STORAGE AND USE OF HIGH HAZARD GAS

1. Definition of High Hazard (HH) Gases

For these guidelines, any gas meeting one or more of the following definitions based on International Fire Code (IFC) and National Fire Protection Association (NFPA) standards:

1.1. Flammable gas – a material that is a gas at 68ºF (20ºC) or less at an absolute pressure of 14.7 psi (101.325 kPa) when in a mixture of 13% or less by volume with air, or that has a flammable range at an absolute pressure of 14.7 psi (101.325 kPa) with air of at least 12%, regardless of the lower limit

1.2. Pyrophoric gas – a gas with an autoignition temperature in air at or below 130ºF (54.4ºC)

1.3. Health Hazard 3 (HH3) gas – material that, under emergency conditions and according to the standards, can cause serious or permanent injury

1.4. Health Hazard 4 (HH4) gas – material that, under emergency conditions and according to the standards, can be lethal

The storage and usage of a gas or gases meeting any of the above definitions must follow all applicable IFC and NFPA guidelines and the requirements outlined in this document.

2. Notification Requirements Prior to Obtaining High Hazard Gases

2.1. Environmental Health and Safety (EH&S) must be notified prior to obtaining High Hazard gases (regardless of quantity) via email (safety@ehs.pitt.edu) or phone (412-624-9505).

2.2. The following information must be provided to EH&S concerning High Hazard gases:

2.2.1. Type and concentration of compressed or liquefied gas
2.2.2. Quantity (net weight) of compressed or liquefied gas
2.2.3. Type / size of gas cylinder
2.2.4. Storage and use location(s)
2.2.5. Research plans for gas usage
2.2.6. Vendor source, including written acknowledgement / agreement confirmation that the vendor will accept the “used” cylinders for return

3. Documentation Requirements to Possess and Use High Hazard Gases

3.1. The Principal Investigator must document a description of the research project and the associated risk assessment prior to obtaining the High Hazard gas. The documents should include the following lab specific information:
3.1.1. Laboratory entrance requirements
3.1.2. Personal Protective Equipment
3.1.3. Safe Work Practices

3.1.4. Safe Storage and Handling
3.1.5. Waste Disposal
3.1.6. Chemical Spill or Release Response Procedures
3.1.7. Other Emergency Procedures
3.1.8. Safety Manual Review Signoff Page
3.1.9. Laboratory Personnel Training Requirements
3.1.10. Laboratory Personnel Emergency Contact Information (contact EH&S for guidance concerning additional emergency phone numbers for safety and facility related personnel)

3.2. The documents mentioned in Section 3.1 must be submitted to EH&S for review prior to use of High Hazard gas.

3.3. Certain High Hazard gases may be subject to the reporting requirements of the Department of Homeland Security Chemical Facility Anti-Terrorism Standard. EH&S must be contacted prior to ordering a High Hazard gas to determine permissible quantity and concentration of gas.

4. Storage and Use of High Hazard Gases

4.1. Exhausted gas cabinets or certified chemical fume hoods must be utilized for all storage and usage of High Hazard gases.

4.2. Quantities of High Hazard gases in storage and usage must be limited to comply with IFC standards at all times. Contact EH&S for specific guidance.

4.3. High Hazard gas cylinders must be ordered with the smallest orifice as practicable (recommend 0.006 inch and not to exceed 0.010 inch).

4.4. High Hazard gas systems must have excess gas flow controls installed.

4.5. Only compatible and approved regulators, valves, piping, and fittings must be used with all gas system installations. Consult your gas supplier for approved materials for each gas.

4.6. High Hazard gas cylinder set-up should be equipped with an automatic shut off valve in the event of gas detection at any of the monitoring points. High Hazard gas cylinder set-up should be equipped with a manual shut-off valve when feasible.

4.7. High Hazard gas systems should be limited to a single gas line running from the gas containment device (gas cabinet or chemical fume hood) to the equipment; multiple lines and valve points should be avoided.

