liquid phase.
Ammonia, Chemical & Physical Properties

- Ammonia is a liquefied gas which is flammable at concentrations higher than the DOT definition and highly corrosive. Outside the US it is classified as a Toxic Gas
- Anhydrous Ammonia, NH₃
- CAS# 7664-41-7
- UN# 1005
- Molecular Weight 17.03
- Liquefied Gas with Vapor Pressure of 114.4 psig @ 70°F (21°C)
- Gas Density of 0.045 lb/ft³ (0.724 gm/l) @ 70°F (21°C)
- Liquid Density of 38.0 lb/ft³ (609 gm/l) @ 70°F (21°C)
- Corrosive Gas with PEL of 50 ppm, LC₅₀ of >7300 ppm, IDLH of 300 ppm
- DOT Nonflammable Gas with LFL of 16% and UFL of 25%
- Boiling Point, 1 atm. -28.1°F (-33.4°C)
- Freezing Point, 1 atm. -107.9°F (-77.7°C)
- Critical Temperature 271.4°F (133°C)
Ammonia Leaker
Inert Gases

- Argon
- Nitrogen
- Helium
- Neon
- Krypton
- Sulfur Hexafluoride
- Carbon Tetrafluoride
- Xenon

HAZARD: Oxygen Deficiency
Nitrogen
Chemical & Physical Properties

- Nitrogen is a compressed gas which is inert
- Pure element, N₂
- CAS# 7727-37-9
- UN# 1066 for gas and 1977 for liquid
- Molecular Weight 28.01
- Compressed gas filled in cylinders to pressures >2000 psig
- Gas Density of 0.072 lb/ft³ (1.153 gm/l) @ 70°F (21°C)
- Liquid Density of 50.47 lb/ft³ (808 g/l) @ boiling point
- Specific Gravity of Gas @ 70°F (air = 1) 0.967
- Boiling Point, 1 atm. -320°F (-196°C)
- Freezing Point, 1 atm. -346°F (-210°C)
- Critical Temperature -232°F (-147°C)
Oxygen Deficiency

The normal oxygen content of air is 20.9%. Depletion of oxygen content in air, either by combustion or displacement with inert gas, is a potential hazard to personnel throughout industry. A general indication of what can potentially occur relative to the percentage of oxygen available is given in the table below.

Note: These indications are for a healthy average person at rest. Factors such as individual health (e.g., smoker), degree of physical exertion, and high altitudes can affect these symptoms and the oxygen levels at which they occur.

<table>
<thead>
<tr>
<th>Oxygen Content</th>
<th>Effects and Symptoms of Acute Exposure (at Atmospheric (% by Volume))</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-19%</td>
<td>Decreased ability to perform tasks. May impair coordination and may induce early symptoms in persons with heart, lung, or circulatory problems.</td>
</tr>
<tr>
<td>12-15%</td>
<td>Breathing increases, especially in exertion. Pulse up. Impaired coordination, perception and judgment.</td>
</tr>
<tr>
<td>10-12%</td>
<td>Breathing further increases in rate and depth, poor coordination and judgment, lips slightly blue.</td>
</tr>
</tbody>
</table>
Gases With Multiple Hazards

- Many gases have multiple hazards
- Chlorine Trifluoride is one of the gases with the most hazards
  - Toxicity
  - Corrosivity
  - Oxidizer
  - Reactivity
- Very little energy is required to cause it to react with most materials
- Hypergolic with flammable liquids and solids.
Chlorine Trifluoride ER & Safety Information

- Vapor Pressure 6.8 PSIG (46.85 kPa)
- Gas Density 0.244 lb/ft³ (3.908 kg/m³)
- Specific Gravity (air=1) 3.19
- Boiling Point 53.2°F (11.75°C)
- Freezing Point –105.4°F (-76.3°C)
- Dissociation starts at 250°C with 50% at 450°C
Chlorine Trifluoride Exposure Testing

- Liquid Onto Asphalt
- Liquid Onto Oil Film
- Liquid Onto Raw Chicken
- Vapor Onto Raw Chicken
Self Reacting Gases

- Gases which can react with themselves given sufficient energy.
- Ignition outside of the cylinder can flashback into the cylinder.
- The heat given off by the decomposition or polymerization accelerates the reaction.
Self Reacting Gases/Liquids

