

CGA G-18—2016
HYDROGEN SELENIDE
FIRST EDITION

PREFACE

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has issued **CGA G-18, Hydrogen Selenide**, jointly produced by members of the International Harmonization Council and originally published by the Japan Industrial and Medical Gases Association (JIMGA) as JIMGA-T-S/85/12 *Hydrogen Selenide*.

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

Hydrogen selenide is a highly toxic, flammable, colorless gas with a disagreeable penetrating odor at room temperature and atmospheric pressure [1]. It is shipped as a liquefied compressed gas under its own vapor pressure of 138 psia at 70 °F (0.950 MPa, abs at 21.1 °C) [2]. It is also supplied in a gaseous state, diluted with other gases under pressure.

The use of hydrogen selenide has constantly been growing and this usage is expected to continue throughout the world. The issue of the safe handling of hydrogen selenide is a very important and relevant topic to the compressed gas industry as well as the user community of this electronic specialty gas.

Hydrogen selenide is used to prepare metallic selenides and organoselenium compounds. It is used in doping gas mixtures for the preparation of semiconductor materials containing a controlled amount of a significant impurity [3]. It is also used to manufacture photovoltaic cells such as copper-indium selenide/sulfide (CIS) or copper-indium-gallium-selenide (CIGS) as in thin-film deposition of multiple junction photovoltaic cells.

Hydrogen selenide can be safely handled if equipment is properly designed, maintained, and employees are trained. As a minimum, all personnel should have access to a hydrogen selenide safety data sheet (SDS) and training in the use of the SDS and other reference material.

NOTE—In this publication, hydrogen selenide is understood to be in the gaseous phase unless otherwise stated.

2 Scope and purpose

2.1 Scope

This publication is intended for the suppliers, distributors, and users of hydrogen selenide and its handling equipment. The publication includes guidance for design of equipment, cylinders and valve usage, handling controls, and safety. Guidelines on the operational steps associated with the use of hydrogen selenide and hydrogen selenide mixtures as well as fire protection, gas detection, ventilation, and related safeguards are also included. The manufacture, purification, and analysis of hydrogen selenide are beyond the scope of this publication, although the general guidance given is also relevant to these processes.

2.2 Purpose

This publication was written to address the high toxicity and flammability of hydrogen selenide where the consequences of improper handling of hydrogen selenide could cause injury, death, and/or facility damage. This publication will provide a description of the potential hazards involved in handling hydrogen selenide and the guidelines to be taken to minimize risk potential.

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 Absolute pressure**

Based on a zero reference point, the perfect vacuum. Measured from this reference, the standard atmospheric pressure at sea level is 14.696 psia (101.325 kPa, abs); however, local atmospheric pressure can deviate from this standard value because of weather conditions and the elevation above or below sea level.

3.2.2 Apparatus

Accessory equipment such as valves, pressure relief devices (PRDs), regulators, and non-return valves (check valves) used with compressed gas.

3.2.3 ADR/RID

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

3.2.4 Containers

Vessels of various shapes, sizes, and materials of construction such as cylinders, portable tanks, or stationary tanks, of designs meeting the specifications of the American Society of Mechanical Engineers (ASME), Transport Canada (TC), U.S. Department of Transportation (DOT), European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR), Japanese Industrial Standard (JIS), or national authorities and are filled with compressed gases.

3.2.5 Corrosive

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

3.2.6 Critical temperature

Temperature above which a pure gas cannot be liquefied, regardless of the degree of compression.

3.2.7 Cryogenic liquid

Refrigerated liquefied gas having a boiling point lower than -130°F at 14.696 psia (-90°C at 0.101 MPa, abs).

3.2.8 Cylinder

Transportable pressure receptacle having a water capacity that does not exceed 150 L that can be filled with a gas under pressure.

NOTE—For pure hydrogen selenide or hydrogen selenide mixtures that are classified as highly toxic, some countries prohibit the use of cylinders larger than 57 L.

3.2.9 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.