4.8. Entry doors to the laboratory or storage room in which High Hazard gas is stored must have appropriate warning signs. Signage must include name of the gas, room entry instructions for alarm or emergency conditions and emergency contact(s) information.

5. Gas Detection and Alarm Systems

5.1. Gas detection devices or systems are required in the gas cabinet or chemical fume hood and at all potential release points of the High Hazard gas system (per manufacturer's recommendations). Contact EH&S for specific guidance

5.2. Gas detection system consists of gas sensors and/or flame detectors depending on the high hazard gas (or gases) being stored and used in the laboratory space. Contact gas detection vendor for specific guidance on devices required and placement location.

5.3. An alarm system (local, audible, and visual) must be installed at locations inside and outside the laboratory or use site. If the alarm system is not feasible due to a set-up in the chemical fume hood, then ventilation flow rate alarms are required on the fume hood.

5.4. Emergency power must be provided for the gas cabinet exhaust, system shut offs, monitoring, alarms, and associated components.

6. Certification and Testing Requirements

6.1. Upon installation of the gas cabinet and cylinder and prior to initial use, the entire system (including, but not limited to detection system, alarms, etc.) must be certified by the installer and the documentation confirming the testing must be provided to the University.

6.2. Gas detection and alarm system must be serviced and maintained according to manufacturer's guidelines.

6.3. EH&S recommends annual testing / calibration of the alarm system by a qualified vendor.

6.4. Certification of testing equipment and maintenance of test records must be done on an annual basis.

APPENDIX A – HIGH HAZARD GASES
(The following table of HIGH HAZARD gases, is not an all-inclusive list, and is provided as a reference)

Health Hazard 3 and 4 Gases	CAS	Health Hazard 3 and 4 Gases	CAS
Acetylene	74-86-2	Hydrogen Fluoride, anhydrous	7664-39-3
Ammonia, anhydrous	7664-41-7	Hydrogen Selenide	7783-07-5
Arsenic Pentafluoride	7784-36-3	Hydrogen Sulfide	7783-06-4
Arsine	7784-42-1	Methane	74-82-8
Boron Tribromide	10294-33-4	Methylchlorosilane	68937-17-7
Boron Trichloride	10294-34-5	Methyl Mercaptan	74-93-1
Boron Trifluoride	7637-07-2	Nitric Oxide	10102-43-9
Carbon Monoxide	630-08-0	Nitrogen Dioxide	10102-44-0
Carbonyl Fluoride	353-50-4	Nitrogen Trioxide	10544-73-7
Carbonyl Sulfide	463-58-1	Nitrosyl Chloride	2696-92-6
Chlorine	7782-50-5	Oxygen Difluoride	7783-41-7
Chlorine Dioxide	10049-04-4	Ozone	10028-15-6
Chlorine Monoxide	7791-21-1	Pentaborane	19624-22-7
Chlorine Pentafluoride	13637-63-3	Perchloryl Fluoride	7616-94-6
Chlorine Trifluoride	7790-91-2	Phosgene	75-44-5
Cyanogen	460-19-5	Phosphine	7803-51-2
Cyanogen Chloride	506-77-4	Phosphorus Trichloride	7719-12-2
Diazomethane	334-88-3	Propane	74-98-6
Diborane	19287-45-7	Selenium Hexafluoride	7783-79-1
Dichlorosilane	4109-96-0	Silane	7803-62-5
Dinitrogen Tetroxide	10102-44-0	Silicon Tetrafluoride	7783-61-1
Ethane	74-84-0	Stibine	7803-52-3
Ethylene Oxide	75-21-8	Sulfur Dioxide, anhydrous	7446-09-5
Fluorine, compressed	7782-41-4	Sulfur Tetrafluoride	7783-60-0
Germane	7782-65-2	Sulfuryl Fluoride	2699-79-8
Germanium Tetrafluoride	7783-58-6	Tellurium Hexafluoride	7783-80-4
Hexafluoracetone	684-16-2	Tetrafluorohydrazine	10036-47-2
Hydrogen	1333-74-0	Titanium Tetrachloride	7550-45-0
Hydrogen Bromide	10035-10-6	Trifluoroacetyl Chloride	354-32-5
Hydrogen Chloride, anhydrous	7647-01-0	Tungsten Hexafluoride	7783-82-6
Hydrogen Cyanide, anhydrous, stabilized	74-90-8		

