



SAFE HANDLING OF ELECTRONIC SPECIALTY GASES

AIGA 018/05

Asia Industrial Gases Association

298 Tiong Bahru Road, #20-01 Central Plaza, Singapore 168730

Tel : +65 6276 0160 • Fax : +65 6274 9379

Internet : <http://www.asiaiga.org>



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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, the Asian Industrial Gases Association has written this safety guide to assist both the packager and user of these gases.

It is the intention of the Association to promulgate standards which will enhance safety in the workplace where these gases and mixtures are prepared, when these materials are transported from the production site to the ultimate user, and as they are stored and eventually consumed by the end user.

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

Electronic specialty gases encompass gases and mixtures that are primarily used in the electronics industry. Because of the inherent need for very high purity, extraordinary precautions are taken to ensure that the gases are packaged in cylinders with valves that have extremely low leak rates, and that the stability of the gas specification is maintained for the entire specified shelf life of the package. However, 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 they are deemed to be inert.

Further, in the wake of the events of September 11, 2001, some electronic specialty gases can also be considered as potential weapons of mass destruction. The guidelines noted in this standard 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 the potential hazards of both the containers and the gases, as well as direction for handling problem containers, are presented in this document. Additionally, guidelines are provided on general safety considerations.

The information contained in this publication is designed to provide awareness and guidance for personnel working in a facility that packages or distributes gases used primarily in the electronic industry, such as the manufacture of semiconductors, TFT-LCD, fibre optics and opto-electronic devices. It is not meant to take the place of Work Instructions or Standard Operating Procedures, 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 the 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.

To the extent possible, each section will provide guidance and direction as to where additional information can be found in the literature of the Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), ISO, the European Road and Rail Regulations (ADR/RID), as well as the Regulations promulgated by the United Nations in the "Orange Book".

Where the word "shall" is used, it will be understood to mean that the steps or directions outlined are mandatory. On the other hand, when the word "should" is used, it will be understood to mean that the recommendation, when followed, will result in benefits; however, alternate arrangements may also be considered to achieve the desired result.

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 or

non-liquefied gas, this will be highlighted. The information contained in this document was collected from sources that are believed to be accurate. However, it should not be understood that every potential aspect of the safe handling of electronic gases has been considered, and the reader is encouraged to take steps to ensure that such a comprehensive review is undertaken.

3 Definitions

Absolute Pressure: is based on a zero reference point, the perfect vacuum. Measured from this reference, the standard atmospheric pressure at sea level is 1.013 bars (101.325 kPa), abs; however, local atmospheric pressure may deviate from this standard value because of weather conditions and the distance above or below sea level.

Apparatus: Accessory equipment, such as valves, pressure relief devices, regulators, etc., used with compressed gas.

ADR/RID: European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR) and Rail (RID).

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

Bundle: A bundle is a pack containing two or more gas cylinders, manifolded together, with a common valve connection for filling and use.

CFR: Code of Federal Regulations in the United States.

Compressed Gas: A substance or mixture of substances that (1) is a gas at 20 °C (68 °F) or less at an absolute pressure of 101.325 kPa, abs (14.696 psia) and (2) has a boiling point of 20 °C (68 °F) or less at an absolute pressure of 101.325 kPa, abs (14.696 psia) and that is liquefied, non-liquefied, or in solution, except those gases that have no other health or physical hazard properties are not considered to be compressed gases until the pressure in the packaging exceed an absolute pressure of 280 kPa, abs (40.6psia) at 20 °C (68 °F).

(See Appendix 1 for more information)

Containers (Compressed Gas): Vessels of various shapes, sizes, and materials of constructions such as cylinders, portable tanks, or stationary tanks, and of designs meeting the specifications of either the ASME, TC, DOT, ADR, JIS, or national authorities, and are filled with compressed gases.

Corrosive Gas: A gas that in contact with materials or living tissue can cause damage or destruction.

Critical Temperature: The critical temperature is the temperature above which the compressed gas cannot exist in the liquid state.

Cryogenic Liquid: A refrigerated liquefied gas having a boiling point lower than –90 °C at 101.325 kPa, abs.

Cylinder: Container (compressed gas) having a water capacity that does not exceed 150 litres.
See Appendix 1 for more information.

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

Filling Ratio: This is the ratio of the mass of liquefied gas introduced in a container to the mass of water at 15 °C that would fill the same container fitted ready for use. Also known as fill density, filling factor, maximum fill degree, maximum fill pressure.

Filling ratio may be applied to some non-liquefiable gases for safety reasons such as auto-decomposition, e.g. nitrous 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 must be ascertained.

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 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 pressure and at a temperature of 20 °C.

Gas Mixture: A gas mixture is a mixture of two or more components, either liquid or gaseous, which has been deliberately filled for use from the cylinder as a blended mixture, and which exerts a pressure of equal to or more than 150 kPa, abs at 15 °C.