NOTE—Also known as fill density, filling factor, maximum fill degree, or maximum fill pressure.

3.2.10 Flammable gas

When either a mixture of 13% or less (by volume) with air is ignitable at 14.696 psia (0.101 MPa, abs) or has a flammable range with air of at least 12% regardless of the lower limit. These limits shall be determined at 14.696 psia (0.101 MPa, abs) pressure and at a temperature of 68°F (20°C).

3.2.11 Gas

Gas or gas under pressure as defined in United Nations (UN) *Recommendations on the Transport of Dangerous Goods, Model Regulations* and in Globally Harmonized System of Classification and Labelling of Chemicals (GHS) [4, 5].

A gas is a substance that (a) At 50°C has a vapor pressure greater than 300 kPa; or (b) Is completely gaseous at 20°C at a standard pressure of 101.3 kPa.

3.2.12 Gas supplier

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

3.2.13 Handling

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

3.2.14 Hazard

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

3.2.15 Highly toxic

Gases that have an LC_{50} in air less than or equal to 200 ppm for a 1 hr exposure. National regulations may have additional classifications.

NOTE—In this publication, ppm means parts per million by volume.

3.2.16 Hot zone

Area immediately around the chemical spill and the surrounding region that may be in serious danger from physical hazards such as fire, explosion, or chemical exposure. Generally, only firefighters and emergency response team who are members of a specialized hazardous material (HAZMAT) team will enter the hot zone.

3.2.17 Inert gas

Gas that is not toxic, doesn't support human breathing, and reacts scarcely or not at all with other substances.

3.2.18 LC_{50}

Concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50% of the entire defined experimental animal population.

NOTE—Usually measured as ppm or mg/m^3 .

3.2.19 Lower flammability limit (LFL)

Lower limit of flammability (point at which a flame just starts to propagate) of a gas or vapor at ordinary ambient temperatures and pressures expressed in percent of the gas or vapor in air by volume. The LFL will vary with temperature and pressure.

NOTE—Also referred to as lower explosive limit (LEL).

3.2.20 National standards, guidelines, regulations

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

3.2.21 Oxidizer

Gas or gas mixture that is able, at atmospheric pressure, to support the combustion more than a reference oxidizer consisting of 23.5% oxygen in nitrogen (for example, gaseous oxygen, nitrous oxide, or fluorine).

3.2.22 Pressure

Force per unit of area exerted by a gas to its surroundings. The term megapascal (MPa) will be the standard term for pressures used in this publication. 1 MPa = 1000 kPa = 20,885.4 psf = 145 psi = 10 bar.

3.2.23 Pressure relief device

Pressure and/or temperature activated device that may be used to prevent the pressure from rising above a predetermined maximum and thereby prevent equipment or container failure due to overpressurization.

3.2.24 Safety data sheet (SDS)

Written or printed information concerning a hazardous material (properties, precautions, etc.) following national regulations.

3.2.25 Test pressure

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

3.2.26 Toxic gas

Compressed gas that has an LC₅₀ in air of less than or equal to 5000 ppm but greater than 200 ppm for a 1 hr exposure. National regulations may have additional classifications.

3.2.27 Threshold limit value—Time-weighted average (TLV®—TWA)

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

3.2.28 Upper flammability limit (UFL)

Upper limit of flammability (point at which a flame can still nominally propagate) of a gas or vapor at ordinary ambient temperatures and pressures expressed in percent of the gas or vapor in air by volume. The UFL will vary with temperature and pressure.

NOTE—Also referred to as upper explosive limit (UEL).

3.2.29 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.

3.2.30 Valve protection cap

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

4 Gas properties**4.1 General**

Hydrogen selenide is a hydride gas with the chemical formula H₂Se. It is highly toxic with an established LC₅₀ of 0.3 ppm/8 hr inhalation-guinea pig. In addition to its toxicity, it is also flammable and is capable of forming flammable mixtures when mixed with air. It possesses a disagreeable, unpleasant odor. The odor threshold is less than 0.1 ppm. At higher concentrations, olfactory fatigue can rapidly occur with loss of any awareness of the gaseous odor [7].

