STORAGE AND HANDLING OF FLAMMABLE AND PYROPHORIC GAS

These guidelines provide requirements for all University faculty, staff, and students using, handling, or storing flammable and pyrophoric gas. These requirements are established to ensure faculty, staff and students know the physical characteristics of the material used and the protective measures necessary to prevent fire, explosion, or violent reaction.

1. Definitions

1.1. Compressed Gas: Any material or mixture having, when in its container, an absolute pressure exceeding 40 psi (an absolute pressure of 276 kPa) at 70°F (21.1°C) or, regardless of the pressure at 70°F (21.1°C), having an absolute pressure exceeding 104 psi (an absolute pressure of 717 kPa) at 130°F (54.4°C).

1.2. Flammable Gas: A material that is a gas at 68°F (20°C) or less at an absolute pressure of 14.7 psi (101.325 kPa), that is ignitable at an absolute pressure of 14.7 psi (101.325 kPa) when in a mixture of 13 percent 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 percent, regardless of the lower limit.

1.3. Liquefied Petroleum Gas (LP-Gas): Any material having a vapor pressure not exceeding that allowed for commercial propane that is composed predominantly of the following hydrocarbons, either by themselves or as mixtures: propane, propylene, butane (normal butane or isobutane), and butylenes.

1.4. Pyrophoric Gas: A gas with an autoignition temperature in air at or below 130°F (54.4°C).

1.5. Fire Area: An area of a building separated from the remainder of the building by construction having a fire resistance at least 1 hour.

1.6. Gas Cabinet: A fully enclosed, noncombustible enclosure used to provide an isolated environment for compressed gas cylinders in storage and use arranged as follows:

1.6.1. Constructed of not less than 12-gauge (2.5 mm or 0.097 in.) steel, coated to prevent corrosion and provided with a self-closing and self-latching cylinder access door.

1.6.2. Provided with a noncombustible safety window (6.4 mm or 0.25 in. wire-reinforced safety glass or equal) that allows viewing of equipment controls and provided with self-closing access port(s) or windows of sufficient size that allow hand access to equipment controls.

1.6.3. Provided with an approved automatic sprinkler.

1.6.4. Provided with makeup air inlets that allow air circulation throughout the cabinet when the access port(s) or windows are closed.

1.6.5. Provided with exhaust ventilation that ensures the cabinet is at negative pressure in relation to the surrounding area and an average velocity of air flow at the face of open access ports or windows of 200 fpm (1.02 m/s) with a minimum of 150 fpm (0.75 m/s) at any measurement point.

1.6.6. Provided with gas detection and/or ventilation monitoring to signal both an audible and visual alarm in the event of gas leakage and/or a drop-in velocity below the limits outlined above.

1.6.7. Gas cabinets shall NOT contain more than three containers, cylinders, or tanks.

1.6.8. Incompatible gases must be stored or used in separate gas cabinets.

1.7. <u>Gas Room:</u> A separately ventilated, fully enclosed room in which only compressed gases, associated equipment and supplies are stored or used which meets the construction, arrangement and protection requirements of the City of Pittsburgh, NFPA and International Building and Fire Code standards as follows:

1.7.1. Walls, floors and ceilings must be constructed of non-combustible materials and have a fire-resistive rating of not less than one hour. In some cases, a 2-hour rating may be necessary and/or explosion venting may be required.

1.7.2. Approved fire doors must be provided and kept closed and latched at all times (or arranged to close automatically in case of fire).

1.7.3. The entrance to the room should be labeled in accordance with NFPA 704 – Identification of the Hazards of Materials for Emergency Response.

1.7.4. Proper ventilation must be provided. Storage and other materials should not obstruct the exhaust ventilation.

1.7.5. Lighting, heating and electrical service must be properly rated for the gases being stored.

1.7.6. The room should be kept free of all combustible materials such as empty boxes, trash containers and other miscellaneous items.