Gas Pressure: The 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 document.

Gas Supplier: A business that produces, fills, and/or distributes compressed gases and compressed gas containers.

Handling: Moving, connecting or disconnecting a gas container under normal conditions

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

Highly Toxic: Gases that have an LC₅₀ in air less than or equal to 200 ppm for a one-hour exposure.

Inert Gas: A gas which is not toxic, which doesn't support human breathing and which reacts scarcely or not at all with other substances.

LC₅₀: The median lethal concentration of gas, when administered by continuous inhalation for an hour to 10 albino rats weighing between 200 and 300 grams each, causes death to 50% of the population within 14 days.

LFL (Lower Flammability Limit): The minimum concentration in air of a gas which would burn when ignited.

Material Safety Data Sheet (MSDS): Written or printed information concerning a hazardous material (properties, precautions, etc.) following national regulations.

National Standards, Guidelines, Regulations: These are the technical standards set by the 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.

Nesting: A 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 2 for more information.

Oxidising Gas: A gas that, in the presence of a fuel, supports and may vigorously accelerate combustion.

Passivation: Passivation is a 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 is

usually carried out using a mixture containing a reactive gas diluted in an inert gas, sometimes followed by the pure reactive gas. As an example, in the specific case of fluorine or fluorinated gases, passivation ensures that any residual contaminants will react in a controlled manner and will create an inert fluoride layer.

Pressure Relief Device: A 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.

Refrigerant Gas: Liquefied compressed gases at room temperature typically used for a mechanical cooling system.

Shall: The use of the word “shall” in this document implies a strong concern or instruction.

Should: The use of the word “should” in this document indicates a recommendation.

Tare Weight: The tare weight is the mass of the container and other fittings not removed during the container’s fill or use. It would include the valve, dip tube and any permanently or semi-permanently fixed valve protection device.

Test Pressure: The test pressure of a container is the pressure at which the container is hydraulically or pneumatically tested and is the pressure which must not be exceeded under any foreseeable normal operating conditions (e.g. during filling).

Toxic Gas: A compressed gas that has a LC₅₀ in air of less than or equal to 5000 parts per million (ppm) for a one-hour exposure. National regulations may have additional classifications.

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. (This is the definition from ACGIH - American Conference of Governmental Industrial Hygienist).

UFL (Upper Flammability Limit): The maximum concentration in air of a gas, which would burn when ignited.

Valve Outlet Caps and Plugs: Removable attachments that usually form a gas-tight seal on valve outlets provided by the gas supplier with certain gases. (Some caps are designed only for valve thread protection and are not gas-tight.)

Valve Protection Cap: A rigid removable cover provided for container valve protection during handling, transportation, and storage.

Valve Protection Device: A 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 (ESGs) used in the manufacture of semi-conductor and electronic components are often hazardous due to their inherent physical properties, and chemical and biological reactivity. Most gases possess more than one hazard.

Material Safety Data Sheets (MSDS) provided by gas suppliers for individual gases should be consulted for better understanding of the hazards of each product. They provide a wealth of information and recommendations for the safe handling of electronic specialty gases.

4.1 Physical hazards

4.1.1 Gas pressure

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

4.1.2 Extreme cold

Gases handled in liquid form, cryogenic or refrigerated can pose various hazards such as:

- frostbite
- metal embrittlement
- mist formation
- thermal expansion
- freezing

4.2 Chemical hazards

4.2.1 Flammability

A flammable gas requires two additional components to burn, an ignition source and an oxidizer. The flammable gas will only burn when the mixture with air is within a range of flammable limits, called the Lower Flammability Limit (LFL) and Upper Flammable Limit (UFL). Mixtures outside this range will not generally burn.

Some gases not classified as flammable for transportation purpose can burn under certain ambient conditions, e.g. ammonia.

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

A flammable gas mixture normally needs an ignition source to start the radical chain-reaction. Some flammable gases which have an auto-ignition temperature of less than 54.4 °C may ignite when released into the atmosphere. These are classified as pyrophoric gases.

4.2.2 Oxidizing gases

Oxidizing gases accelerate combustion but are not flammable by themselves, e.g. chlorine, fluorine and nitrous oxide. Their reactivity is dependent on the chemical being oxidized and on the pressure and temperature of the reactants.

Substances stable in air at ambient temperatures and pressures, e.g. grease and stainless steel, react violently with oxidizing gases at elevated temperatures and pressures. It is therefore vital that all pipelines and equipment handling oxidizing gases be cleaned for oxygen service.

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

Materials that normally will not burn at room temperature become flammable in the presence of strong oxidizing gases, such as fluorine and chlorine trifluoride.