Hydrogen selenide is routinely shipped in seamless steel or aluminum alloy cylinders. For safety reasons, cylinders used for pressurized hydrogen selenide will have a test pressure of 609 psi (4.2 MPa). Some national bodies mandate higher test pressures. The vapor pressure of hydrogen selenide is 138 psia at 70 °F (0.950 MPa, abs at 21.1 °C) [2].

Table 1 shows properties of hydrogen selenide.

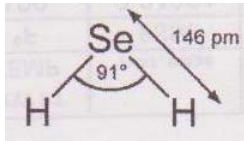
4.2 Physical properties

Hydrogen selenide is a weak acid. It is less thermally stable than hydrogen sulfide. It decomposes to elemental selenium at about 320 °F (160 °C). If ignited, it burns to give off selenium dioxide and water [3, 8]. Hydrogen selenide will react violently with nitric acid [11].

It is best to avoid sources of ignition, sparks, and flames because of the flammable properties of hydrogen selenide. The concern for explosions shall be recognized. Hydrogen selenide poses a severe fire hazard and a moderate explosion risk.

A flammable mixture of hydrogen selenide in air requires an ignition source to ignite and is not pyrophoric. The autoignition temperature of hydrogen selenide is not defined.

Table 1—Properties of hydrogen selenide

Property	SI Units	U.S. Units	Reference
Synonyms	Selenium hydride; hydrogen selenide, anhydrous; hydroselenic acid, anhydrous; dihydrogen selenide; selenium dihydride; selenane		[1]
Chemical formula	H ₂ Se		
CAS number	7783-07-5		
UN number	UN 2202		
Physical state	Gas		
Color	Colorless		[3]
Odor	Disagreeable, unpleasant. Similar to decayed horseradish or garlic		[3, 8, 1]
Molecular weight	80.976		[9]
Boiling point	−41 °C	−42 °F	[9]
Freezing point	−64 °C	−83 °F	[9]
Decomposition temperature	160 °C	320 °F	[3]
Critical temperature	138 °C	280.4 °F	[3]
Critical pressure	9017 kPa, abs	1308 psia	[2]
Critical volume	112.24 cm ³ /mol		[3]
Critical density	675.7 kg/m ³	42.18 lb/ft ³	[2]
Critical compressibility factor	0.274		[3]
Density of the liquid at −42 °F (−41 °C)	2004 kg/m ³	125.1 lb/ft ³	[2]
Density of the gas (1 atm) at −68 °F (20.0 °C)	3.348 kg/m ³	0.209 lb/ft ³	[2]
Relative density of gas at 70 °F (21.1 °C) at 101.325 kPa (air=1)	2.796		
Vapor pressure at 70 °F (21.1 °C)	0.950 MPa, abs	138 psia	[2]
Solubility in water, vol gas/vol water at 32 °F (0 °C) and 1 atm	2.05 vol/vol		[2]
pH	Acidic		[1]
Volatility	Not applicable		
Odor threshold (varies with impurities)	0.1 ppm		[1]
Lower flammability limit (LFL)	4.0%		[9, 10]
Upper flammability limit (UFL)	67.5%		[2]
Molecular shape	Bent		
Standard enthalpy of formation at 25 °C, Δ _f H ⁰ gas	+29.7 kJ/mol		[3]
Structure: H ₂ Se adopts a “bent” structure with a H-Se-H bond angle of 91°. Consistent with this structure, three IR-active vibrational bands are observed: 2358, 2345, and 1034 cm ^{−1} .			