1.7.7. As applicable, automatic detection and/or suppression systems are required in new or renovated rooms.

1.8. <u>Closed System:</u> The use of a hazardous material (flammable/combustible liquid, gas, solid) involving a closed vessel or system that remains closed during normal operations where vapors or gas are not liberated outside of the vessel or system and the product is not exposed to the atmosphere during normal operations. An example of a closed system is product conveyed through a piping system into a closed vessel or piece of equipment.

1.9. Open System: The use of a hazardous material (flammable/combustible liquid or solid) involving a vessel or system that is continuously open to the atmosphere during normal operations and where vapors are liberated, or the product is exposed to the atmosphere during normal operations. An example of an open system is dispensing to or from an open beaker, container or dip tank. **Use of an open system does not apply to any gas use covered in this section.**

2. General Hazards Description

A great variety of compressed gases in cylinders are stored and handled in University laboratories and in other University operations such as cutting, welding, and outdoor cooking. The use of compressed gas has the potential to introduce hazards of fire and explosion, increased rates of combustion, exothermic reactions, or serious interference with manual firefighting efforts depending on the characteristics and properties of the specific gases.

Escape of flammable compressed gases due to failure of equipment, human failure, premature operation of safety relief devices, or rupture of cylinders exposed to fires in other materials has caused severe fires and explosions. Since the gases are contained in heavy, highly pressurized metal containers, the large amount of potential energy resulting from compression of the gas makes the cylinder a potential rocket or has the potential to violently rupture the cylinder into fragments.

Automatic sprinklers provide effective control of fires involving flammable-gas cylinders by cooling and preventing gas discharge caused by melting of fusible plugs or released by relief valves of exposed cylinders. Provision of gas cabinets, shutdown of gas flow, leak detection and alarms may be required for certain gasses or to allow additional storage amounts without the need for a gas room.

3. General Guidelines for Flammable Gases

3.1. The volume of flammable gas in a lab, room or location is restricted by University guidelines and International Fire Codes. EH&S should be contacted regarding any questions or for additional guidance.

3.2. The volume of flammable gas shall be kept to the minimum necessary for the work being done. Just in time delivery should be used where possible.

3.3. The maximum internal volume (water volume) of all cylinders in each of the listed classifications, in use in the laboratory work area or single fire area, shall comply with the following based on internal cylinder volume at 70°F (21°C).

3.3.1. For a laboratory work area of 500 ft^2 or less, the internal cylinder volume equals 6.0 ft^3 or approximately three (3) “K” (9.25-inch diameter, 60-inch height) sized cylinders.

3.3.2. For a laboratory work area greater than 500 ft^2, the internal cylinder volume is 0.012 ft^3 per ft^2 lab work area, but not to exceed the maximum cubic feet of gas from the chart below (approximately five (5) "K" sized cylinders for flammable gas except hydrogen – see Section 4).

Material	Storage	Use-Closed System	Use-Open System
	Cubic Feet	Cubic Feet	Cubic Feet
Oxidizing Gas	1,500	1,500	NA
Flammable Gas	1,000	1,000	NA
Pyrophoric Gas	50	10	NA

3.3.3. The maximum quantity of lecture bottles in a single fire area should not exceed 20. The University strongly discourages the use of any non-returnable, non-refillable compressed gas cylinders (lecture bottles).

3.4. Flammable gasses should be separated by 20 ft. (6.1 m) from all pyrophoric, oxidizing and corrosive gasses except as follows:

3.4.1. The 20 ft distance shall be reduced without limit when separated by a barrier of noncombustible materials at least 5 ft (1.5 m) high that has a fire resistance rating of at least 30 minutes.

3.4.2. The 20 ft distance shall be reduced to 5 ft where one of the gases is enclosed in a gas cabinet or without limit where both gases are enclosed in gas cabinets.

3.4.3. Cylinders without pressure-relief devices shall be stored separately from flammable and pyrophoric gases with pressure-relief devices.

3.5. The following are requirements for outdoor storage of flammable gas:

3.5.1. The cylinders should not be stored within 10 ft of windows, doors, or other openings nor shall they be stored within 50 ft of ventilation intakes.