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

4.2.3 Corrosive gases

Generally, corrosive gases can cause harm or damage to human tissue or materials when in contact with moisture. In dry environments, corrosive gases have negligible effects on metals. In practice however, minute leaks of gases combine with atmospheric moisture to corrode metal containers, valves and fittings. All efforts must be made to minimise the contact of corrosive gases with water.

There are acidic corrosive gases, e.g. hydrogen chloride, and alkaline corrosive gases, e.g. ammonia. When combined in an enclosed environment, they may react violently releasing much energy.

4.2.4 Self-reacting gases

These are gases that react on their own under certain conditions. The products of the reaction may 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, di-borane and the polymerization of ethylene oxide. Many polymerizable gases have inhibitors added.

4.3 Biological hazards

4.3.1 Toxicity and carcinogens

The most common route of toxic gas ingress into the body is inhalation through the lungs. A less common route is absorption through the skin.

Acute toxicity may result in rapid death of an individual, e.g. exposure to arsine, carbon monoxide

Chronic toxicity can result in deterioration of health due to accumulation of toxins (e.g. arsenic trihydride), damage to vital tissues, e.g. lung (e.g. nitrous oxide), or recurrent pain (e.g. hydrogen fluoride). Some gases such as ethylene oxide may pose a carcinogenic hazard. Mortality may not be rapid but the gas is believed to cause mutation in the genetic code of human cells which may lead to a malignant carcinogenic condition over a period of time.

4.3.2 Asphyxia

Asphyxia 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 breathing. This is not limited to inert gases such as nitrogen, helium, or argon, but can be any gas, e.g. hydrogen. Oxygen concentrations that are less than 19.5% are identified as oxygen deficient.

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, e.g. helium and hydrogen, may accumulate in ceiling spaces.

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

- a) entry into confined spaces which had not been sufficiently purged with a breathable atmosphere
- b) process lines which had not been adequately isolated
- c) leaks from cylinders or hoses
- d) spillage from dewars
- e) process vents which had not been routed to a safe area

5 Gas container and valves

5.1 Container construction and certification

The materials used in the construction of containers are predominantly carbon steel and aluminium. For low pressures, welded carbon steels are used. At higher pressures, seamless carbon steel and aluminium 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 follow national standards or the container manufacturer's country laws and regulations, whichever is more stringent. Containers failing to meet these standards must 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 1 shows the component parts of a gas container.