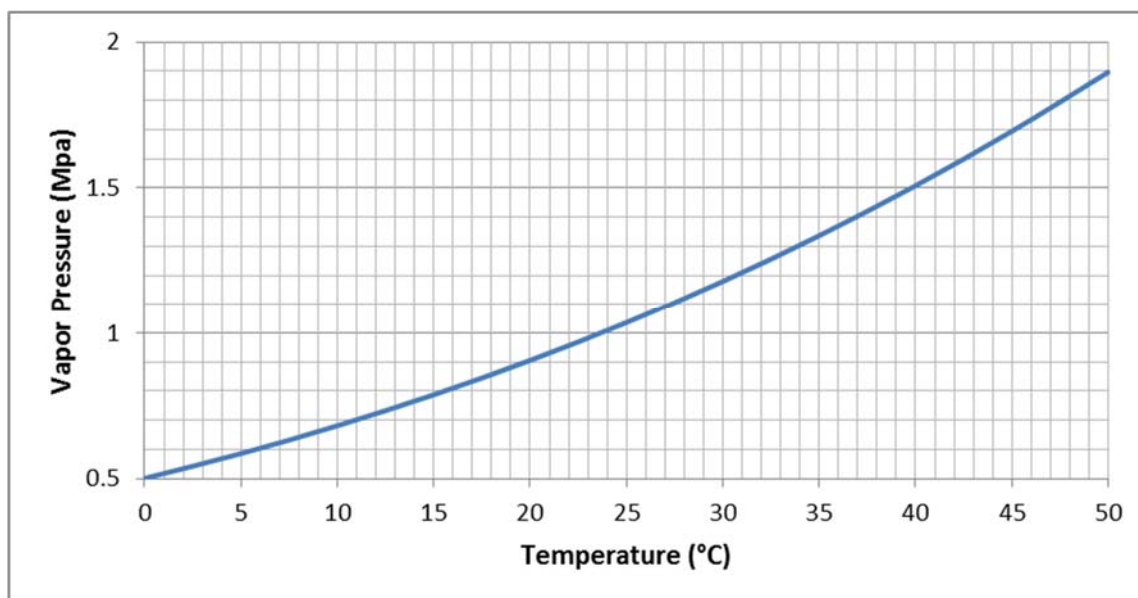


Figure 1—Hydrogen selenide vapor pressure versus temperature (SI units) [9]

