

CGA G-17—2018

PHOSPHINE

SECOND EDITION

PREFACE

As part of a program of harmonization of industry standards, the Compressed Gas Association (CGA) has issued [CGA G-17, Phosphine](#), jointly produced by members of the International Harmonization Council and originally published by the Asia Industrial Gases Association (AIGA 051) and Japan Industrial and Medical Gases Association (JIMGA T-S/37) *Code of Practice Phosphine*.

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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NOTE—Technical changes from the previous edition are underlined.

NOTE—Appendix A (Normative) is a requirement.

NOTE—Appendices B and C (Informative) are for information only.

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Contents	Page
1 Introduction.....	1
2 Scope and purpose	1
2.1 Scope	1
2.2 Purpose	1
3 Definitions.....	1
4 Gas properties.....	4
4.1 General.....	4
4.2 Physical properties	4
4.3 Chemical properties.....	4
4.4 Health properties	4
4.5 Pyrophoric and flammability properties	4
4.6 Environmental properties.....	7
5 Gas major hazards.....	7
5.1 Fire and explosion hazards [21, 22, 23, 24, 25]	7
5.2 Toxicology	8
6 Gas handling equipment—general considerations.....	10
6.1 Materials of construction.....	11
6.2 Compatibility of sealing compounds	11
6.3 System pressures and overpressure protection	12
6.4 Valve types and filter types	12
6.5 Tubing.....	13
6.6 Purity	13
6.7 System leak tests and purge	13
6.8 System temperature control	13
6.9 Use of electrical control and use of <u>electrically classified</u> equipment.....	13
6.10 Monitoring system	14
6.11 Abatement system.....	15
6.12 System vent.....	15
7 Process and operation	15
7.1 Life safety control (gas detection and alarm systems)	15
7.2 Operational procedures and personnel	17
7.3 Ventilation.....	17
7.4 On-going maintenance and preventive maintenance programs.....	19
8 Gas cylinder filling/packaging.....	19
8.1 Filling facility consideration.....	19
8.2 Containers	19
8.3 Filling equipment	20
9 Storage and Handling.....	21
9.1 General guidelines	21
9.2 Storage.....	21
9.3 Handling	22
9.4 Security.....	23
10 Gas supply to point-of-use	24
10.1 Process line control	24
10.2 Regulators	24

11	Gas abatement systems.....	24
11.1	Basic principles of abatement.....	24
11.2	User requirements	27
11.3	Waste stream disposal	27
11.4	Waste management	27
12	Emergency response	28
12.1	Preparation	28
12.2	Response	29
13	References	29

Tables

Table 1—Properties of phosphine.....	5
Table 2—Regulatory exposure limits for phosphine	10
Table 3—Material compatibility guide [33]	11

Figures

Figure 1—Phosphine vapor pressure curve (SI Units).....	6
Figure 2—Phosphine vapor pressure curve (U.S. Units)	6

1 Introduction

Phosphine is a toxic, colorless gas with an odor of decaying fish or more commonly like that of welding grade acetylene. It is shipped as a liquefied compressed gas under its own vapor pressure of 516 psi (3558 kPa). It is also supplied in a gaseous state, diluted with other gases under pressure. It is flammable, pyrophoric, and highly toxic.

The issue of the safe handling of phosphine is a very important and relevant topic to the compressed gas industry as well as the user community of this specialty gas.

Phosphine is used as a doping agent for silicon-based solid state electronic devices. It is thermally diffused into the silicon layer using furnaces or by an ion implantation system (n-type dopant). It is also used to manufacture compound semiconductors such as light-emitting diodes (LEDs) by reaction with a metal organic such as trimethyl gallium forming a gallium phosphide layer. Phosphine is also used in the semiconductor industry to grow a capping layer. Phosphine can be inadvertently generated in mining and manufacturing processes involving phosphorous compounds and paints and herbicides containing phosphorous compounds. Phosphine is also used as a fumigant for grain.

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

NOTE—In this publication, phosphine 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 phosphine and its handling equipment. This publication includes guidance for design of equipment, selection of cylinders and valves, handling controls, and safety practices. Guidelines on the operational steps associated with the use of phosphine and phosphine mixtures as well as fire protection, gas detection, ventilation, and related safeguards are also included. The manufacture, purification, and analysis of phosphine 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 phosphine where the consequences of improper handling of phosphine could cause injury, death, and/or facility damage. This publication provides a description of the potential hazards involved in handling phosphine and the guidelines to follow 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 101.325 kPa, abs (14.696 psia); 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, non-return valves (check valves) used with compressed gas.

3.2.3 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)* [1, 2].

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 [1, 2].

3.2.4 Containers

Vessels of various shapes, sizes, and materials of constructions such as cylinders, portable tanks, or stationary tanks, and of designs meeting the specifications of the American Society of Mechanical Engineers (ASME), Transport Canada (TC), United States 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].

3.2.5 Critical temperature

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

3.2.6 Cylinder

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

3.2.7 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.

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

3.2.8 Flammable gas

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

3.2.9 Gas supplier

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

3.2.10 Handling

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

3.2.11 Hazard

Any condition that could cause injury to personnel or property.