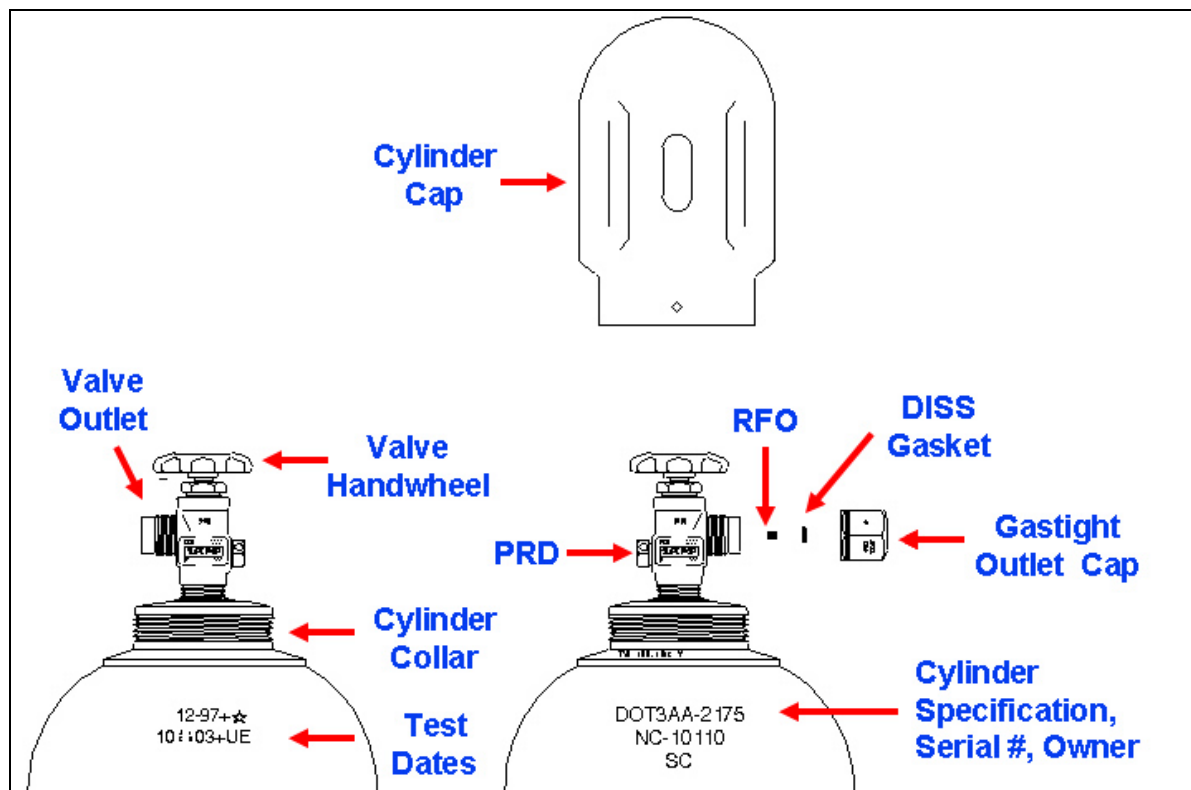


Figure 1: Drawing showing cylinder components (From Air Products and Chemicals, Inc)

5.2 Container weight

The empty or tare weight of a large compressed gas container can exceed 200 kg. When filled, the total weight of the container with gas can exceed 1000 kg. This can present a significant handling hazard.

5.3 Container identification

Each container has its basic information stamped on the body shoulder. This stamp may include container material specification, first test date, weight, volume, pressure rating, and manufacturer or re-test 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 should include gas name, brief description of properties, explosion prevention/control measures, and first aid and manufacturer information. Labels should be read before use, along with the MSDS.

Some countries have colour codes on the container to identify the gas inside; however; there is no unified international colour coding system for gases.

5.4 Valve construction

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

Figure 2 shows a section view of a valve with its various components: body, seat, handle, container connection, outlet connection, pressure relief device and restrictive orifice.

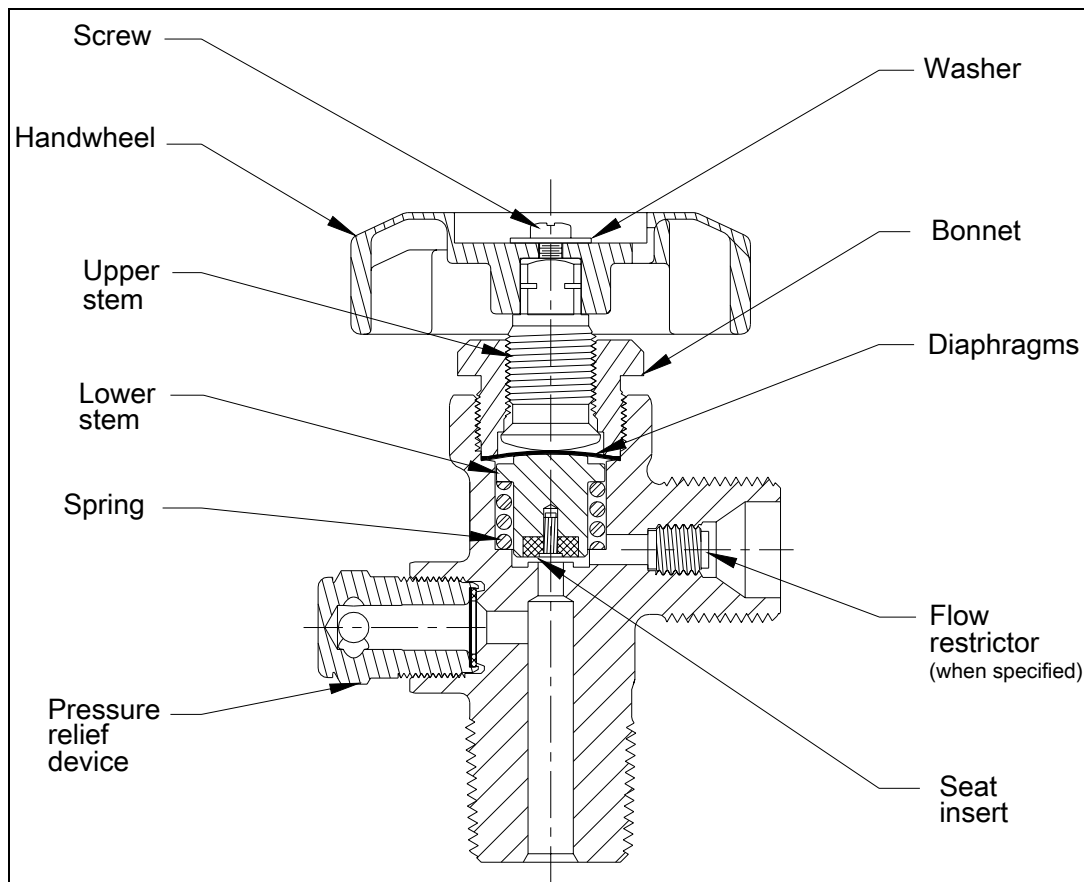


Figure 2—Diaphragm packless valve®

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.

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Valves can be operated

- using handwheels,
- using wrenches, or
- pneumatically.

