SAFE HANDLING OF ELECTRONIC SPECIALTY GASES

Doc 199/15

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As part of a programme of harmonization of industry standards, the European Industrial Gases Association (EIGA) has issued Doc 199 *Safe Handling of Electronic Speciality Gases*, jointly produced by members of the International Harmonization Council and originally published by the Asia Industrial Gases Association (AIGA) as AIGA 018, *Safe Handling of Electronic Specialty Gases*.

This publication is intended as an international harmonized publication for the worldwide use and application by all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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1 Introduction

With the worldwide proliferation of electronic gases and recognizing that these gases present certain inherent dangers and risks with their use, this safety publication has been written to assist both the packager and user of these gases.

This publication is intended to recommend best practices, which will enhance safety in the workplace where these gases and mixtures are prepared and during transport from the production site to the ultimate user, where they are stored and used. Since these gases are usually packaged at high pressure and can be reactive, flammable, toxic, or corrosive, great care should be exercised in their use even if mixtures containing these gases are classified as inert.

While the information contained in this publication is applicable, in principle, to all compressed gas packages, this publication is primarily focused on electronic specialty gases.

Electronic specialty gases encompass gases and mixtures that are primarily used in the semiconductor and photovoltaic industry (hereafter called the electronics industry). Because of the inherent need for very high purity, extraordinary precautions are taken in this publication to ensure that the gases are packaged in cylinders with valves that have extremely low leak rates, and that the stability of the contained gas or mixture is maintained for the entire specified shelf life of the package.

In addition, some electronic specialty gases can also be considered as potential chemical weapons. The guidelines in this publication will assist in raising the level of safety and security on sites that process and handle these materials.

2 Scope and purpose

These recommendations form the basis for the safe storage, handling, and use of electronic specialty gases that are packaged in containers. Information on potential hazards of these gases, containers, and gas supply systems also includes direction for handling problem containers.

The information contained in this publication is designed to provide awareness and guidance for personnel working in facilities that package, distribute and use gases primarily in the electronic industry, such as the manufacture of semiconductors, thin film transistor-liquid crystal display (TFT-LCD), fibre optics, opto-electronic devices, and solar cells. It is not meant to take the place of work instructions or standard operating procedures (SOPs), but rather to assist personnel to identify generic steps that need to be taken in their routine operations as well as to recognize issues that could result in injury to personnel or damage to equipment.

Where practical, the theory pertaining to these principles being discussed is presented. However, this coverage is meant to provide a very minimal overview of pertinent technical facts that would explain the reasons for taking or avoiding certain practices.

Each section will provide guidance and direction as to where additional information can be found in the literature of Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), Japan Industrial and Medical Gases Association (JIMGA), International Organization for Standardization (ISO), European Agreements Concerning the International Carriage of Dangerous Goods by Road (ADR) and by Rail (RID) as well as the Model Regulations promulgated by the United Nations (UN), *Recommendations on the Transport of Dangerous Goods*, *Model Regulations* also known as the "Orange Book" [1, 2, 3][1].

The term "gas", when used in this publication, can encompass both a pure material and a mixture of several individual pure gases. If there is a specific distinction between a compressed gas, a liquefied gas, or non-liquefied gas this will be highlighted. The information contained in this publication was collected

[1] References are shown by bracketed numbers and are listed in order of appearance in the reference section.

from sources that are believed to be accurate. However, it should be understood that every potential aspect of the safe handling of electronic gases has not been considered and the reader is encouraged to take steps to ensure that such a comprehensive review is undertaken.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. Shall is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 ADR/RID

European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) and Rail (RID) [1, 2].

3.2.2 Bar

Standard unit of pressure, equal to 100 kPa. The term bar and kPa will be used as a standard reference for pressure.

3.2.3 Gas

Substance that at 50 °C (122 °F) has a vapour pressure greater than 300 kPa (43.5 psi) or is completely gaseous at 20 °C (68 °F) at a standard pressure of 101.3 kPa (14.7 psia).

3.2.4 Gases under pressure

Gases that are contained in a receptacle at a pressure not less than 200 kPa (29.0 psi) at 20 °C (68 °F) or as a refrigerated liquid. They comprise compressed gases, liquefied gases, dissolved gases, and refrigerated liquefied gases.

See Appendix A for more information.

3.2.5 Containers

Vessels of various shapes, sizes, and materials of constructions such as cylinders, portable tanks, or stationary tanks that meet the specifications of either American Society of Mechanical Engineers (ASME), Transport Canada (TC), U.S. Department of Transportation (DOT), ADR, Japanese Industrial Standards (JIS), or national authorities, and are filled with gases under pressure.

3.2.6 Corrosive gas

Gas that in contact with materials or living tissue can cause damage or destruction by chemical action.

3.2.7 Critical temperature

Temperature above which the gas cannot exist in the liquid state.

3.2.8 Cryogenic liquid

Refrigerated liquefied gas having a boiling point lower than –90 °C (–130 °F) at 101.325 kPa, abs (14.7 psia).

3.2.9 Cylinder

Pressure receptacle having a water capacity that does not exceed 150 L.

See Appendix A for more information.

3.2.10 Dewar

Open-mouthed, non-pressurized portable liquid containers that are vacuum-jacketed or insulated vessels designed to hold cryogenic liquids.

3.2.11 Exhausted enclosure

Appliance or piece of equipment that consists of a top, a back and two sides providing a means of local exhaust for capturing gases, fumes, vapours, and mists. Such enclosures include laboratory hoods, exhaust fume hoods and similar appliances, and equipment used to locally retain and exhaust the gases, fumes, vapours, and mists that could be released.

3.2.12 Filling ratio

Ratio of the mass of liquefied gas introduced in a container to the mass of water at 15 °C (59 °F) that would fill the same container fitted ready for use. Also known as fill density, filling factor, maximum fill degree.

Lower filling ratio or fill pressure may be applied to some gases for safety reasons such as auto-decomposition, e.g., nitric oxide and germane.

NOTE The water capacity stamped on the cylinder may apply to the minimum water capacity designed without internal fittings, in which case, the net water capacity shall be determined.

3.2.13 Flammable gas

A gas is considered flammable when either a mixture of 13% or less (by volume) with air is ignitable at 101.325 kPa, abs (14.7 psia) or has a flammable range with air of at least 12% regardless of the lower limit. These limits shall be determined at 101.325 kPa, abs (14.7 psia) pressure and at a temperature of 20 °C (68 °F).

3.2.14 Gas cabinet

Fully enclosed, exhausted, and non-combustible enclosure used to provide an isolated environment for gas cylinders in storage or use. Doors and access ports for exchanging cylinders and accessing pressure-regulating controls are allowed to be included. A gas cabinet operates at negative pressure relative to the surrounding atmosphere.

3.2.15 Gas mixture

Mixture of two or more components, either liquid or gaseous, which has been deliberately filled for use from the cylinder as a blended mixture.

3.2.16 Gas pressure

Force per unit of area exerted by a gas to its surroundings. The term kilopascal (kPa), along with the term “bar” will be the standard term for pressure used in this publication.

3.2.17 Gas supplier

Business that produces, fills, and/or distributes gases and gas containers.

3.2.18 Handling

Moving, connecting, or disconnecting a gas container under normal conditions.

3.2.19 Hazard

Any condition that could potentially cause injury to personnel or property.

3.2.20 Highly toxic

Gases that have an LC_{50} in air less than or equal to 200 ppm for a one-hour exposure.

3.2.21 Inert gas

Gas that is not toxic, which does not support human breathing and which reacts scarcely or not at all with other substances.

3.2.22 $LC_{50/rat.1H}$

Median lethal concentration of gas that, when administered by continuous inhalation for an hour to 10 albino rats weighing between 200 g and 300 g each, causes death to 50% of the population within 14 days.

3.2.23 Lower flammability limit (LFL)

Minimum concentration in air of a gas that would burn when ignited. Also known as the lower explosive limit (LEL).

3.2.24 Mass weight

The weight of the empty cylinder including all permanent attachments (collar, neckring, or footring) but not including: the cylinder cap; the valve; the valve outlet cap/plug; or an eductor tube.

3.2.25 National standards, guidelines, regulations

Technical standards set by regulatory authorities of the country in which the equipment/facility is used, with respect to their design, construction testing, and use. Where available and applicable, these standards should be followed.