3.5.2. Storage areas shall be kept clear of dry vegetation and combustible materials for a minimum distance of 15 ft.

3.5.3. Cylinders stored outside shall not be placed on the ground (earth) or on surfaces where water can accumulate.

3.5.4. Storage areas shall be provided with physical protection from vehicle damage.

3.5.5. Storage areas shall be permitted to be covered with canopies of noncombustible construction.

3.6. All compressed gas cylinders shall be stored in an upright position.

3.7. All flammable gas cylinders, full or empty, shall be handled in the same manner. Store empty cylinders separately from full cylinders.

3.8. Compressed flammable gas cylinders, whether full or partially full, shall not be exposed to or heated by devices that could raise the temperatures above 125°F (52°C).

3.9. Always use non-sparking tools on compressed gas cylinders.

3.10. Static-producing equipment located in flammable gas areas shall be grounded.

3.11. Signs should be posted in areas containing flammable gases communicating that smoking or the use of open flame, or both, is prohibited within 25 ft of the storage or use area perimeter.

3.12. Compressed flammable gas cylinders should not be placed where they could become a part of an electrical circuit.

3.13. Compressed flammable gas cylinders shall not be exposed to dampness, salt, corrosive chemicals or fumes that could damage the cylinders or valve-protective caps.

3.14. Leaking, damaged, or corroded compressed flammable gas cylinders should be removed from service.

3.15. **EXCESS FLOW VALVE.** A valve inserted into a compressed gas cylinder, portable tank or stationary tank that is designed to positively shut off the flow of gas in the event that its predetermined flow is exceeded. Excess flow valves are intended to automatically shut off the flow due to releases caused by line breakage or other upset conditions. The valve is closed by the differential pressure produced by a larger than normal flow rate through the valve. Excess flow valves are tested and rated to close when flow exceeds a predetermined rate for a given mounting position (vertically upward, horizontal, etc.). They must be installed in the correct direction. Excess flow valves are recommended because they can be effective in achieving prompt shutdown of flow following a large break and sudden release and they are considered a complementary safeguard to manual and automatic isolation.

3.16. **RESTRICTED ORIFICE REDUCED FLOW VALVE.** A valve equipped with a restricted flow orifice (RFO) and inserted into a compressed gas cylinder, portable tank or stationary tank that is designed to reduce the maximum flow from the valve under full-flow conditions. The maximum flow rate from the valve is determined with the valve allowed to flow to atmosphere with no other piping or fittings attached. In laboratory applications where very low flow rates will be needed, use of an RFO may be feasible. A cylinder fitted with an RFO might take several hours to empty, compared with just a few minutes if the cylinder valve is open all the way with unrestricted flow. To be considered reliable, the RFO must be installed in the cylinder valve outlet by the gas supplier. Gas suppliers will usually provide gas cylinders fitted with restrictive flow orifices upon request by the customer.

4. Hydrogen

Hydrogen gas has several unique properties that make it potentially dangerous. It has an extremely wide flammability range (LEL 4%, UEL 74.5%) that makes it easier to ignite than most flammable gases. Unlike most other gases, hydrogen's temperature increases during expansion. Many hydrogen fires result from the self-ignition of sudden hydrogen release through rupture disks and pressure relief valves.

Observe the following guidelines for hydrogen use and storage:

4.1. Limit the number of hydrogen cylinders to approximately 400 ft^3 or two (2) “K” type cylinders in a laboratory or single fire area.

4.2. Adequate ventilation should be provided and maintained throughout the area where hydrogen cylinders are in use.

4.3. Open the cylinder valve slowly. If a cylinder valve is opened too quickly, the static charge generated by the escaping gas may cause it to ignite.

4.4. Hydrogen embrittlement can weaken carbon steel, therefore cast-iron pipes and fittings should not be used.

4.5. 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.

4.6. 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 1000°F (538°C).

4.7. Provide 20 ft of separation from Class I, II and IIIA flammable liquids, oxidizing gases and readily combustible materials.

4.8. Locate the cylinders 25 ft from open flames and other sources of ignition.

4.9. Hydrogen burns with an invisible flame. Caution should therefore be exercised when approaching a suspected hydrogen flame.