Pressure relief devices are sometimes fitted to valves to prevent the rupture of containers. There are generally four types:

- metal diaphragm;
- fusible plug;
- spring; and
- a combination of diaphragm and fusible plug in series.

If a pressure relief device is used, it should be appropriate for the gas being filled and should follow national standards.

Valve outlet connections are designed to prevent incompatible gases from being connected, or to prevent system pressures exceeding design. Connections should follow national standards if any.

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

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

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

Some good practices for storage and use of electronic specialty gases are listed below with recommendations included in Section 6.3 to address specific chemical properties of various electronic specialty gases.

6.1 Handling and use

- a) All facilities must have an emergency response plan which should include the plan for gas releases and emergency evacuation (more information in AIGA 004/04 and EIGA 30/04)
- b) Only trained and qualified personnel should handle electronic specialty gases.
- c) Have on hand the MSDS to handle the electronic specialty gases.
- d) Use appropriate materials of construction compatible for handling electronic specialty gases. This information can be obtained from the MSDS.
- e) Always wear proper personal protective equipment when handling gas containers. Steel-capped safety shoes, safety glasses with side shields and leather gloves are recommended.
- f) Good housekeeping is essential, e.g. keeping combustible material away from container storage or use areas.
- g) Practice First-In-First-Out (FIFO) cylinder management.
- h) 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. The threads on the valve inlet must match the 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.

- i) Care must be exercised to ensure that a container about to be filled has not been previously damaged.
- j) Pre-fill inspection of containers and correct verification of their pressure rating prior to filling is very important.
- k) Check for insects or foreign material before removing the valve protection cap.
- l) Remove valve outlet plug or connections slowly and look for signs of leakage before removing completely.
- m) Always stand at the side of the valve outlet plug or connection when removing the plug or breaking a connection.
- n) Check cleanliness of the valve outlet and hoses.
- o) Adaptors shall not be used to connect containers.
- p) Always open valves slowly and carefully.
- q) Do not over-tighten valves.
- r) The valve protection device shall always be kept in place except when the container is being filled or used.
- s) Never drag or slide the containers.
- t) During transportation of hazardous gases, handwheel valves should have the handwheel tied shut to prevent accidental release.
- u) Never lift the container by the valve protection cap.
- v) Use proper cylinder trolleys or appropriate moving devices to minimize rolling of cylinders over long distances.
- w) Always restrain the containers whether during transportation, storage or use.
- x) Never strike an arc (with welding electrode) on the container.
- y) Never allow containers to contact electrical circuits.
- z) Never expose containers to corrosive chemicals or vapours, e.g. bleach or seawater.
- aa) Never use cylinders as a roller to move equipment.
- bb) Containers with residual gas should be treated as if they were full.
- cc) Always purge piping systems with inert gas before introduction of flammable, toxic and corrosive gases.
- dd) Always purge piping systems with inert gas before disconnection of flammable, toxic and

corrosive gases.

6.2 Storage

6.2.1 General guidelines

- a) Containers should be stored under dry conditions.
- b) Containers should be stored on level ground to minimize toppling.
- c) Always segregate full and used containers.
- d) Group containers according to the gas hazard they pose.
- e) In storage, separate incompatible groups 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.
- f) Store containers in such a way as to prevent the temperature of the containers from exceeding the national guideline or a maximum of 53 °C, e.g. by avoiding direct sunlight. See Appendix 1 for more information on Temperature Effects.
- g) Some gases require low temperature storage, e.g. –10 °C for di-borane, to minimize auto-decomposition.
- h) Quantity of gases stored should not exceed the design of the facility and should comply with national regulations.
- i) Cylinders when stored vertically shall be secured (nested, palletised or chained) to prevent accidental tip-over.
- j) Certain cylinders are designed to be stored horizontally such as ton containers. Other small cylinders such as lecture bottles are more conveniently stored horizontally. In these cases, precaution must be taken to ensure that they are secured.

6.2.2 Ventilation

- a) Store containers in well ventilated areas.
- b) For outdoor storage, forced ventilation is generally not required.
- c) Gas densities must be considered in the design of ventilation requirements.
- d) For indoor storage, forced ventilation is required and should follow national regulations.

6.2.3 Fire fighting systems

Fire fighting systems must be considered for storage areas and should follow national regulations.

6.2.4 Life safety systems

- a) 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 (PEL) generally do not require leak detection devices outdoors.)
- b) 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.
- c) Gas storage areas should be designed with more than one exit.

6.2.5 Security

Appropriate security measures should be implemented to prevent access to hazardous cylinders by unauthorized personnel. For more details refer to AIGA Doc. 003/04 'Security guidelines'.

6.3 Guidelines for specific gas types

6.3.1 Flammable gases

Precautions to be taken are outlined below.