3.2.26 Nesting

Method of securing flat bottomed cylinders upright in a tight mass using a contiguous three-point contact system whereby all cylinders within a group have a minimum of three points of contact with other cylinders, walls, or bracing.

See Appendix B for more information.

3.2.27 Oxidising gas

Gas that can cause or contribute to the combustion of other material more than air does. Oxidising ability is determined either by tests or by calculation methods adopted by ISO (see ISO 10156: *Gases and gas mixtures—Determination of fire potential and oxidising ability for the selection of cylinder valve outlets*) [4].

3.2.28 Passivation

Procedure that is applied when there is a possibility of a reaction between a reactive gas and the container or system into which it is going to be introduced. Passivation ensures that any reaction takes place under controlled conditions. Passivation may also be used to ensure the stability of a gas mixture. Passivation is usually carried out using a mixture containing a reactive gas diluted in an inert gas, sometimes followed by the pure reactive gas.

3.2.29 Pressure relief device (PRD)

Pressure and/or temperature activated device used to prevent the pressure from rising above a predetermined maximum and thereby prevents rupture of a normally charged container when subject to a standard fire test, see CGA C-14, *Procedures for Fire Testing of DOT Cylinder Pressure Relief Device Systems* [5].

3.2.30 Safety data sheet (SDS)

Written or printed information concerning a hazardous material (properties, precautions, etc.) following national regulations. Previously known as material safety data sheet (MSDS).

3.2.31 Test pressure

Pressure at which a container is hydraulically or pneumatically tested and is the pressure that shall not be exceeded under any foreseeable normal operating conditions (e.g., during filling).

3.2.32 Threshold Limit Value—Time Weighted Average (TLV®—TWA)

The concentration to which a person may be exposed, 8 hours a day, 40 hours a week, without harm [6].

3.2.33 Toxic gas

A gas that has a LC_{50} in air of less than or equal to 5000 ppm for a one-hour exposure. National regulations may have additional classifications.

3.2.34 Upper flammability limit (UFL)

Maximum concentration in air of a gas that would burn when ignited. Also known as upper explosive limit (UEL).

3.2.35 Valve outlet caps and plugs

Removable attachments that usually form a gastight seal on valve outlets provided by the gas supplier with certain gases

NOTE Some caps are designed only for valve thread protection and are not gastight.

3.2.36 Valve protection cap

Rigid removable cover provided for container valve protection during handling, transportation, and storage.

3.2.37 Valve protection device

Device attached to the neck ring or body of the cylinder for the purpose of protecting the cylinder valve from being struck or damaged by impact resulting from a fall or an object striking the cylinder.

4 Hazards of electronic specialty gases

Electronic specialty gases used in the manufacture of semi-conductor and electronic components are often hazardous due to their inherent physical properties and chemical and biological reactivity. Thus, there are four categories of hazards of electronic specialty gases, physical, chemical, health, and environmental hazards. Most gases possess more than one hazard.

Safety data sheets provided by gas suppliers for individual gases should be consulted for better understanding of hazards of each product. They provide information and recommendations for the safe handling of electronic specialty gases.

4.1 Physical hazards

There are two primary physical hazards, gas pressure and extreme cold.

4.1.1 Gas pressure

Gases under pressure are at a higher state of energy (pressure) than unconfined gases and this energy gradient can pose a hazard. Uncontrolled releases of gases due to human error or equipment failure can result in severe injury or damage. In unusual circumstances such as a fire, stresses exerted on the container wall can exceed the bursting strength of the container causing it to rupture. Overfilled containers can pose a similar hazard.

4.1.2 Extreme cold

Gases handled in liquid form at very low temperatures, described with the term cryogenic or refrigerated can pose various hazards such as:

- frostbite;

- embrittlement of the material due to low temperature;
- mist formation;
- thermal expansion or contraction; and
- freezing.

4.2 Chemical hazards

There are four primary chemical hazards, flammability, oxidising potential, corrosivity, and reactivity.

4.2.1 Flammability

A flammable gas requires two additional conditions to burn: an ignition source and an oxidizer. The flammable gas will only burn when the mixture with air or oxidizer is within a range of flammable limits, called the lower flammability limit (LFL) and upper flammability limit (UFL). Mixtures outside this range will not generally burn.

Some gases not classified as flammable for transportation purposes can burn under certain ambient conditions, for example, ammonia.

Some gases when released can detonate in the presence of an ignition source. The sudden rise in pressure can cause the surrounding enclosure to rupture.

Some flammable gases which have an auto-ignition temperature of less than 54°C (130 °F) can ignite when released into the atmosphere. These are classified as pyrophoric gases.

Fire will occur when air (oxidizer), fuel, and an ignition source are provided at the same time as shown in Figure 1.

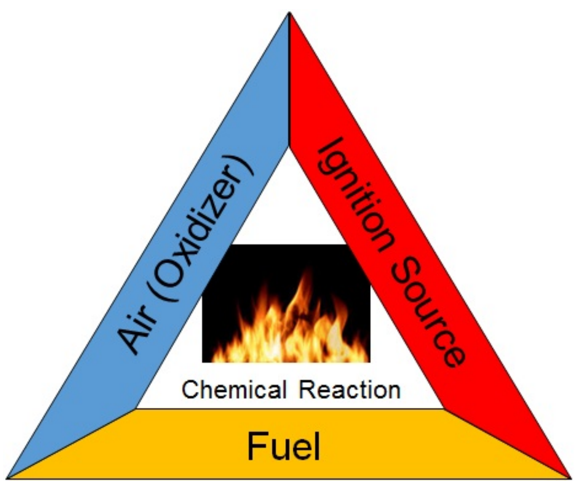


Figure 1 Fire triangle

4.2.2 Oxidising potential

Oxidising gases accelerate combustion but are not flammable by themselves, e.g., oxygen, chlorine, fluorine, and nitrous oxide. The oxidation reaction is dependent on the chemical being oxidized and on the pressure and temperature of reactants. Materials that normally will not burn at room temperature can do so in the presence of strong oxidising gases such as fluorine and chlorine trifluoride.

Substances that are stable in air at ambient temperatures and pressures, e.g., grease and stainless steel, react violently with oxidising gases at elevated temperatures and pressures. It is, therefore, vital that all pipelines and equipment handling oxidising gases be cleaned for oxygen service. Refer to EIGA Doc, *Cleaning of equipment for oxygen service;* for more information [7, 8, 9, 10].

Fluorine is the most reactive oxidising gas. Equipment and pipelines handling fluorine need to be passivated before use.

Certain finely divided metals such as aluminium, carbon steel, or/and stainless steel can also spontaneously combust in the presence of oxidising gases.

4.2.3 Corrosivity

Generally, corrosive gases can cause harm or damage to human tissue or materials when in contact with moisture or mucous membranes of the body (e.g., eyes, mouth, throat, etc.). In dry environments, corrosive gases have negligible effects on metals; however, minute leaks of gases combine with atmospheric moisture to corrode metal containers, valves, and fittings. All efforts shall be made to prevent the contact of corrosive gases with water or moisture of any kind.

There are acidic corrosive gases (e.g., hydrogen chloride) and alkaline corrosive gases (e.g., ammonia) that when combined in an enclosed environment can react violently releasing a large amount of energy.

4.2.4 Reactivity

Self-reactive gases react on their own under certain conditions. Products of the reaction can cause a rise in pressure and temperature of the container sufficient to rupture it. Examples of such reactions are the self-decomposition of nitric oxide, germane, diborane, and the polymerization of ethylene oxide. Many polymerisable gases have inhibitors added.

4.3 Health hazards

There are various categories of health hazards detailed in the *Globally Harmonised System of Classification and Labelling* (GHS), Part 3:

- acute toxicity;
- mutagenicity, carcinogenicity, and reproductive toxicity;
- specific target organ/systemic toxicity; and
- asphyxiation. [11].

Note: Asphyxiation is not considered as a distinct hazard class in the Regulation (EC) 1272/2008 (CLP)

4.3.1 Toxicity

The most common route of toxic gas exposure is inhalation. A less common route is absorption through the skin.

Acute toxicity refers to those adverse effects occurring following oral or dermal administration of a single dose of a substance or multiple doses given within 24 hours, or an inhalation exposure of 4 hours.

Acute toxicity can result in rapid death of an individual, for example, exposure to arsine, carbon monoxide.