APPENDIX B – INFORMATION ON SPECIFIC HIGH HAZARD GASES
(The following list of gases is NOT all-inclusive and is provided as a reference)

Carbon Monoxide (CO)

- Poison and flammable gas
- Chemical asphyxiant
- University Guideline (EH&S #04-014) "Carbon Monoxide Gas Usage in Laboratories" provides specific guidance for work with CO.[5]

Additional Requirements/Considerations for Carbon Monoxide Use

1. A functioning CO gas detector, with visual and audible alarms, must be used in laboratory spaces where CO gas cylinders are stored and / or actively used.
2. Operation of the CO gas detector must be checked on a regular basis (monthly) and batteries must be replaced every 6 months.

Chlorine (Cl_2)

- Poison gas
- Respiratory irritant
- Listed as a Department of Homeland Security Chemical of Interest (DHS COI). EH&S must be contacted prior to ordering to determine permissible quantity and concentration of gas.

Additional Requirements/Considerations for Chlorine Use:

1. Steel piping is recommended for dry chlorine gas systems; the system must be kept dry due to the presence of moisture causing corrosive conditions in the steel pipe (formation of hydrochloric and hypochlorous acids).[1]
2. Precautions should be taken to keep chlorine cylinders and equipment free of moisture.[1]
3. Chlorine equipment and handling systems should be designed by engineers familiar with chlorine.[1]
4. Chlorine is classified as an oxidizer and must be stored away from flammable gases (hydrogen, acetylene, ethane, methane, etc.) and other hydrocarbons.[2] EH&S recommends storing oxidizers are stored at least 20 feet from flammable gases and other flammable materials.

Diborane (B_2H_6)

- Pyrophoric, autoignition temperature of 40-50ºC (105-122ºF)
- Poison and flammable gas
- Diborane in the range of 0.9 to 98% forms a flammable mixture with air.[1]
- Listed as a Department of Homeland Security Chemical of Interest (DHS COI). EH&S must be contacted prior to ordering to determine permissible quantity and concentration of gas.
- University Guideline (EH&S #02-004) "Flammable and Pyrophoric Gas" (Section 8) provides guidance for work with pyrophoric material.

Additional Requirements/Considerations for Diborane Use:

1. Diborane must be obtained in the smallest sized cylinder possible and the cylinder should be returnable to the gas vendor.
2. Diborane cylinder must only be kept on site for 3 months (pure diborane) or 6 months (diborane mixtures).
3. Pure diborane at ambient temperatures will undergo 10 to 20% decomposition per month.[1]
4. Piping and appurtenances for undiluted diborane must be designed by experienced engineers in conjunction with safety and fire safety professionals.[1]
5. All diborane system lines must be constructed of stainless steel, maintained with the shortest possible run distances, should not be branched, should not have any 'dead ends', and should have welded fittings.
6. For systems downstream of the cylinder valve, only welded and VCR-type fittings should be used in order to prevent leakage both in and out, under vacuum and pressure.[1]
7. Remote manual shutdown devices for diborane gas flow must be provided outside each gas cabinet or near each gas panel. Interlocks tied into the fire protection system should activate an automatic shutdown devices for the pyrophoric gas flow upon gas leak detection.
8. Diborane gas flow, purge, and exhaust systems must have redundant controls that prevent diborane gas from igniting or exploding. These controls include excess flow valves, flow orifices, mass flow controller sizing, process bypass line elimination or control, vacuum-pump inert-gas purging, dilution of process effluent with inert gas and ventilation, controlled combustion of process effluent, ventilation monitoring, and automatic gas shutdown.
9. Emergency back-up power must be provided for all electrical controls, alarms and safeguards associated with the storage and process system.
10. All diborane process lines and equipment must be adequately purged using a dedicated inert gas cylinder.