4.10. Provide 50 ft of separation from other flammable gas storage.

5. **Acetylene**

Acetylene is flammable gas with a normal explosive range with air of 2.3 to 80% acetylene. Special cylinders used for acetylene contain a porous material and acetone, in which the gas dissolves and becomes practically stable. The porous filler absorbs the acetone and eliminates large voids in which decomposition might occur. Because of its tendency to break down and release energy, acetylene is highly reactive and is widely used in chemical processes. The temperature of the oxyacetylene flame, 5400 to 6300°F (3000 to 3500°C), is the highest for any commercially practical mixture of gases.

The minimum autoignition temperature for acetylene-air mixtures is about 571°F (300°C). The presence of catalytic impurities such as rusts, scale, silica gel, charcoal, or potassium hydroxide can lower the ignition temperature substantially. The presence of copper, silver, or mercury acetylides combined with light shock can result in ignition or decomposition of acetylene at room temperatures.

Observe the following guidelines for acetylene use and storage:

5.1. Do not handle cylinders roughly, subject cylinders to hydrostatic test, or take any other action that can create large voids in the mineral filler.

5.2. Provide separate storage locations for acetylene and oxygen or chlorine cylinders. A gas-tight non-combustible partition will serve to separate a storage area for this purpose.

5.3. Store and use cylinders in an upright position to prevent loss of acetone.

5.4. Do not withdraw acetylene from a cylinder or manifold at a rate in excess of one-seventh of the total cylinder capacity per hour. Provide additional cylinders if needed to supply higher demand without exceeding this rate.

5.5. Use a pressure regulator at the discharge of an individual cylinder or manifold to reduce the gas pressure to 15 psi (105 kPa) or less.

5.6. Keep acetylene cylinder valves closed when gas is not being used and open the valves only 1-1⁄2 turns when in use.

5.7. Use wrought-iron or steel pipe and steel or malleable-iron fittings. Welded joints are preferable because of the reduced probability of leakage. Alloys containing more than 67% copper should not be used for piping, valves, or fittings (with the exception of a torch tip, which is pure copper).

6. Liquefied Petroleum Gas (LPG)

Although Liquefied Petroleum Gases (LPG) are transported and stored as liquids, they are gases at atmospheric pressures and normal temperatures. They are as hazardous as other combustible gases, with the added danger that they are heavier than air, tend to remain in low places for a somewhat longer period, and have little or no natural odor.

The discharge from tank relief valves, if ignited, can create a large torch fire. The intense, radiated heat may seriously expose buildings and contents. If ignition is delayed, the discharge from tank relief valves may travel hundreds of feet and settle in low-lying areas or enter below grade building openings. If the gas enters a building, ignition may result in an explosion. Once ignited, the resulting flashback to the tank may involve other structures and contents.

Observe the following guidelines for LPG use and storage:

6.1. Containers of LPG should be stored outside of buildings at least 10 ft. from any doorway or other opening with the following exceptions:

6.1.1. For temporary demonstration purposes, a container with a maximum water capacity of 12 pounds (5 pounds of LPG) may be used.

6.1.2. For hand torches or similar appliances, a container with a maximum water capacity of 2.5 pounds (1 pound of LPG) may be used.

6.2. Cylinders should not be filled past their rated capacity. The weight limit is usually specified on the cylinder. If it has been overfilled, the pressure relief valve may release propane as the cylinder warms. Overfilling can lead to flash fires and explosions.

6.3. All cylinders having a propane capacity of 4 pounds through 40 pounds fabricated after 1998 must be equipped with an overfill prevention device (OPD) as a secondary means of protecting against overfilling (the primary means is to determine the fill limit by weight). Cylinders equipped with OPD's will have a triple-notched valve handwheel with the letters "OPD."

6.4. Used cylinders must be retrofitted with UL listed OPD's when being requalified under DOT regulations. Affected cylinders cannot be filled unless they are equipped with UL listed OPD's.

6.5. Cylinders should be kept away from heat sources, as the heat can build up pressure inside the cylinder and may cause the pressure relief valve to release propane.