Chronic toxicity can result in deterioration of health due to accumulation of toxins (e.g., arsenic trihydride, carbon monoxide), damage to vital tissues for example lungs (e.g., nitrous oxide), or recurrent pain (e.g., hydrogen fluoride).

4.3.2 Mutagenicity, carcinogenicity, and reproductive toxicity

4.3.2.1 Mutagenicity

This hazard is primarily concerned with chemicals that can cause mutations in cells of humans that can be transmitted to the progeny.

4.3.2.2 Carcinogenicity

Carcinogens are chemical substances or mixtures that induce cancer or increase its incidence.

Some gases such as ethylene oxide may also pose a carcinogenic hazard. These gases are believed to cause mutation in the genetic code of human cells that can lead to a malignant carcinogenic condition over a period of time.

4.3.2.3 Reproductive toxicity

Reproductive toxicity includes adverse effects on sexual function and fertility in adult males and females as well as developmental toxicity in the offspring.

4.3.3 Specific target organ/systemic toxicity

Specific target organ/systemic toxicity can occur by any route that is relevant for humans, i.e., principally oral, dermal, or inhalation and can occur after single or repeated exposure.

4.3.4 Asphyxiation

Asphyxiation is a condition caused by deprivation of oxygen.

Any gas or mixture with the exception of oxygen or air released into a confined space can displace oxygen to concentrations below that needed for sustaining life. This is not limited to inert gases such as nitrogen, helium, or argon, but can be any gas, for example, hydrogen. Typically oxygen concentrations that are less than 19.5% are identified as oxygen deficient. Some countries identify lower oxygen concentrations as oxygen deficient, for example, 18% in Japan.

Gases with higher density than air, especially gases below ambient temperatures, can flow to low lying spaces, e.g., basement rooms, sewer manholes, pits, wells, and pump sumps.

Gases with lower density than air, for example, helium and hydrogen, can accumulate in ceiling spaces.

Fatal accidents due to oxygen-deficient atmospheres (asphyxiation) have been caused by:

- entry into confined spaces that had not been sufficiently purged with a breathable atmosphere;
- process lines that had not been adequately isolated;
- leaks from cylinders or hoses;

- spillage from dewars; and
- process vents that had not been routed to a safe area.

4.4 Environmental hazards

With proper control, these gases pose no significant threat to human life and the environment. But when certain gases (e.g., toxic gases) are accidentally released to the environment, they can contaminate land, water, and/or air with potentially disastrous results. Most countries have strict regulations and measures to be taken if a release occurs. Users of these gases should review regulations that apply.

Establishing emergency response programs, obtaining guidance documents from the local government agency to offer direction in following regulations, controlling emissions, and characterizing risks to human health and the environment on the basis of locally measured or predicted exposure scenarios are strongly recommended.

5 Gas packaging

This section covers material of construction, container, valve construction, and filling ratio.

5.1 Material of construction

Selection of metals and non-metals shall take into account the compatibility of the gas and the material used. It is extremely important that all gas equipment be compatible with the gas being passed through it. The use of a device that is not compatible with the gas service can damage the unit and cause a leak that could result in personal injury or property damage. If a material is required to be used in the gas service for the first time and is thought to be compatible it should be tested to confirm suitability prior to use under defined temperature, pressure, and flow conditions.

5.2 Container

5.2.3 Container construction and certification

Materials used in the construction of containers are predominantly carbon steel and aluminium alloy. For low pressures, welded carbon steels are used. At higher pressures, seamless carbon steel and aluminium alloy are used. Sometimes, other materials such as nickel and stainless steel are used depending on purity and compatibility requirements.

Containers shall be certified and tested regularly in compliance with national standards. Container re-test shall meet the requirements of national standards or the container manufacturer’s country laws and regulations, whichever is more stringent. Containers failing to meet these standards shall be removed from service. If they can be repaired to meet the standards, they can be put back to use; otherwise they shall be scrapped.

Use of valves should also comply with national standards.

Figure 2 shows component parts of a gas container.

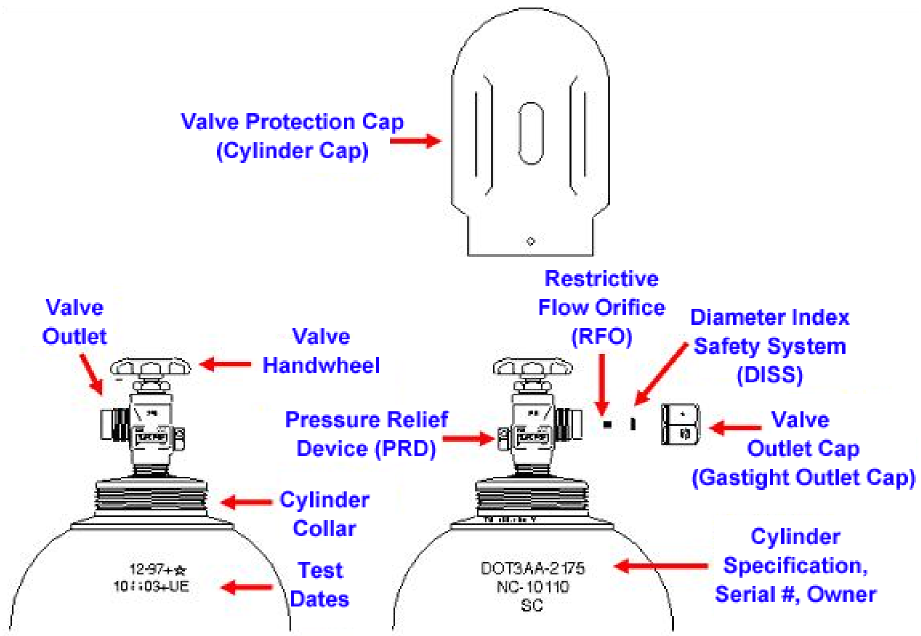


Figure 2 Cylinder components (courtesy of Air Products and Chemicals Inc.)

5.2.2 Container weight

The empty or mass weight of a large compressed gas container can exceed 200 kg, (440 lb). When filled, the total weight of the container with gas can exceed 1000 kg (2200 lb). This can present a significant handling hazard.

5.2.3 Container identification

Each container has its basic information stamped on the body shoulder according to local regulations (for example, the ADR/RID in Europe) [1, 2]. This stamp may include container material specification, first test date, weight, volume, pressure rating, chemical name of the gas, manufacturer, and retest date. This basic information helps to identify the container's physical strength and usability. A container that becomes due for periodic inspection or re-qualification shall not be refilled until the testing is successfully completed.

Users should rely primarily on labels attached by the supplier and cylinder markings to identify gas contents and hazards. The label affixed in accordance with local regulations (such as the classification, labelling, and packaging of substances and mixtures (CLP) regulation in Europe) should include gas name, brief description of properties, generic hazards prevention measures, first aid, and manufacturer information [12]. Labels should be read before use along with the SDS.

Many countries have colour codes for key gases (in Europe, see EN1089-3, *Transportable gas cylinders. Gas cylinder identification (excluding LPG). Colour coding*); however; there is no universally accepted international colour coding system for gases [13].

5.2.4 Container internal surface treatment

Containers used in high purity gas service usually have special internal pre-treatment to maintain gas purity.

5.3 Valve construction

Valves are specially designed for safe use on a pressurized container.

Figure 3 shows a section view of a valve with its various components: body, seat, handle, container connection, outlet connection, PRD, and restrictive orifice.