Germane (GeH_4)

- Pyrophoric, ignites spontaneously in air
- Poison and flammable gas
- Listed as a Department of Homeland Security Chemical of Interest (DHS COI). EH&S must be contacted prior to ordering to determine permissible quantity and concentration of gas.
- University Guideline (EH&S #02-004) "Flammable and Pyrophoric Gas" (Section 8) provides guidance for work with pyrophoric material.

Additional Requirements/Considerations for Germane Use:

1. Germane must be obtained in the smallest sized cylinder possible and should be returnable to the gas vendor.

2. All germane system lines must be constructed of stainless steel, maintained with the shortest possible run distances, should not be branched, should not have any 'dead ends', and should have welded fittings.
3. Remote manual shutdown devices for germane gas flow must be provided outside each gas cabinet or near each gas panel. Interlocks tied into fire protection should activate automatic shutdown devices for pyrophoric gas flow and/or detection must be provided.
4. Germane gas flow, purge, and exhaust systems must have redundant controls that prevent silane gas from igniting or exploding. These controls include excess flow valves, flow orifices, mass flow controller sizing, process bypass line elimination or control, vacuum-pump inert-gas purging, dilution of process effluent with inert gas and ventilation, controlled combustion of process effluent, ventilation monitoring, and automatic gas shutdown.
5. Emergency back-up power must be provided for all electrical controls, alarms and safeguards associated with the storage and process system.
6. All germane process lines and equipment must be adequately purged using a dedicated inert gas cylinder

Hydrogen (H_2)

- Flammable gas
- Forms explosive mixtures with air within a wide range, 4-74% by volume in air[2]
- University Guideline (EH&S #02-004) "Flammable and Pyrophoric Gas" (Section 4) provides specific guidance for work with hydrogen.

Additional Requirements/Considerations for Hydrogen Use:

1. Limit the number of hydrogen cylinders to approximately 400 ft^3 or two full size cylinders in a laboratory or single fire area (an area of a building separated from the remainder of the building by construction having a fire resistance of at least 1 hour).[4]
2. Piping, tubing, fittings, gaskets and thread sealants should be suitable for hydrogen service at the pressures and temperatures involved. Refer to American Society of Mechanical Engineers Code for Process Piping, ASME B31.3.[4]
3. For gaseous hydrogen service, joints in piping and tubing should be made by welding or brazing or by use of flanged, threaded, socket, slip or compression fittings. Brazing materials should have a melting point above 1000ºF (538ºC).[4]
4. Provide 20 feet of separation from Class I, II and IIIA flammable liquids, oxidizing gases and readily combustible materials.

Hydrogen Sulfide (H_2S)

- Poison and flammable gas
- Chemical asphyxiant
- Forms explosive mixtures with air within a wide range of 4.3-45% by volume in air[2]
- Listed as a Department of Homeland Security Chemicals of Interest (DHS COI). EH&S must be contacted prior to ordering to determine permissible quantity and concentration of gas.

Additional Requirements/Considerations for Hydrogen Sulfide Use:

1. Do not store hydrogen sulfide near oxidizing materials, acids or other corrosive materials.[1]
2. Use isolated storage areas clear of large accumulations of flammable materials.[1]

Phosgene (CCl_2O)

- Poison gas
- Phosgene exposure can be treacherously dangerous, due to the fact that there may not be any immediate irritation even at lethal concentrations. The initial symptoms are mild. However, severe congestion of lungs or pneumonia occurs 6-24 hours after exposure.[2]
- Listed as a Department of Homeland Security Chemicals of Interest (DHS COI). EH&S must be contacted prior to ordering to determine permissible quantity and concentration of gas.