6.6. The cylinders should be kept in a secure upright position with the valves closed and the thread caps secured when they are transported, stored, or used.

6.7. When disconnecting cylinders, whether full or empty, first close the shut-off valve, then disconnect the cylinder and snugly seal the valve with a plug, cap, or approved quick-closing coupling.

6.8. Never use propane from a cylinder without a regulator (except for forklift cylinders). Protect the regulator connector from scratches and dents. Ensure the regulator vent is clean and pointed downward, and the regulator is protected.

6.9. Cylinders that are visibly rusted or damaged shall not be refilled.

7. **Oxygen**

Oxygen is neither combustible nor explosive. However, the intensity of any ordinary fire or explosion increases as the amount of oxygen in the surrounding air increases. Materials, such as grease or oils that produce intense fires with air, burn in an atmosphere of enriched oxygen with explosive violence. Explosions have occurred in oxygen pressure gauges after being tested on common oil-filled gauge testers. Oxygen at atmospheric pressure in a closed system can combine explosively with lubricating oil at temperatures above 340°F (170°C).

Observe the following guidelines for oxygen use and storage:

7.1. Separate oxygen cylinders from cylinders or manifolds containing flammable gases and other combustible or easily ignited materials such as wood, paper, oil, and grease. Gas-tight fire partitions having at least ½ hour fire resistance rating are suitable as cutoffs. **Note:** This does not apply to properly arranged and safeguarded oxygen and acetylene tanks used for cutting and welding torches.

7.2. Do not use oil or grease for lubricating valves, gauge connections, or other parts of the oxygen system.

7.3. Use extra-heavy steel or nonferrous pipe and fittings if the oxygen pressure is over 150 psi (1 MPa). For lower pressures, standard-weight pipe and fittings are satisfactory. Cast-iron fittings should not be used.

In medical oxygen gas systems, Type K or L (ASTM B-88) copper tubing may be used. Brazed fittings should be used for 3⁄4-inch (19-mm) and larger tubing. Flared-type tubing fittings may be used in smaller sizes where the fitting is visible in the room.

7.4. Use welded joints whenever possible. If threaded joints are necessary, they should be carefully made using litharge and glycerin or proprietary materials compounded for oxygen service. Compounds containing oils should not be used. Gaskets should be entirely of noncombustible materials.

8. Pyrophoric Gas

Pyrophoric chemicals are those substances that react so rapidly with air and its moisture that the ensuing oxidation and/or hydrolysis lead to ignition. Ignition may be instantaneous or delayed. Spontaneous (instantaneous) ignition or combustion occurs when a substance reaches its ignition temperature without the application of external heat.

An example of a pyrophoric gas is silane. Silane has caused major losses due to fires in ducts, gas cabinets and supply systems; and explosions in ducts, vacuum pumps and cross-contaminated cylinders. These incidents have occurred in research facilities. The hazards are pyrophoric fires, explosions and/or deflagrations, and autoignition of a vapor cloud. All of these conditions can occur depending on leak location, excess flow control and shutdown of the silane gas. Pyrophoric fires are difficult to extinguish. When pyrophoric fires are extinguished, the gas supply must be shut down promptly by interlocks tied into fire protection and/or detection, because resulting pyrophoric gas build up has the potential to create vapor cloud detonation.

Observe the following guidelines when storing or using pyrophoric gas:

8.1. Minimally sized cylinders of pyrophoric gases shall be limited per the above table and kept in approved gas cabinets.

8.2. Remote manual shutdown devices for pyrophoric gas flow should be provided outside each gas cabinet or near each gas panel. Automatic shutdown devices for pyrophoric gas flow activated by interlocks tied into fire protection and/or detection should be provided.

8.3. Pyrophoric gas flow, purge, and exhaust systems should have redundant controls that prevent pyrophoric 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.

8.4. Order cylinders with the smallest orifice as practicable (0.006 inch and not to exceed 0.010 inch).

8.5. Emergency back-up power should be provided for all electrical controls, alarms and safeguards associated with the storage and process systems.

8.6. All process systems components and equipment should be adequately purged using a dedicated inert gas cylinder.