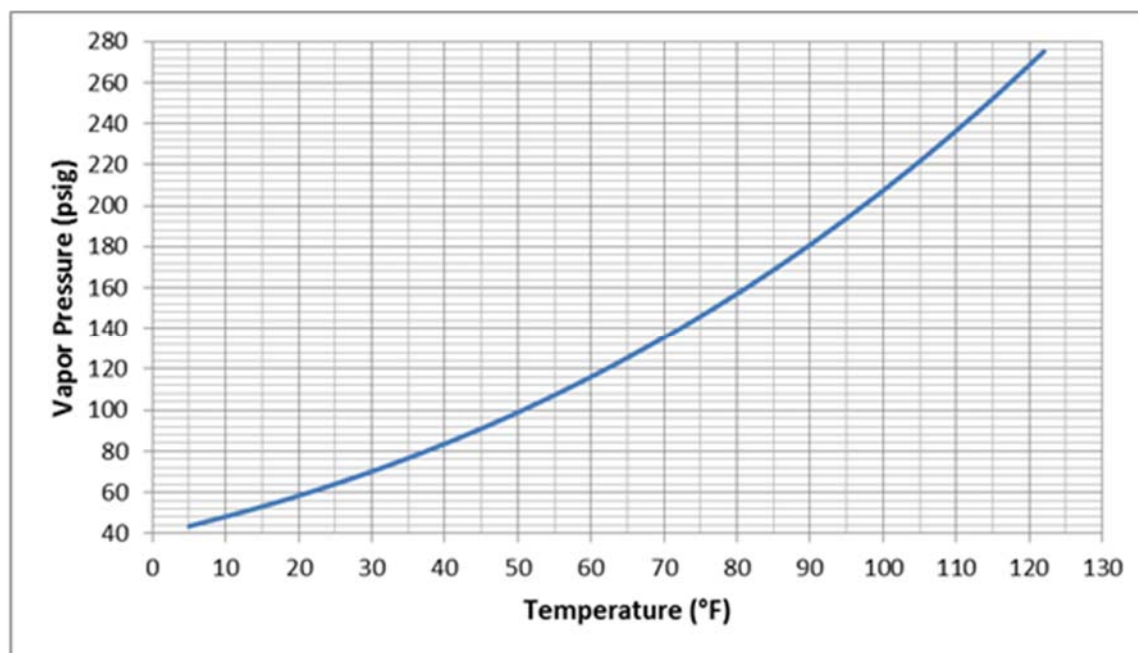


Figure 2—Hydrogen selenide vapor pressure versus temperature (US units) [9]

4.3 Chemical properties

Hydrogen selenide is incompatible with oxidizing materials, members of the halogen family, acids, other combustible materials, and will react slowly with water. Hydrogen selenide is a strong reducing agent and reacts vigorously with oxidizers such as potassium permanganate, sodium hypochlorite, oxygen, ozone, chlorine, fluorine, and nitric oxide. Hydrogen selenide can react with the alkali metal family. Hydrogen selenide, like other hydrides, is not known to polymerize.

4.4 Health properties

Refer to 5.2.

4.5 Flammability properties

Refer to 5.1.

4.6 Environmental properties

If hydrogen selenide enters the environment through an accidental release, it can contaminate land, water, and air with potentially disastrous results. Many countries have strict regulations and measures to be taken should a release occur. The users of hydrogen selenide should review the regulations that apply.

- Selenium compounds including hydrogen selenide are considered hazardous air pollutants (HAPs) in certain jurisdictions. These pollutants are known or suspected to cause liver disorders, respiratory disorders, other serious health effects, and adverse environmental effects. There is no information that hydrogen selenide will cause cancer [8, 12];
- Hydrogen selenide users should employ a variety of tools to prevent direct pollutant discharges into waterways, municipal wastewater treatment facilities, or allow polluted runoff;
- Emergency response programs are established and at times mandated to eliminate any danger to the public and the environment posed by hazardous substance releases. To help fulfill this mission, local governments may require that the person or organization responsible for hydrogen selenide use notify the government when the amount onsite reaches a predetermined limit;
- If a release or spill of hydrogen selenide occurs, the government may require additional notifications be made. These requirements vary by governments;
- Guidance documents should be obtained from the local government agency to offer direction in following regulations and control emissions. Legal action may be undertaken to pursue those who do not fully comply with the requirements of environmental legislation; and
- Risks to human health and the environment will vary considerably depending upon the type and extent of exposure. Hydrogen selenide users are strongly encouraged to characterize risk on the basis of locally measured or predicted exposure scenarios.

National agencies such as the United States Environmental Protection Agency (EPA) establish drinking water standards and have determined that selenium is a health concern at certain high levels of exposure. Pure selenium is also an essential nutrient at low levels of exposure. This inorganic chemical is found naturally in food and soils. EPA has set the drinking water standard for selenium at 0.05 ppm to protect against the risk of adverse health effects. Drinking water that meets EPA's standard is associated with little to no risk and is considered safe with respect to selenium [13]. In Japan, there is a limit of 0.01mg/l for hydrogen selenide and selenium compounds.

Risk assessment values or other media quality standards may be used in countries to evaluate the health risks posed by exposures to toxic chemicals. These values are typically specified as concentration limits that shall not be exceeded to avoid health risk. These published values can be compared directly to information about the concentration of a chemical in the environment to identify potential health hazards. If a chemical concentration exceeds a relevant media quality standard, action to reduce environmental contamination or exposure is warranted.

5 Gas hazards

5.1 Fire and explosion hazards [11, 14, 15, 16]

Hydrogen selenide is flammable and presents a severe fire hazard. The vapors are heavier than air. Vapors can ignite at ignition sources downstream and flash back to the leaking source. Vapor and air mixtures are explosive. Containers can rupture or explode if exposed to heat. The low vapor pressure of hydrogen selenide generally