- **Acetylene**
  - is absorbed into acetone and in a solid matrix

- **Ethylene Oxide**
  - Stabilized by mixing with Carbon Dioxide or Freon. 60 lb cylinders will not explode because the heat is adsorbed. Will create a lot of polymer

- **Germane**
  - Fill limit based on complete reaction

- **Hydrogen Cyanide**
  - Stabilized with 0.06% Sulfuric or Hydrochloric acid

- **Tetrafluoroethylene**
  - Stabilized with D-Limonene. Without it, it can explode at 2.7 atm (39 psia)

- **Nitric oxide**
  - Pressure is limited to 480 psig

- **Nitrous Oxide**
  - Reaction can only propagate in gas phase

- **Tetrafluorohydrazine**
Linde AG, Nitrous Oxide Explosion 2001
Dry Pump Caused Overtemperature
Matheson Germane Explosion

- Incident on Nov. 26, 1984 at Nippon Sanso Kawasaki facility in Japan
- Two workers injured in explosion
- MITI investigation
- 44 liter cylinder filled with 10 kg which is 5% full of liquid
- Germane has negative heat of formation
- Will heat byproducts of decomposition (Germanium & Hydrogen) to 1719°F

\[
\text{GeH}_4 \rightarrow \text{Ge} + 2\text{H}_2 + \text{Heat}
\]

- Decomposition is deflagration in 100 milliseconds with a pressure of over 9000 psig
- Germane is now filled to 25% of original
Basic Gas Safety Rules

- Limit Inventory and store in the approved location
- Do not mix incompatibles
- Review MSDS for Hazards
- Leakcheck cylinder and system before use
- Purge system with inert gas before and after use
- Wear appropriate PPE
Potential Leak Points

- Gas or Vapor
- Tight Outlet
- Cap
- Pressure
- Relief Device
- Valve Thread
Cylinder Safety Rules

Cylinders and Containers present a physical hazard when handling

- Proper lifting techniques should be used in lifting
- Use approved handcart to move >6 ft
- Do not lift using cylinder cap
- Move with cylinder cap and vaportight cap/plug in place
- Cylinders shall not be marked “Empty” unless they have been purged with inert gas
- Do not reduce pressure to <10 psig
- Do not fill cylinder with another gas
- Heat cylinders only with approved devices and never above 125°F
- Do not cool cylinders below -20°F
- Do not allow cylinders to become part of an electric circuit
A Safety Alert By Willard Graham, Mine Safety & Health Administration, Dept. of Labor

On January 2, 2003 three employees were attempting to plug a tire on a Ford F-250 pickup. Earlier in the day they had inflated the left rear tire with a can of "fix-a-flat" and topped it off with oxygen from the cutting torch tanks mounted on the truck. They had plugged the front tire of the truck and noticed the rear tire was leaking again. An employee had reamed the hole in the rear tire and as he reached for the plug tool, another employee knelt down and removed the reamer from the tire, at which point the tire exploded. All three employees were blown ~10 ft away from the truck, resulting in critical injuries to one employee and serious injuries to the other two. Currently, one of the employees with serious injuries has been released from the hospital and the most critically injured employee remains in the trauma center and is expected to recover after several surgeries and lengthy recovery.
Air Products
Product Information Sources

- Air Products Product Safety Web Site
  www.airproducts.com/productstewardship

- Air Products Technical Information Center at:
  800-752-1597

- Air Products MSDS’s
- Air Products Safetygrams
- Air Products Gases and Equipment Fact Book
### Material Safety Data Sheet

#### SECTION 1. PRODUCT IDENTIFICATION

- **PRODUCT NAME:** Nitrogen, refrigerated liquid
- **CHEMICAL NAME:** Nitrogen
- **SYNONYMS:** Liquid Nitrogen, LIN, Cryogenic Liquid Nitrogen, Nitrogen
- **MANUFACTURER:** Air Products and Chemicals Inc.
  