Additional Requirements/Considerations for Phosgene Use:

1. Gas systems must be constructed of aluminum, copper, pure iron or cast iron, or steel.
2. Pressure relief devices are prohibited for use on phosgene cylinders.[1]
3. Valves must be either a nonperforated diaphragm type (with outlets sealed with a solid metal cap or plug) or packed type provided the assembly is made gas-tight by means of a seal cap to the valve body or to the cylinder.[1]

Propane (C_3H_8)

- Flammable gas
- University Guideline (EH&S #02-004) "Flammable and Pyrophoric Gas" (Section 6) provides specific guidance for work with propane.

Additional Requirements/Considerations for Propane Use:

- Propane (Liquefied Petroleum Gas, LPG) is restricted to a cylinder with a maximum water capacity of 2.5 pounds (1 pound of LPG) to be used within a research laboratory.

Silane (SiH_4)

- Pyrophoric, ignites spontaneously in air
- Flammable gas
- Listed as a Department of Homeland Security Chemical of Interest (DHS COI). EH&S must be contacted prior to ordering to determine permissible quantity and concentration of gas.
- University Guideline (EH&S #02-004) "Flammable and Pyrophoric Gas" (Section 8) provides guidance for work with pyrophoric material.

Additional Requirements/Considerations for Silane Use:

1. Silane must be obtained in the smallest sized cylinder needed to complete the research.
2. Per the International Fire Codes, Chapter 41, Pyrophoric Materials, Section 4104.2, any sized cylinder of silane with a concentration of 1.37% or higher must be stored within an exhausted gas cabinet.[3]
3. Storage of silane gas, and gas mixtures with a silane concentration of 1.37% or higher by volume, must be in accordance with the Compressed Gas Association (CGA) G-13 guidance.[3]
4. Storage of silane gas and gas mixtures with a silane concentration of 1.36% or lower outside of an exhausted gas cabinet must be stored in quantities that do not exceed those allowed by the International Fire Codes, Chapter 41, Pyrophoric Materials.[3]
5. All silane system lines must be constructed of stainless steel, maintained with the shortest possible run distances, should not be branched, should not have any 'dead ends', and should have welded fittings.
6. Remote manual shutdown devices for silane gas flow must be provided outside each gas cabinet or near each gas panel. Interlocks tied into fire protection should activate automatic shutdown devices for pyrophoric gas flow and/or detection must be provided.
7. Silane gas flow, purge, and exhaust systems must have redundant controls that prevent silane gas from igniting or exploding. These controls include excess flow valves, flow orifices, mass flow controller sizing, process bypass line elimination or control, vacuum-pump inert-gas purging, dilution of process effluent with inert gas and ventilation, controlled combustion of process effluent, ventilation monitoring, and automatic gas shutdown.
8. Emergency back-up power must be provided for all electrical controls, alarms and safeguards associated with the storage and process system.
9. All silane process lines and equipment must be adequately purged using a dedicated inert gas cylinder.

APPENDIX C – REFERENCES

[1] - *Handbook of Compressed Gases*, 3rd Edition, Compressed Gas Association, Inc., 1990.

[2] - *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 3rd Edition, Pradyot Patnaik, 2007.

[3] – *International Fire Code (IFC)*, International Code Council, 2009.

[4] – University of Pittsburgh Guideline for Storage and Handling of Flammable and Pyrophoric Gas (EH&S #02-004), http://www.ehs.pitt.edu/assets/docs/flam-gas.pdf.

[5] – University of Pittsburgh Guideline for Carbon Monoxide Gas Usage in Laboratories (EH&S #04-014), http://www.ehs.pitt.edu/assets/docs/CO-usage.pdf.