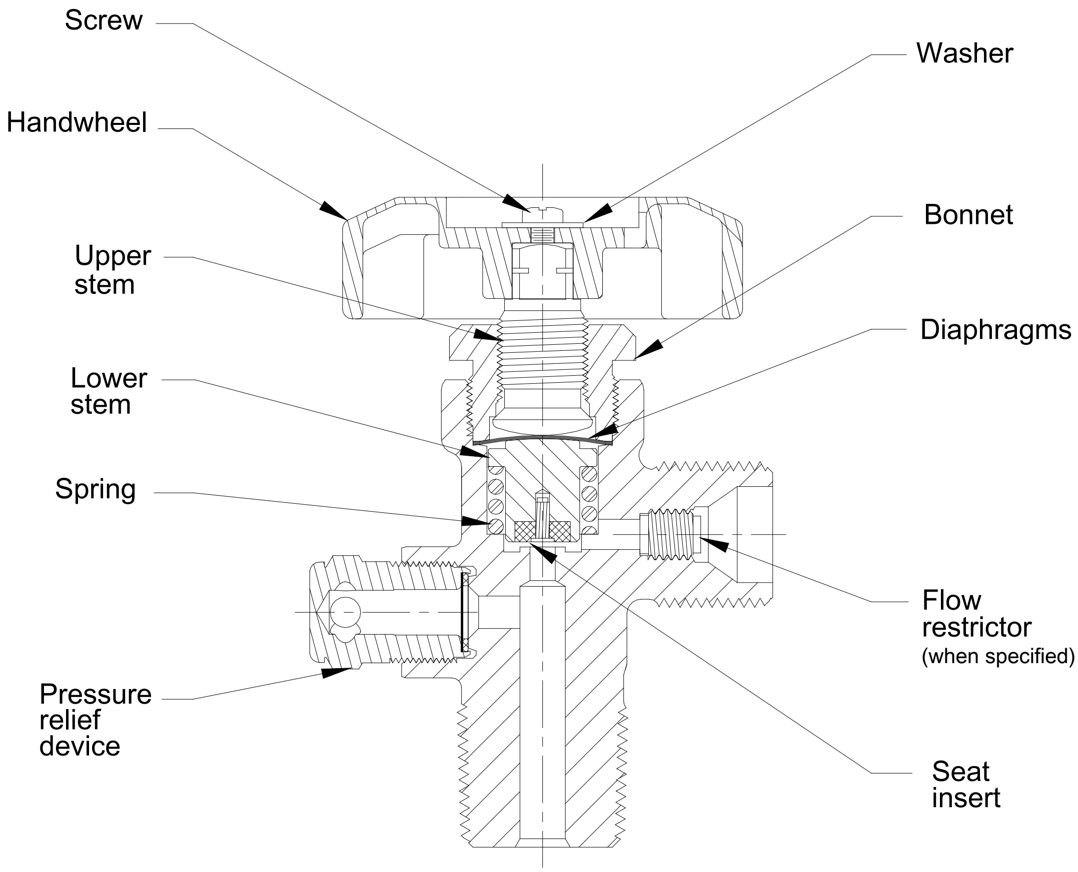


Figure 3 Diaphragm packless valve

A container valve is fitted on a container to allow flow into or out of it. The valve body is typically made of brass, bronze, stainless steel, or other compatible metals.

A variety of seats are used, the most common being metal and soft seats made of polymers.

The valve stem is typically sealed by packing or with a metal diaphragm depending on purity and compatibility requirements.

Valves can be operated using hand wheels or wrenches. Since the 1980s, pneumatically actuated valves have also been used. They allow for remote opening and closing of the cylinder valve and afford an extra measure of safety both at the filling as well as at the point of use.

PRDs are sometimes fitted to valves or cylinders to prevent the rupture of normally charged containers when it is over pressurized such as when in a fire. There are generally four types:

- metal diaphragm or rupture disk;
- fusible plug;
- a combination of diaphragm and fusible plug in series; and

- spring.

If a PRD is used, it should be appropriate for the gas being filled and shall meet the requirements of national standards.

NOTE In certain countries, the storage of liquefied gas containers is in the area protected from sunlight.

Valve outlet connections are designed to prevent incompatible gases from being connected or to prevent system pressures exceeding design limits. Connections should follow national standards where these exist.

Use of the torque wrench is recommended for tightening a valve. There are torque wrenches specifically designed for the valve handwheel. Torque is pre-set so that damage to internal valve components such as diaphragm, valve seat, etc., does not occur when the valve is closed. Additionally, there are other types of torque wrenches designed for cylinder valve outlet caps. Torque is also preset for the type of outlet such as Diameter Index Safety System (DISS), metal to metal, gaskets seal, etc. See Figure 4.

Figure 4 Typical handwheel torque wrench and an air actuated valve with a DISS outlet

Some valves are fitted with restrictive flow orifices (RFO) to limit the maximum flow from the container, for example, silane, arsine, and phosphine.

Some containers (especially those containing highly toxic gases and pyrophoric gases) are fitted with valve outlet caps or plugs to prevent accidental release and shall be designed to withstand expected container pressures.

The regulatory body of each country stipulates direction on the use of PRDs. These regulations shall be followed. It is recognized that there are differences in the assignment of PRDs from country to country.

5.4 Filling ratio

When filling a liquefied gas into a gas cylinder, a specified filling ratio shall be maintained to ensure that cylinder does not become liquid full at 55 °C (131 °F) or exceed pressure requirements as stated in national regulations.

While the UN Model Regulations P200 Packing Instructions prescribe filling ratios, some countries such as Japan and the U.S. use different filling ratios, which are prescribed by their country regulations [3].

Local regulations on filling ratio shall be checked when filling liquefied gases.

6 Good practices for handling, use and storage of electronic specialty gases containers

The following are some good practices for storage and use of electronic specialty gases with recommendations included in 6.3 to address specific chemical properties of various electronic specialty gases.

6.1 Handling and use

- All facilities shall have an emergency response plan that should include the plan for gas releases and emergency evacuation (for more information in EIGA Doc 80, *Handling gas container emergencies* and EIGA Doc 30, *Disposal of gases* [14, 15]);

- Only trained and qualified personnel should handle electronic specialty gases;

- Have the SDS on hand to handle electronic specialty gases;

- Use appropriate materials of construction compatible for handling electronic specialty gases. This information can be obtained from the SDS or by contacting the gas manufacturer;

- Always wear proper personal protective equipment (PPE) when handling gas containers. Steel-toed safety shoes, safety glasses with side shields, and leather gloves are recommended. Refer to Appendix B for PPE;

- Good housekeeping is essential, e.g., keeping combustible material away from container storage or use areas;

- Practice first-in-first-out (FIFO) cylinder management;

- There are a variety of different cylinder valve inlets that are in use today. There are also a variety of cylinder neck threads that are used worldwide. Threads on the valve inlet shall match threads on the container neck. It is very dangerous to match cylinders and valves that have been manufactured to different national standards since the possibility exists that the valve, under pressure, could be ejected from the cylinder;

- Care shall be exercised to ensure that a container including the container valve about to be filled has not been previously damaged;

- Pre-fill inspection of containers and correct verification of their pressure rating prior to filling is very important;

- Check for insects or foreign material before removing the valve protection cap;

- Remove valve outlet plug or connections slowly and look for signs of leakage before removing completely;

- Always stand at the side of the valve outlet plug or connection when removing the plug or breaking a connection;

- Check cleanliness of the valve outlet and of the connection of hoses or pigtails;

- Adaptors shall not be used to connect containers of different gases since it is very dangerous to use them;

- Always open valves slowly and carefully;

- Do not over-tighten valves;
- Removable valve protection devices shall always be kept in place except when the container is being filled or used;
- Never drag or slide containers;
- During transportation of highly toxic hazardous gases, handwheel valves should have the handwheel tied shut to prevent accidental opening of the valve;
- Never lift the container by the valve protection cap;
- Use proper cylinder trolleys or appropriate moving devices to minimize rolling of cylinders;
- Always restrain containers whether during transportation, storage, or use;
- Never strike an arc (with welding electrode) on the container;
- Never allow containers to contact electrical circuits;
- Never expose containers to corrosive chemicals or vapours, for example, bleach or seawater;
- Never use cylinders as a roller to move equipment;
- Containers with residual gas should be treated as if they were full;
- Always purge and/or evacuate piping systems with inert gas before introduction or disconnection of flammable, toxic, and corrosive gases. Pulling vacuum instead of purging with an inert gas may also be used or a combination of both; and
- Connections (e.g., cylinder pigtail connections), which are routinely re-made in the process, should be leak checked at a pressure not less than the maximum operating pressure before system purging.