  7201 Hamilton Boulevard
  
  Allentown, PA 18195-1601

- **PRODUCT INFORMATION:** 1-800-752-1597
- **MSDS NUMBER:** 1041

#### SECTION 2. COMPOSITION/INFORMATION ON HAZARD

#### Safetygram - 7

**Liquid Nitrogen**

- **General:** Liquid nitrogen is inert, colorless, odorless, noncorrosive, nonflammable, and extremely cold. Nitrogen makes up the major portion of the atmosphere (78.03% by volume, 75.5% by weight). Nitrogen is inert and will not support combustion; however, it is not life supporting. Nitrogen is inert except when heated to very high temperatures where it combines with some of the more active metals, such as lithium and magnesium, to form nitrides. It will also combine with oxygen to form oxides of nitrogen and when combined with hydrogen in the presence of heat can form nitrogen compounds.

- **Manufacture:** Nitrogen is produced at air separation plants by fractional distillation of air where it is separated from the other atmospheric gases.

- **Toxicity:** In general, it is safe to work with nitrogen under normal conditions. However, it can cause hypothermia in high concentrations for extended periods of exposure. It is also inert and does not support combustion.

- **Fire and Explosion Hazards:** Nitrogen is not flammable; however, it can displace oxygen and cause asphyxiation.

- **Health and Environmental Hazards:** Nitrogen is a colorless, odorless, non-toxic, non-flammable gas. It is not harmful to humans in normal concentrations.

- **Safety Precautions:** When working with nitrogen, wear appropriate personal protective equipment (PPE) such as gloves, goggles, and respiratory protection. Ensure proper ventilation and do not inhale nitrogen for extended periods of time.

- **Spill Procedures:** In case of a spill, isolate the area and ventilate the area to allow the gas to disperse. Use a vacuum or a non-conducting tool to contain the spill. Avoid inhalation of nitrogen and be aware of potential asphyxiation hazards.

- **Disposal:** Disposal of nitrogen should be in accordance with local regulations. It is not hazardous for the environment and can be disposed of as a non-hazardous waste.

- **MSDS References:** For more detailed information, refer to the Material Safety Data Sheet (MSDS) provided by the manufacturer.
Air Products Safetygrams

Safetygram-1: Gaseous Oxygen
Safetygram-2: Gaseous Nitrogen
Safetygram-3: Gaseous Argon
Safetygram-4: Gaseous Hydrogen
Safetygram-5: Gaseous Helium
Safetygram-6: Liquid Oxygen
Safetygram-7: Liquid Nitrogen
Safetygram-8: Liquid Argon
Safetygram-9: Liquid Hydrogen
Safetygram-10: Handling, Storage, and Use of Compressed Gas Cylinders
Safetygram-11: Emergency Action in Handling Leaking Compressed Gas Cylinders
Safetygram-12: Regulator Selection, Installation, and Operation
Safetygram-13: Acetylene
Safetygram-14: Don’t Turn a Cylinder Into a Rocket
Safetygram-15: Cylinder Pressure-Relief Devices
Safetygram-16: Safe Handling of Cryogenic Liquids
Safetygram-17: Dangers of Oxygen-Deficient Atmospheres
Air Products Safetygrams

Safetygram-18: Carbon Dioxide
Safetygram-19: Gaseous Carbon Monoxide
Safetygram-20: Nitrous Oxide
Safetygram-21: Safe Handling Procedures for Medical Oxygen Cylinders and the Use of Regulation Equipment
Safetygram-22: Liquid Helium
Safetygram-23: Cylinder Valves
Safetygram-24: Hydrogen Chloride
Safetygram-25: 20% Fluorine/Nitrogen Mixture
Safetygram-26: Silane
Safetygram-27: Cryogenic Liquid Containers
Safetygram-28: Nitrogen Trifluoride Safe Handling Practices
Safetygram-29: Treatment Protocol for Hydrofluoric Acid Burns
Safetygram-30: Handling Liquefied Compressed Gas
Safetygram-31: Cylinder Valve Outlet Connections
Air Products Safetygrams

Safetygram-33: The Hazards of Oxygen and Oxygen Enriched Mixtures
Safetygram-34: The Toxic metal Hydrides
Safetygram-35: Air Products Policy on Oxygen Sales to Oxygen Bars
Safetygram-36: Recommendation to Air Products' Customers for the Transportation of Hazardous Chemicals
Safetygram-37: Chemical Security
Safetygram-38: Product Migration of Liquefied Gases in Manifolded Systems
Safetygram-39: Chlorine Trifluoride
Safetygram-40: Epoxy Systems Spray Coating Operations
Safetygram-41: APEC UHP Developer Safe Handling Practices
Safetygram-42: Fluorine