- a) Leak check containers and connection before use.
- b) 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.
- c) Flammable gases shall be separated from other hazards. (See Section 6.1.)
- d) An energy relief wall or blast roof should be incorporated into the design if flammable gases are stored in large quantities indoors. This wall or roof is designed to allow dissipation of pressure arising from an explosion.
- e) The use of portable electronic devices, e.g. mobile handphones and walkie-talkies, is prohibited, unless the devices have been proven to be intrinsically safe.
- f) Do not vent flammable gases to the atmosphere except through a properly designed system.
- g) National regulations may limit the total quantity of flammable gases allowed to be stored and may require a risk assessment.
- h) Prohibit sources of ignition, e.g. cigarette smoking.
- i) 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 IEC (International Electro-technical Commission) or NEC (National Electrical Code).
- j) Non-sparking tools are to be used when working around flammable gases.
- k) All piping, cabinet and equipment used to handle flammable gases should have electrical continuity sources and should be earthed.
- l) Flashback arrestors should be used, where appropriate, in pipes containing flammable gases.

6.3.2 Oxidizing gases

Precautions to be taken are outlined below.

- a) Leak check containers and connection before use.
- b) Oxidizing 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.
- c) Oxidizing gases shall be separated from other hazards. (See Section 6.1.)
- d) Use only equipment designed for oxygen service.
- e) Keep oxygen systems free from external contamination.
- f) Use only oxygen compatible lubricants or sealants.
- g) Do not vent oxidizing gases to the atmosphere except through a properly designed system.
- h) Oxygen cylinders used in work areas with inadequate ventilation should have oxygen monitors to ensure that oxygen concentrations are kept below 23.5%. (See AIGA Doc. 005/04 "Fire hazards of oxygen and oxygen enriched atmospheres".)
- i) Equipment handling fluorine or fluorinated compounds may require passivation.

6.3.3 Toxic gases

Precautions to be taken are outlined below.

- a) Leak check containers and connection before use.
- b) Toxic gases shall be stored in well-ventilated areas, away from flammable gases, pyrophoric gases, flammable liquids, open flames, sparks and sources of heat.
- c) Toxic gases shall be separated from other hazards. (See Section 6.1.)
- d) Prior to entry, enclosed spaces containing highly toxic gases, including shipping containers, should be checked for leaks of the toxic gas in the absence of a maintained stationary detection system.
- e) Do not vent toxic gases to the atmosphere except through a properly designed system.
- f) Emergency showers, eyewash station and first aid stations may be required.
- g) National regulations may limit the total quantity of toxic gases allowed to be stored and may require a risk assessment review.
- h) 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.
- i) 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 be taken when handling corrosive gases are:

- a) Use the appropriate protective equipment to prevent skin contact.
- b) Equipment such as an emergency shower and eyewash station shall be available.

6.3.5 Inert gases

Inert gases may also be classified as asphyxiant gases.

- a) Leak check containers and connections before use.
- b) For inert gases being filled indoors, oxygen monitors may be required. Also refer to AIGA Doc. 008/04 'Hazards of inert gases'.
- c) Cryogenic liquid containers may continuously vent, indoor areas should be properly ventilated.

6.3.6 Pyrophoric gases

Precautions to be taken are similar to those for flammable gases.

6.3.7 Self-reacting and polymerizable gases

Precautions to be taken when handling self-reacting gases are indicated below.

- a) Leak check containers and connection before use.
- b) Enforce strict compliance to First-In-First-Out (FIFO) usage of the gas in order to control the shelf life of the filled cylinders.
- c) Minimise the causes of self-reaction or polymerization, e.g. high temperature and rust particles.

7 Handling problem gas containers

The 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 documents detail the procedures that are needed to be followed in such a situation. They are AIGA Doc. 004/04 'Handling gas containers emergencies' and EIGA Doc. 30/04 'Disposal of gases'. 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.

7.1 General principles

The general principles relating to the handling of problem containers are listed below.

- a) Only knowledgeable and well-trained response teams should handle problem ESG containers.
- b) If there is any doubt as to how to handle the situation, immediately contact the local fire brigade or emergency response contractor who will be in a better position to handle the incident.
- c) Ensure all sources of ignition are eliminated.
- d) Ensure appropriate personal protective equipment is used.
- e) Move the cylinder to a 'safe location' for disposal work, if possible.
- f) Design the gas scrubber for high temperatures generated from the heat of neutralization.
- g) After scrubbing, the empty cylinder should be marked as defective and then handled in the appropriate manner.
- h) If a valve is not operable, use specialized equipment, e.g. a cylinder drill, to access the contents of the cylinder through the cylinder wall or valve body.
- i) During scrubbing 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.
- j) Only a trained team should attempt to scrub gases from a problem cylinder.
- k) Be aware of the 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.