6.2 Storage

6.2.1 General guidelines

- Containers should be stored under dry conditions wherever possible;
- Containers should be stored on level ground to minimize toppling;
- Always segregate full and used containers;
- Group containers according to the gas hazard they pose;
- Separate incompatible groups of containers (such as those containing flammable and oxidising gases) by appropriate distances or with fire partition with fire resistance of at least 30 minutes. This fire partition should have a minimum height of 1.5 m or at least 0.5 m above the tallest container unless restricted by national regulations;
- Store containers of liquefied gases to prevent the temperature of containers from exceeding the national guideline or a maximum of 50 °C (122 °F), e.g., by avoiding direct sunlight. See Appendix A for more information on temperature effects;

- Some gases require low temperature storage, for example, –10 °C (14 °F) for diborane, to minimize auto-decomposition;

- Quantity of gases stored should not exceed the design of the facility and should comply with national regulations;

- Cylinders when stored vertically shall be secured (nested, palletised, or chained) to prevent accidental tip-over; and

- Certain gas containers are designed to be stored and used horizontally such as pressure drums, tubes, or tonne containers. Other small cylinders such as lecture bottles are more conveniently stored horizontally. In these cases, precaution shall be taken to ensure that they are secured properly and in accordance with national regulations and codes.

6.2.2 Ventilation

- Store containers in well-ventilated areas;

- For outdoor storage, forced ventilation is generally not required;

- Gas densities shall be considered in the design of ventilation requirements:

    - For gases that are heavier than air, exhaust should be taken near the floor

    - For gases that are lighter than air, exhaust should be taken near the ceiling; and

- For indoor storage, natural or forced ventilation is required and shall meet the requirements of national regulations.

6.2.3 Firefighting systems

- Firefighting systems shall be considered for storage areas and shall meet the requirements of national regulations; and

- Where practical, a deluge system can be of benefit in a storage area and may be considered.

6.2.4 Life safety systems

- Appropriate leak detection devices should be installed to trigger emergency response actions in compliance with national regulations, if any.

  NOTE Gases with human detection limits below permissible exposure limits (PELs) generally do not require leak detection devices outdoors.

- Appropriate gas scrubbing or ventilation systems should be installed to handle gas leaks. National regulations, if any, may require gas scrubbing or ventilation to handle gas leaks; and

- Gas storage areas should be designed with more than one exit required by local regulations.

6.3 Guidelines for specific gas types

There are seven specific gas types such as flammable, oxidising, toxic, corrosive, inert, pyrophoric, self-reactive, and polymerisable gases. The following guidelines are in addition to those listed in 6.1 and 6.2. It is recognized that there could be a degree of duplication of requirements noted in 6.1 and 6.2. Specific requirements noted in this section will take precedence.

6.3.1 Flammable gases

The following are precautions to take when handling flammable gases:

- Use the appropriate protective equipment to prevent potential flash or burn injury;
- Leak check containers and connections before use;
- Flammable gases shall be stored in well-ventilated areas, away from oxidizers, pyrophoric gases, highly toxic gases, flammable liquids, open flames, sparks, and sources of heat;
- Flammable gases shall be separated from other hazards (see 6.1);
- Where required by national codes, an energy relief wall or blast roof may be required. This wall or roof is designed to allow dissipation of pressure arising from an explosion;
- The use of non-classified portable electronic devices, for example, mobile phones and walkie-talkies, is prohibited;
- Do not vent flammable gases to the atmosphere except through a properly designed system;
- National regulations may limit the total quantity of flammable gases allowed to be stored and may require a risk assessment;
- Prohibit sources of ignition, e.g., cigarette smoking. Minimize to the extent possible all sources of ignition. This would also include static electric charges;
- Electrical equipment in the vicinity of flammable gases should be intrinsically safe following zoning guidelines in national regulations. If national regulations are not available, consult the International Electrotechnical Commission (IEC) or NFPA 70, *National Electrical Code®* [16, 17];
- Use of non-sparking tools shall be considered when working on or close to systems containing flammable gases;
- All piping, cabinets, and equipment used to handle flammable gases should have electrical continuity sources and should be earthed; and
- Flashback arrestors should be used, where appropriate, in pipes containing flammable gases.

6.3.2 Oxidising gases

The following are precautions to take when handling oxidising gases:

- Leak check containers and connections before use;
- Oxidising gases shall be stored in well-ventilated areas, away from flammable gases, pyrophoric gases, highly toxic gases, flammable liquids, open flames, sparks, and sources of heat;
- Oxidising gases shall be separated from other hazards (see 6.1);
- Use only equipment designed for oxygen service;

- Keep oxygen systems free from external contamination;
- Use only oxygen compatible lubricants or sealants;
- Do not vent oxidising gases to the atmosphere except through a properly designed system;
- Oxygen cylinders used in work areas with inadequate ventilation should have oxygen monitors to ensure that oxygen concentrations are kept below 23.5%, see EIGA Doc 04, *Fire hazards of oxygen and oxygen enriched atmospheres* [18]; and
- Equipment handling fluorine or oxidising fluorinated compounds can require passivation.

6.3.3 Toxic gases

The following are precautions to take when handling toxic gases:

- Leak check containers and connections before use;
- Toxic gases shall be stored in well-ventilated areas, away from flammable gases, pyrophoric gases, flammable liquids, open flames, sparks, and sources of heat;
- Toxic gases shall be separated from other hazards (see 6.1);
- Prior to entry, enclosed spaces containing highly toxic gases, including cylinder packaged inside shipping containers, should be checked for leaks of the toxic gas in the absence of a maintained stationary detection system;
- Do not vent toxic gases to the atmosphere except through a properly designed system;
- Emergency showers, eyewash station, and first aid stations may be required;
- National regulations may limit the total quantity of toxic gases allowed to be stored and may require a risk assessment review;
- The filling and use of highly toxic gases should be done in exhausted enclosures or rooms with the discharge treated properly to below acceptable levels before emission into the atmosphere; and
- Since many toxic gases are also corrosive, care should be taken in selecting the appropriate construction material.

6.3.4 Corrosive gases

Corrosive gases are also toxic and should be treated as such. Additional precautions to take when handling corrosive gases are:

- Use the appropriate protective equipment to prevent skin and eye contact; and
- Equipment such as an emergency shower and eyewash station should be available. The use of such equipment is mandatory in certain jurisdictions.

6.3.5 Inert gases

Inert gases can also be classified as asphyxiant gases. Additional precautions to take when handling inert gases are:

- Leak check containers and connections before use;
- For inert gases being filled and used indoors, oxygen monitors may be required. Also refer to EIGA Doc 44, *Hazards of inert gases and oxygen depletion* [19]; and
- Cryogenic liquid containers can continuously vent, indoor areas should be properly ventilated.

6.3.6 Pyrophoric gases

Precautions to take are at a minimum the same as to those for flammable gases as listed in 6.3.1.

6.3.7 Self-reactive and polymerisable gases

The following are precautions to take when handling self-reactive gases:

- Leak check containers and connections before use;
- Enforce strict compliance to FIFO usage of the gas in order to control the shelf life of filled cylinders; and
- Minimise causes of self-reaction or polymerization, e.g., high temperature and rust particles.

7 Other equipment for the electronic specialty gases supply system

This section includes other equipment for supplying electronic specialty gases such as regulators, gas monitoring systems, cylinder gas cabinets, and gas abatement systems.

7.1 Regulators

Regulators are used in gas delivery systems to reduce and control the pressure from a high pressure source to a safe working pressure for use. All internal regulator parts should be compatible with the gas used under normal operating conditions.

A regulator for semiconductor applications is functionally the same but has different features than that of a regulator designed for general duty use. Regulators designed for controlling gases in semiconductor processes are typically constructed of 316 or 316L stainless steel (SS), and at times electro polished. Regulators with stainless steel diaphragms should be used to avoid the potential of gas diffusion through porous elastomer diaphragms and the potential diffusion of contaminants that are adsorbed on elastomeric diaphragms. Other materials of construction such as brass may be used depending on the specific gas in question. Once a regulator has been used in the particular gas service, it should not be used for other gas service unless it has been reconditioned.

7.2 Gas monitoring system

For some gases, there is a need to ensure that each individual is protected by gas detection systems.

Many gases are colourless, flammable, or toxic. Some have odours that cannot be detected until the concentration reaches dangerous levels. Some gases are non-irritating and produce no immediate symptoms. Persons exposed to hazardous levels can be unaware of its presence. A gas monitoring system will ensure that any gas leak is detected and annunciated at predetermined levels. These levels for toxic gases may be alerted at 50% of TLV-TWA and alarm at the 100% of TLV-TWA. For flammable gases, it may be alerted at 25% of LFL and alarm at 50% of LFL. A gas monitoring system continuously monitors primary locations for the gas including, but not limited to the following areas:

- storage areas;
- operation area;
- cylinder gas cabinets;
- fume hoods; and
- process rooms.

