

CGA P-46—2015

**SAFE HANDLING OF
ELECTRONIC SPECIALTY GASES**

FIRST EDITION

PREFACE

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has issued [CGA P-46](#), *Safe Handling of Electronic Specialty 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 standard for the worldwide use and application of 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), fiber 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 AIGA, CGA, EIGA, JIMGA, International Organization for Standardization (ISO), U.S. Department of Transportation (DOT), Transport Canada (TC), European Agreements Concerning the International Carriage of Dangerous Goods by Road (ADR) and by Rail (RID) as well as the regulations promulgated by the United Nations (UN), *Recommendations on the Transport of Dangerous Goods* (Orange book) [1, 2, 3, 4, 5].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 nonliquefied gas this will be highlighted. The information contained in this document was collected 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.

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

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. It 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) [3, 4].

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.²

3.2.3 Gas

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

3.2.4 Gases under pressure

Gases that are contained in a receptacle at a pressure not less than 29.0 psi (200 kPa) at 68 °F (20 °C) 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.

² kPa shall indicate gauge pressure unless otherwise noted as (kPa, abs) for absolute pressure or (kPa, differential) for differential pressure. All kPa values are rounded off per [CGA P-11](#), *Metric Practice Guide for the Compressed Gas Industry* [6].

3.2.8 Cryogenic liquid

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

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, nonpressurized 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, vapors, and mists. Such enclosures include laboratory hoods, exhaust fume hoods and similar appliances, and equipment used to locally retain and exhaust the gases, fumes, vapors, 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 59°F (15°C) 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 autodecomposition, 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 ascertained.

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 14.7 psia (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 14.7 psia (101.325 kPa, abs) pressure and at a temperature of 68°F (20°C).

3.2.14 Gas cabinet

Fully enclosed, exhausted, and noncombustible 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 psi along with the term kilopascal (kPa), 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 doesn't support human breathing and, which reacts scarcely or not at all with other substances.

3.2.22 LC₅₀

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 Oxidizing gas

Gas that can cause or contribute to the combustion of other material more than air does. Oxidizing 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*) [7].

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* [8].

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 [9].

3.2.33 Toxic gas

Compressed gas that has a LC₅₀ 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 gas-tight 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 gas-tight.

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 semiconductor 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, namely physical, chemical, health, and environmental hazards. Most gases possess more than one hazard.

Safety data sheets (SDS) 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

There are two primary physical hazards, namely 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, namely flammability, oxidizing 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, e.g., 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 autoignition temperature of less than 130 °F (54 °C) 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.

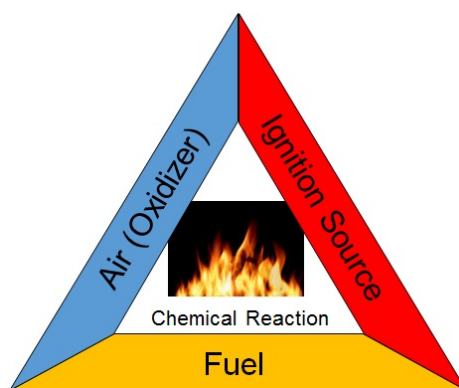


Figure 1—Fire triangle

4.2.2 Oxidizing potential

Oxidizing 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 oxidizing 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 oxidizing gases at elevated temperatures and pressures. It is, therefore, vital that all pipelines and equipment handling oxidizing gases be cleaned for oxygen service. Refer to [CGA G-4.1, Cleaning Equipment for Oxygen Service](#) for more information [10].

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

Certain finely divided metals such as aluminum, carbon steel, or/and stainless steel can also spontaneously combust in the presence of oxidizing 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 polymerizable 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, namely:

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

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, e.g., 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 such as the 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.