7.2 Flammable gases

- a) If the valve is operable, use it to vent the flammable gas to a "safe area".
- b) It is always preferable to vent the flammable gas to an incinerator or burner.

7.3 Oxidizing gases

Acidic oxidizing 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. Oxidizers such as oxygen and nitrous oxide can be vented to a safe area.

If there is any doubt on how to handle the situation, immediately contact the local fire brigade or emergency response contractor who will be in a better position to handle the incident.

7.4 Corrosive gases

Corrosive gases are either acidic or alkaline:

Acid gases

- Scrub acidic gases with a 15% w/w alkaline solution.

Alkaline gases

- Scrub alkaline gases with a 10%-20% w/w acid solution.

7.5 Inert gases

- a) Leaking inert gases can become **asphyxiants** if they are vented into a confined area.
- b) The cylinder can be vented to a safe location which must be away from a confined space.

7.6 Toxic gases

If there is any doubt as to how to handle the situation, immediately contact the local fire brigade or emergency response contractor who will be in a better position to handle the incident.

- a) For toxic gases that are **acidic**, please refer to the section above entitled, "Acid Gases".
- b) For toxic gases that are **alkaline**, please refer to the section above entitled, "Alkaline Gases".
- c) For toxic gases that are **oxidizers**, please refer to the section above entitled, "Oxidizing Gases".
- d) For toxic gases that are metal **hydrides**, refer to the two referenced documents above and/or immediately contact the emergency response contractor who will be in a better position to handle the incident.

8 References

AIGA 003/04	Security guidelines
AIGA 004/04	Handling gas container emergencies
AIGA 005/04	Fire hazards of oxygen and oxygen enriched atmospheres
AIGA 008/04	Hazards of inert gases
AIGA 009/04	Safety training of employees
AIGA 011/04	Work permit systems
AIGA 012/04	Cleaning of equipment for oxygen service
AIGA 014/05	Safety audit guidelines
AIGA 017/05	Labelling of gas containers (and associated equipment)
EIGA 13/02	Oxygen pipeline systems
EIGA 30/04	Disposal of gases
EIGA 52/04	Load securing of Class 2 receptacles
EIGA 92/03	Code of Practice – nitrogen trifluoride

Note: Additional information on handling problem cylinders can be found in the following publications:

"Disposal of Leaking Cylinders" in the seventh edition of the *Matheson Gas Data Book*, published by McGraw-Hill.

British CGA Code of Practice CP-18, "The Safe Storage, Handling and Use of Special Gases in the Micro-electronics Industry".

Compressed Gas Association P-1, "Safe Handling of Compressed Gases in Containers".

Compressed Gas Association P-22, "The Responsible Management & Disposition of Compressed Gases & Their Containers".

ISO 11625, "Gas cylinders – Safe Handling"

Appendix 1: Additional explanatory notes

1-1 Compressed gases

a) State of gases

The physical state of the compressed gas will determine, in large measure, the hazard properties. As an example, there are subsets of a compressed gas which include, but are not limited to, physical states such as liquefied, refrigerated, cryogenic, etc.

As a further example of these subsets, a high-pressure liquefied gas has a critical temperature of between -50°C and 65°C , while a low pressure liquefied gas has a critical temperature of above 65°C .

It should be noted that hydrogen fluoride and hydrogen cyanide by definition are not compressed gases; however, they are treated as such in this document, 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 or lower at 101.325 kPa (14.696 psia). Refrigerated liquids, such as nitrous oxide and carbon dioxide which have boiling points of higher than -90°C are liquid, and should not be confused with refrigerant or fluorocarbon gases. To further illustrate the impact that the physical state has on the hazard properties of the material, consider carbon dioxide (CO_2). It can be shipped as a compressed liquefied gas with UN1013, as a refrigerated liquid 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.

b) Definition of gas cylinder

In this document, a gas cylinder is defined as a container with a water capacity that does not exceed 150 litres (under section 3)

US regulations define a cylinder as a compressed gas container having a maximum water capacity of 454 litres. Newer U.S. specifications permit the use of larger sized containers having a water capacity of approximately 2268 litres.

1-2 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 a temperature of 60°C . The hydraulic forces from a liquid full container can potentially cause the container walls to rupture catastrophically. High pressure liquefied gases cannot be filled to exceed the recommended filling ratio to ensure that it will not exceed the cylinder test pressure at 65°C .

Aluminium containers when heated to a temperature of higher than 177°C can exhibit embrittlement of the aluminium alloy and should be avoided.

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

1-3 Safe handling of cryogenic gases

Cryogenic gas containers should be placed in well-ventilated areas to minimize asphyxiation, flammability, and oxidizing hazards from gases escaping from pressure relief devices. Vents from pressure relief devices must also be piped away from enclosed or poorly ventilated areas.