Selection criteria are detection method, sensitivity, response time, reproducibility, selectivity, and stability.

Further, gas detection systems should be accurate, efficient, economic, and easy to use and maintain.

It is desirable to have a system capable of networking existing systems from various manufacturers and the ability to accommodate ongoing expansion.

7.3 Cylinder gas cabinets

Cylinder gas cabinets are commonly used for flammable and/or toxic gases at the semiconductor manufacturing facility.

A cylinder gas cabinet is made of metal and usually consists of a gas panel, a cylinder, and a purge gas cylinder. It is connected to a ventilation system to capture any leaks that can occur. A ventilation system exhausts a toxic gas to a scrubbing system.

The cylinder gas cabinet is required to be designed, assembled, operated, and maintained based on local regulations. Incompatible gas cylinders shall not be placed in the same gas cabinet nor directly interconnected in the same system.

7.4 Gas abatement systems

Many electronic specialty gases possess dangerous properties such as flammability, toxicity, oxidation, and corrosivity. When these gases are released or accidentally leaked to the atmosphere, there are risks of fire and explosion as well as personal injury and environmental contamination. Further, dangerous and harmful particles can be generated by combustion, oxidation, etc., of these gases.

In order to reduce the previously mentioned risks, it is important to install gas abatement systems for the purpose of abating these gases. Many national regulations require abatement systems to reduce the worst case of release from the container to a prescribed level.

Selection of a specific gas abatement system that is reliable and economical is essential in consideration of properties, concentration, flow rate, pressure, life of abatement material, etc., of the gas and the surrounding related system, etc.

Main gas abatement methods that are in use currently are physical adsorption and chemical reaction on solid media, catalytic oxidation, incineration, and wet scrubbing.

Refer to EIGA Doc 30 for more information [15].

8 Handling problem gas containers

Handling of cylinders that are involved in an emergency situation requires detailed and exact procedures to correct the situation as quickly as possible without harm to the emergency response personnel and without damage to the surroundings. Two publications detail procedures that need to be followed in such a situation. They are EIGA Doc 80 *Handling gas container emergencies* and EIGA Doc 30, *Disposal of gases* 14, 15]. The information in these documents can and shall be used in the case of an emergency situation.

The guidelines below provide an overview of general procedures that can also be followed to assess an emergency situation. These guidelines should not be considered to be comprehensive. They are not to be used in place of documented procedures nor should they be deemed a work instruction for dealing with an emergency.

8.1 General principles

The following are general principles relating to the handling of problem containers:

- Only knowledgeable and well-trained response teams should handle problem electronic specialty gases containers;
- If there is any doubt as to how to handle the situation, immediately contact the local fire brigade, an emergency response contractor, or the gas supplier who will be in a better position to handle the incident;
- Ensure all sources of ignition are eliminated;
- Ensure appropriate PPE is used (see Appendix B);
- Move the cylinder to a safe location for disposal work, if possible;
- Design the gas abatement system (scrubber or other equipment) for high temperatures generated from the heat of neutralization;
- After abatement, the empty cylinder should be marked as defective and then handled in the appropriate manner;
- If a valve is not operable, use specialized equipment, e.g., a cylinder drill, to access contents of the cylinder through the cylinder wall or valve body;
- During abatement of a gas from a problem container, ensure that the piping from the leaking container is kept well below the surface of the scrubber solution;
- Only a trained team should attempt to scrub gases from a problem cylinder;
- Be aware of multiple hazards some gases possess, e.g., ammonia is an alkaline gas that is corrosive, toxic, and flammable at concentrations above 16% v/v in air;
- Ensure that an emergency plan is defined, regularly reviewed and updated; and
- Leaking gas cylinders that cannot be repaired at the emergency site may be transported safely inside suitable cylinder recovery vessels or salvage receptacles.

8.2 Flammable gases

- If the valve is operable, use it to vent the flammable gas to a safe area, if it is safe to do so; and
- It is always preferable to vent the flammable gas to a gas abatement system.

8.3 Oxidising gases

Acidic oxidising gases such as fluorine, chlorine, and chlorine trifluoride can be scrubbed with an alkaline solution that is greater than 15% by weight. Acidic gases such as nitric oxide and nitrogen dioxide are more difficult to scrub. Oxygen, nitrous oxide and their mixtures can be vented directly, without a venting system.

8.4 Corrosive gases

Corrosive gases are either acidic or alkaline:

- Acidic gases—Scrub acidic gases with a 15% w/w alkaline solution
- Alkaline gases—Scrub alkaline gases with a 10 to 20% w/w acid solution

8.5 Inert gases

- Leaking inert gases can become asphyxiants if they are vented into a confined area; and
- The cylinder can be vented to a safe location which shall be a well-ventilated, non-confined area.

8.6 Toxic gases

- For toxic gases that are acidic, see 8.4;
- For toxic gases that are alkaline, see 8.4;
- For toxic gases that are oxidizers, see 8.3; and
- For toxic gases that are metal hydrides, see AIGA Doc 004/04 and EIGA Doc 30, and/or immediately contact the emergency response contractor who will be in a better position to handle the incident [14, 15].

9 Safety training and education

Personnel involved in the handling of electronic specialty gases shall be regularly trained and educated on the exposure effects (signs, symptoms, medical attention) of these gases using their SDS and other safety information.

Minimum requirements are that all personnel handling gases (including vehicle drivers) shall be able to identify gases they are handling, be aware of the appropriate properties and hazards, and the action to take in the event of an emergency. Such personnel should be provided with appropriate safety equipment and training in its use.

Only appropriately trained personnel shall respond to emergencies such as fires, gas leaks, etc.

Additional training can be required by local jurisdictions, which include personnel safety, preventive maintenance, and environmental management programs.

10 Security

Security has become an important concern in the industrial gases industry due to the recent development and threat of terrorism and criminal activity in the world.

Some of the gases covered in this publication can be used as a weapon of mass destruction (WMD) in the possession of a terrorist.

Appropriate security measures should be implemented to protect products, facilities, employees, and the community against theft, vandalism, sabotage, workplace violence, and terrorism.

A sale policy for these gases should be in place against illegal use of the gases such as WMD and the manufacture of illicit drugs. A thorough review should be conducted prior to the purchase being approved and the delivery made to ensure that the customer has a valid reason to purchase these gases and that tracking records during shipment of these gases are issued and kept. .

For more detailed information on security, refer to EIGA Doc 922, Site *security*; EIGA Doc 920, *Guidance for Qualifying Customers Purchasing Compressed Gases*; and EIGA Doc 173, *ADR Transport Security Guidelines* [20, 21, 22].

11 References

[1] *European Agreement Concerning the International Carriage of Dangerous Goods by Road* (ADR), www.unece.org

[2] *European Agreement Concerning the International Carriage of Dangerous Goods by Rail* (RID), www.unece.org

[3] *UN Recommendations on the Transport of Dangerous Goods, Model Regulations,* www.unece.org

[4] ISO 10156, *Gases and gas mixtures – Determination of fire potential and oxidising ability for the selection of cylinder valve outlets,* www.iso.org

[5] CGA C-14, *Procedures for Fire Testing of DOT Cylinder Pressure Relief Device Systems,* www.cganet.com

[6] *Threshold Limit Values (TLVs®) and Biological Exposure Indices (BEIs®),* American Conference of Governmental Industrial Hygienists, www.acgih.org

[7] AIGA Doc. 012/04, *Cleaning of equipment for oxygen service,* www.asiaiga.org

[8] CGA G-4.1, *Cleaning equipment for oxygen service,* www.cganet.com

[9] EIGA Doc 33, *Cleaning of equipment for oxygen service,* www.eiga.eu

[10] JIGA-TS/02/03, *Oxygen equipment cleaning guidelines,* www.jimga.or.jp

[11] *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS), www.unece.org

[12] *Classification, labelling, and packaging (CLP) of substances and mixtures,* European Chemicals Agency (ECHA), www.echa.europa.eu

[13] EN 1089-3, *Transportable gas cylinders: Gas cylinder identification (excluding LPG). Colour coding,* www.cen.eu.