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

Positive pressure must 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 the walls and contaminate the cryogenic product.

The external walls of short uninsulated hoses or piping around bulk cryogenic vessels and vaporisers can reach temperatures of below the boiling point of oxygen (-183 °C). This may result in an oxygen-enriched atmosphere in the micro-environment surrounding the cold surfaces, with its inherent hazards. Precautions for oxidizing gases must 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 must also be well covered to minimise exposure of the skin and face from accidental splashes of cryogenic liquids.

The liquefaction of gases or, conversely, the 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 may result.

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-temperature combination 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.

1-4 Flammability

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

1-5 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 quantitative risk assessment taking into account prevailing climatic conditions, population densities and acceptable risk criteria laid down by local authorities.

1-6 Road transportation

For road transportation, containers are to be secured with fastening devices. (See EIGA 52/04 "Load securing of Class 2 receptacles.")

The transportation truck shall display well-positioned placards as required by national regulations. Additionally, information such as Hazchem Code, UN number and emergency contact phone number may or may not be required depending on the quantity of compressed gases shipped.

Only qualified and certified drivers are allowed to transport hazardous gases. The drivers should be trained in First Aid and in the handling of leaking hazardous gas containers.

1-7 Permit to Work system

A comprehensive “Permit to Work” system should check for:

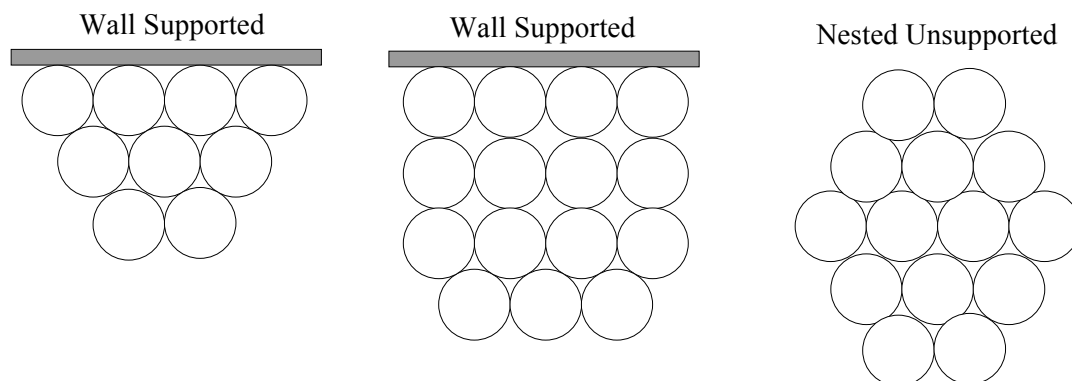
- Method Statements;
- risk assessments of the Method Statement;
- physical isolations;
- safe access and egress;
- standby man and rescue equipment; and
- self-contained breathing equipment.

(See AIGA 011/04 “Work Permit Systems”.)

1-8 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. The 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.



Appendix 2: Emergency response (ER) planning

2-1 Emergency response plan

An emergency response plan shall be created for handling specialty gases. The plan should include, but 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 MSDS with first aid information
- hazards evaluation
- working process of emergency response team
- training requirements

(See AIGA 004/04 "Handling gas container emergencies".)

2-2 Protective equipment

General considerations:

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

- perform hazard assessment of the working process,
- select and use appropriate equipment based on the 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.

Recommended equipment list:

General safety equipment:

- safety shoes
- safety gloves
- safety eye/face protection shields
- eyewash fountains/emergency showers
- safety ropes or tapes

- hazardous gas monitors
- safety signs

Specific equipment in emergency response:

a) Respiratory protection

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

- Self-contained breathing apparatus
 - 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 the airborne contaminants from otherwise respirable air.

b) Protective clothing

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:

- Fire-fighter 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.

c) Maintenance of personal protective equipment:

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

- All types of personal protective equipment (respiratory protection and protective clothing) used in a hazardous material environment must be thoroughly decontaminated before reuse.
- Gas monitors are to be calibrated regularly in accordance with the manufacturer's instructions.
- Respiratory protection equipment must be inspected routinely before and after each use and at least once a month. 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 and leg, and hand protection must be inspected after each use. Chemical exposure may damage protective clothing. Protective clothing should be stored in a proper manner to prevent mechanical damage.

- It is also important to inspect personal protective equipment periodically while in storage.

2-3 Safety audit

All specialty gases handling facilities shall be audited regularly to ensure compliance with the required operating procedures.

The audit personnel shall be qualified to perform the auditing function provided they are independent and knowledgeable of the areas being audited. (See AIGA 014/05 “Safety audit guidelines”.)

Appendix 3: Select properties of commonly used electronic specialty gases

This is published separately as AIGA 018/05 – Appendix 3.