[14] EIGA Doc 80, *Handling gas container emergencies,* www.eiga.eu

[15] EIGA Doc 30, *Disposal of gases,* European Industrial Gases Association, www.eiga.eu

[16] International Electrotechnical Commission (IEC), www.iec.ch

[17] NFPA 70, *National Electrical Code®,* National Fire Protection Association, www.nfpa.org

[18] EIGA Doc 04, *Fire hazards of oxygen and oxygen enriched atmospheres, www.eiga.eu*

[19] EIGA Doc. 44, *Hazards of inert gases and oxygen depletion,* www.eiga.eu

[20] EIGA Doc 922, Site s*ecurity* www.eiga.eu

[21] EIGA Doc 920, *Guidance for Qualifying Customers Purchasing Compressed Gases* www.eiga.eu

[22] EIGA Doc 173, *ADR Transport Security Guidelines*, www.eiga.eu

[23] *Code of Federal Regulations,* Title 49 (Transportation) Parts 100-199, www.gpo.gov

[24] *Directive 2008/68/EC of the European Parliament and of the Council of 24 September 2008 on the inland transport of dangerous goods,* Council of the European Union, www.europa.eu

[25] EIGA Doc. 52, *Load securing of Class 2 receptacles*, www.eiga.eu

[26] *International Maritime Dangerous Goods Code,* International Maritime Organization, www.imo.org

[27] EIGA Doc. 102, *Safety audit guidelines,* www.eiga.eu

12 Additional references

EIGA Doc 23, *Safety training of employees,* www.eiga.eu

EIGA Doc 40, *Work permit systems,* www.eiga.eu

EIGA Doc 169, *Classification, and Labelling Guide in accordance with EC Regulation 1272/2008 (CLP Regulation),* www.eiga.eu

EIGA Doc 176, *Safe practices for storage and handling of nitrous oxide,* www.eiga.eu

EIGA Doc 92, *Code of Practice nitrogen trifluoride,* www.eiga.eu

EIGA Doc 163, *Code of Practice arsine,* www.eiga.eu

EIGA Doc 162, *Code of Practice Phosphine,* www.eiga.eu

EIGA Doc 160, *Storage and handling of silane and silane mixtures,* www.eiga.eu

EIGA Doc 140, *Code of Practice Compressed fluorine and mixtures with inert gases,* www.eiga.eu

CGA P-1, *Safe Handling of Compressed Gases in Containers,* www.cganet.com

CGA P-22, *The Responsible Management and Disposition of Compressed Gases and Their Containers,* Compressed Gas Association, www.cganet.com

CP-18, *The Safe Storage, Handling and Use of Special Gases in the Micro-electronics Industry,* British Compressed Gases Association, www.bcga.co.uk

Matheson Gas Data Book, 7th ed., 1980, www.mathesongas.com

EIGA Doc 13, *Oxygen pipeline systems,* www.eiga.eu

EIGA Doc 92, *Code of Practice – Nitrogen trifluoride,* www.eiga.eu

ISO 11625, *Gas cylinders – Safe handling,*. www.iso.org

Appendix A—Additional explanatory notes

A1 Gases under pressure

A1.1 State of gases

Gases under pressure are further classified, according to their physical state when packaged, in one of four groups in the following table:

Group	Criteria
Compressed gas	A gas that when packaged under pressure is entirely gaseous at –50 °C (–58 °F); including all gases with a critical temperature less than or equal to –50 °C (–58 °F).
Liquefied gas	A gas that when packaged under pressure is partially liquid at temperatures above –50 °C (–58 °F). A distinction is made between: (a) High pressure liquefied gas: a gas with a critical temperature between –50 °C and 65 °C (–58 °F and 149 °F); and (b) Low pressure liquefied gas: a gas with a critical temperature above 65 °C (149 °F).
Refrigerated liquefied gas	A gas that when packaged is made partially liquid because of its low temperature.
Dissolved gas	A gas that when packaged under pressure is dissolved in a liquid phase solvent.

It should be noted that hydrogen fluoride and hydrogen cyanide by definition are not compressed gases; however, they are treated as such in this publication and are handled as low-pressure liquefiable gases, together with other liquids which may be filled into gas cylinders.

Cryogenic liquids are those having a boiling point of –90 °C (–130 °F) or lower at 101.325 kPa, abs (14.696 psia). Refrigerated liquids such as nitrous oxide and carbon dioxide, which have boiling points of higher than –90 °C (–130 °F) are liquid, and should not be confused with refrigerant or fluorocarbon gases. To further illustrate the impact that the physical state has on hazard properties of the material, consider carbon dioxide (CO_2). It can be shipped as a liquefied gas with UN1013, as a refrigerated liquefied gas with UN2187, or as dry ice with UN1845. Each unique UN number identifies a specific set of hazards by virtue of the physical state of the carbon dioxide in each case.

A1.2 Definition of gas cylinder

In this publication, a gas cylinder is defined as a pressure receptacle with a water capacity that does not exceed 150 L (see Section 3).

U.S. regulations define a cylinder as a compressed gas container having a maximum water capacity of

454 L.

NOTE For the purpose of this publication, larger cylinders such as tubes, ISO modules, ISO containers and multiple element gas containers (MEGCs) are also referred to as cylinders and can have capacities in excess of 2200 L..

A2 Temperature effects of gases

Heating a container will in turn raise the temperature and pressure of both liquefied and non-liquefied gases. A liquefied gas when heated will expand. By following and not exceeding the recommended filling ratio for a low pressure liquefied gas, the container will not become liquid full if it is heated to temperatures normally incident to transport. Hydraulic forces from a liquid full container can potentially cause container walls to rupture catastrophically. High pressure liquefied gases shall not be filled to exceed the recommended filling ratio to ensure that it will not exceed cylinder test pressures. Different regulatory authorities can specify different fill ratios. For example, ADR requires that the liquid phase shall not fill the pressure receptacle at a temperature of 60 °C (140 °F) and U.S. DOT requires that the liquid phase shall not fill the pressure receptacle at a temperature of 55 °C (131 °F) [1, 23].

Aluminium containers when heated to a temperature of higher than 77 °C (170 °F) can exhibit over aging of the aluminium alloy and such temperatures should be avoided. Over aging ultimately leads to a reduction in materials properties (loss of strength) and could lead to catastrophic failure of the container. In addition, certain aluminium alloys can be degraded by long term exposure to temperatures of 90 °C (194 °F) and higher, thus making the alloy susceptible to stress corrosion cracking.

Carbon steel can become embrittled at or below temperatures of –40 °C (–40 °F). They shall be allowed to warm slowly back to ambient temperatures to prevent the possibility of thermal induced damage to container walls.

A3 Safe handling of cryogenic gases

Cryogenic gas containers should be placed in well-ventilated areas to minimize asphyxiation, flammability, and oxidising hazards from gases escaping from PRDs. Vents from PRDs shall also be piped away from enclosed or poorly ventilated areas.

Extreme temperature differences compound thermal stresses and care shall be taken during transfer of cryogenic gases into warm containers or piping. Carbon steel cannot be used to handle cryogenic gases; stainless steel is the most common material used.

Positive pressure shall always be maintained in conveying cryogenic gases. This is to minimise the infiltration of air and ambient moisture into containers and piping which may then freeze on walls and contaminate the cryogenic product.

The external walls of short uninsulated hoses or piping around bulk cryogenic vessels and vaporisers can reach temperatures below the boiling point of oxygen (–183 °C (–297 °F)). This can result in an oxygen-enriched atmosphere in the micro-environment surrounding cold surfaces with its inherent hazards. Precautions for oxidising gases shall be taken when working around bulk containers of cryogenic gases and vaporizers.

Contact with a cryogenic liquid will result in what is equivalent to a thermal burn on the skin and is to be treated as such. Insulated leather gloves are recommended for persons handling cryogenic liquids who shall also be well covered to minimise exposure of the skin and face from accidental splashes of cryogenic liquids.

Liquefaction of gases or, conversely, boiling of liquefied gases poses a potential hazard if containers, pumps, and piping are not designed to handle these phase changes. High positive or negative pressures within a container or pipe can result.

The design of facilities has to account for the range of pressures and temperatures expected and all products should be checked for their physical states at all likely pressure and temperature combinations and also meaningful extremes.

In the design of ventilation systems, the proper positioning of sampling points for gas analysers and gas density relative to ambient air in the expected range of operating temperatures have to be considered.

The design should consider the possibility that any cold gas vented has a higher density than air at ambient temperatures, while once it has warmed up it may not.

A4 Flammability

When flammable substances catch fire or burn, the associated rise in temperature and pressure of resultant products of oxidation are dependent on physics of reaction kinetics. The faster the reaction, the quicker the flame spreads and will continue to do so until reactions are quenched and/or components that caused these reactions are removed.

A5 Storage of toxic gases

Toxic gases are to be stored in well-ventilated facilities in accordance with local building and fire prevention codes. The total quantity to be stored on a site should be determined after a quantitative risk assessment taking into account prevailing climatic conditions, population densities, and acceptable risk criteria laid down by local authorities.

A6 Globally Harmonized System of Classification and Labelling of Chemicals (GHS)

The use of chemicals to enhance and improve life is a widespread practice worldwide. But alongside benefits of these products, there is also potential for adverse effects to human health or the environment. To prevent this danger and to ensure the safe use, transport, and disposal of chemicals anywhere in the world, it is necessary to provide an internationally harmonized approach to classification and labelling programs.

GHS addresses classification of chemicals by types of hazard and proposes harmonized hazard communication elements including labels and SDS.

It aims at ensuring that information on physical hazards and toxicity from chemicals are available to enhance the protection of human health and the environment during the handling, transport, and use of these chemicals. GHS also provides a basis for harmonization of rules and regulations on chemicals at national, regional, and worldwide level, an important factor also for trade facilitation.

Most electronic specialty gases fall under GHS and need to meet GHS requirements.

Implementation of GHS has been started and it has already been used in some countries.

A7 Transportation

A7.1 Road transport

In Europe, the transport by road of gases is regulated by the requirements of ADR that is embedded in the national legislations of all member states of the EU through the framework directive on the transport of dangerous goods 2008/68/EC as amended [1, 24].

Drivers and all persons whose duties concern the carriage of dangerous goods shall be trained in the requirements of ADR according to their responsibilities and duties. Employees shall be trained before assuming responsibilities.

In addition, drivers and employees responsible for the loading of packaged goods shall be trained on the most appropriate ways to secure the different types of gas receptacles on the different types of trucks, see EIGA Doc 52, *Load securing of Class 2 receptacles* [25].

A7.2 Air transport

Transport by air of gases is regulated by the requirements of International Civil Aviation Organization (ICAO), supplemented by those of International Air Transport Association (IATA).

The transport by air of gases may be restricted by these regulations to cargo aircrafts only or not allowed at all depending on the hazard classification of the gases and gas mixtures.

Before considering a shipment by air, confirmation should be sought from an employee trained in the requirements of ICAO/IATA or from a specialised shipping agent that the gases are allowed for transport.

A7.3 Sea transport

Transport by sea of gases is regulated by the requirements of the *International Maritime Dangerous Goods Code* (IMDG) [26]. The transport on sea ferries is also governed by IMDG unless there is a special agreement between the countries concerned (e.g., Memorandum of Understanding for the transport of dangerous goods in the Baltic Sea).

There are no restrictions on the transport of gases due to their hazard classification but the IMDG imposes strict rules for the segregation of dangerous goods within a container and aboard the vessel.

Before organizing the shipment of gas receptacles, the segregation rules should be understood and adhered to in order to avoid the shipment being refused before embarking.

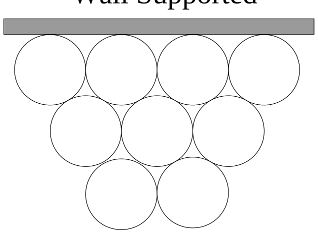
Load securing of the gas receptacles in the container is more severe than for land transport and should be performed by specially trained personnel or subcontracted to specialised firms.

A8 Cylinder nesting

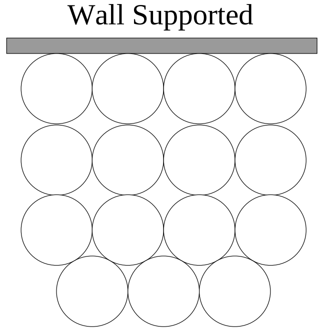
The 3-point contact method (nesting) of cylinders at gas manufacturing and distributing facilities is considered a safer mode of storage than chaining. This method requires that each cylinder makes contact in at least three places with other cylinders, walls, or solid support structure (i.e., rail).

The following three illustrations portray different but acceptable forms of cylinder nesting. The nested unsupported illustration is acceptable for temporary storage (for example, cylinders waiting to be loaded on trucks).

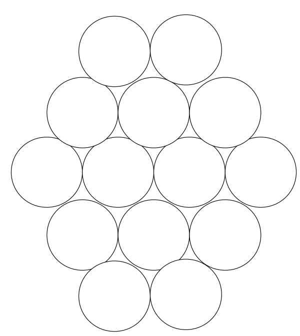
Wall Supported



Wall Supported



Nested Unsupported



A9 Safety audit

Safety audits are a prerequisite to promote, improve, and maintain good safety performance and record and are helpful to the direct prevention of incidents.

They are executed to evaluate the effectiveness of the company's safety effort and make recommendations for the purpose of a reduction in incidents and minimization of business loss.

They are an important part of the company's control system and these checks ensure that deteriorating safety operations and practices are detected.

For detailed practical information about safety audits, refer to EIGA Doc 102, *Safety audit guidelines* [27].

Appendix B—Emergency response planning

B1 Emergency response plan

An emergency response plan shall be created for handling specialty gases. The plan should include, but is not limited to, the following aspects:

- alarm system;
- evacuation plan and roll call;
- safety emergency shutdown system;
- emergency response team contact list;
- emergency equipment locations and list;
- outside parties contact list such as fire brigade, police, hospital, neighbours, etc.;
- communication with media;
- reporting system;
- safety data such as SDS with first aid information;
- hazards evaluation;
- working process of emergency response team; and
- training requirements.

See also EIGA Doc 80; *Handling gas container emergencies* [14].

B2 Personal protective equipment (PPE)

B2.1 General considerations

In the storage, handling, and use of specialty gases, the personnel shall:

- perform hazard assessments of the working process;
- select and use appropriate equipment based on hazards identified;
- ensure that protective equipment shall always be properly maintained for service; and
- ensure that all relevant personnel shall be trained.

It is important to note that no single piece of protective equipment or material of construction will provide protection.

B2.2 Recommended general safety equipment

- safety shoes;
- safety gloves;
- safety eye/face protection shields;
- eyewash fountains/emergency showers;
- safety ropes or tapes;
- hazardous gas monitors; and
- safety signs.

B2.2.2 Specific equipment in emergency response

Respiratory protection safeguards the wearer from the inhalation and ingestion of chemical contaminants. Respiratory protection is divided into three types:

- Self-contained breathing apparatus (SCBA)
  - Uses a source of respirable air carried by the wearer
- Supplied-air respirator
  - Uses air supplied to the wearer from a source at some distance from the work area
- Air-purifying respirator
  - Uses a filter, an absorbent, or combination of filter and an adsorbent to remove airborne contaminants from otherwise respirable air.

Protective clothing is designed to protect the wearer from heat and/or chemicals contacting the skin or eyes. Protective clothing is divided into three types:

- Firefighter protective clothing
  - Designed to protect the wearer from extremes of temperature, steam, hot water, hot particles, and ordinary hazards of structural fire fighting
- Chemical protective clothing
  - Designed to protect the wearer's skin and eyes from direct chemical contact. This type of clothing can be non-encapsulating or encapsulating
- High-temperature protective clothing
  - Designed to protect the wearer from short-term, high-temperature exposure.

All PPE shall be inspected regularly based on its maintenance program and kept in good functional conditions.

- All types of PPE (respiratory protection and protective clothing) used in a hazardous material environment shall be thoroughly decontaminated before reuse;
- Gas monitors should be calibrated regularly in accordance with the manufacturer's instructions or national requirements;
- Respiratory protection equipment shall be inspected routinely before and after each use and periodically. The respiratory equipment should be stored in an accessible location and protected against heat, cold, excessive moisture, damaging chemicals, and mechanical damage;
- The protective clothing for head, eye, face, body, foot, leg, and hand protection shall be inspected after each use. Chemical exposure can damage protective clothing. Protective clothing should be stored in a proper manner to prevent mechanical damage; and
- It is also important to inspect PPE periodically while in storage.