3.2.12 Highly toxic

Gases that have an LC_{50} in air less than or equal to 200 ppm for a 1 hour exposure, which corresponds to gases classified as Acute Toxicity Category 1 according to UN GHS [2]. Refer to 3.2.15.

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

3.2.13 Hot zone

Area immediately around the chemical spill and the surrounding region that could be in serious danger from physical hazards such as fire, explosion, or chemical exposure.

NOTE—Generally, only firefighters and the emergency response team who are members of a specialized hazardous material (HAZMAT) team will enter the hot zone.

3.2.14 Inert gas

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

3.2.15 Lethal concentration 50 (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 population.

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

3.2.16 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 pressure 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).

3.2.17 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.

3.2.18 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).

3.2.19 Pressure

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

3.2.20 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.

3.2.21 Pyrophoric gas

Flammable gas that ignites spontaneously in air at a temperature of 54 °C (129 °F) or less.

3.2.22 Safety data sheet (SDS)

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

3.2.23 Test pressure

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

3.2.24 Toxic gas

Compressed gas that has a LC_{50} in air of less than or equal to 5000 ppm but greater than 200 ppm for a 1-hour exposure, which includes gases classified as Acute Toxicity Category 2 and 3 according to UN GHS [2].

3.2.25 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 [4].

3.2.26 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 pressure 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).

3.2.27 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.

3.2.28 Valve protection cap

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

4 Gas properties**4.1 General**

Phosphine is a metal hydride gas with the chemical formula PH_3 . It is highly toxic with an established LC_{50} 1 hour of 20 ppm and LC_{50} 4 hour of 10 ppm. In addition to its toxicity, it is also flammable and explosive in air, and can autoignite at ambient temperatures. It is not considered to be corrosive in the dry gaseous state. It is slightly soluble in water and soluble in most organic solvents. It possesses an odor of decaying fish and welding grade acetylene [2].

Table 1 shows properties of phosphine.

Figure 1 and Figure 2 show a vapor pressure curve for phosphine.

4.2 Physical properties

Avoid sources of ignition, sparks, and flames due to the flammable properties of phosphine. Avoid contact with air as phosphine is pyrophoric and can form explosive mixtures in concentrations of 1.6% or greater in air. Phosphine poses a severe fire hazard and an explosion risk. Phosphine is stable at room temperature and begins to decompose at approximately 375 °C (707 °F) with complete decomposition at approximately 593 °C (1100 °F) [5].

4.3 Chemical properties

Phosphine is incompatible with oxidizing materials, members of the halogen family, and acids. Phosphine is a strong reducing agent and reacts vigorously with oxidizers such as potassium permanganate, sodium hypochlorite, oxygen, ozone, chlorine, fluorine, and nitric oxide. Phosphine can have some reaction with water and the alkali metal family.

Phosphine is not known to polymerize.

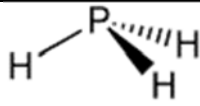
4.4 Health properties

Refer to 5.2.

4.5 Pyrophoric and flammability properties

Refer to 5.1.

Table 1—Properties of phosphine

Property	SI units	U.S. units	Reference
Synonyms	hydrogen phosphide, phosphorous hydride, phosphorated hydrogen		
Chemical formula	PH ₃		
CAS number	7803-51-2		
UN number	UN 2199		
Physical state	Gas		
Color	Colorless		
Odor	decaying fish; <u>welding grade acetylene</u>		
Molecular weight	33.998		
Boiling point at 1atm	−87.74 °C	−125.93 °F	[6]
Melting point at 1 atm	−133.78 °C	−208.8 °F	[6]
Decomposition temperature range	375 °C to 593 °C	707 °F to 1100 °F	[5]
Critical temperature	51.6 °C	124.88 °F	[5]
Critical pressure	6.536 MPa, abs	947.97 psia	[5]
Critical volume	113.32 cm ³ /mol	6.915 in ³ /mol	[6]
Critical density	0.3 g/cm ³	18.7 lb/ft ³	[6]
Critical compressibility factor	0.274		[6]
Density of liquid at 25 °C at 3.46 MPa	0.491 g/cm ³	30.65 lb/ft ³	[6]
Density of gas at 21.1 °C at 101325 Pa	1.408 kg/m ³	0.0879 lb/ft ³	[6]
Specific gravity of gas at 25 °C and 1 atm (air =1)	1.184		
Vapor pressure at 21.1 °C (70 °F)	3558 kPa	516 psi	[7, 8]
Latent heat of vaporization at 25 °C (77 °F)	204.7 kJ/kg	88 Btu/lb	
Solubility in water at 25 °C and 101325 Pa	269.7 ppm (wt)		[6]
pH	Not applicable		
Volatility	Not applicable		
Odor threshold (varies with impurities)	0.03 ppm to 3 ppm		[9, 10]
Evaporation rate	Not applicable		
Flash point	Not applicable		
Lower flammability limit (LFL)	1.6, 1.8%		[11, 12, 13]
Upper flammability limit (UFL)	98%		[14, 15]
Autoignition temperature	37.8 °C	100 °F	[5, 15, 16]
Molecular shape	trigonal pyramidal		
Dipole moment	0.58 D		[17, 18]
Standard enthalpy of formation at 25 °C, ΔH ⁰ _{gas}	+5.4 kJ/mol		[19, 20]
Structure			

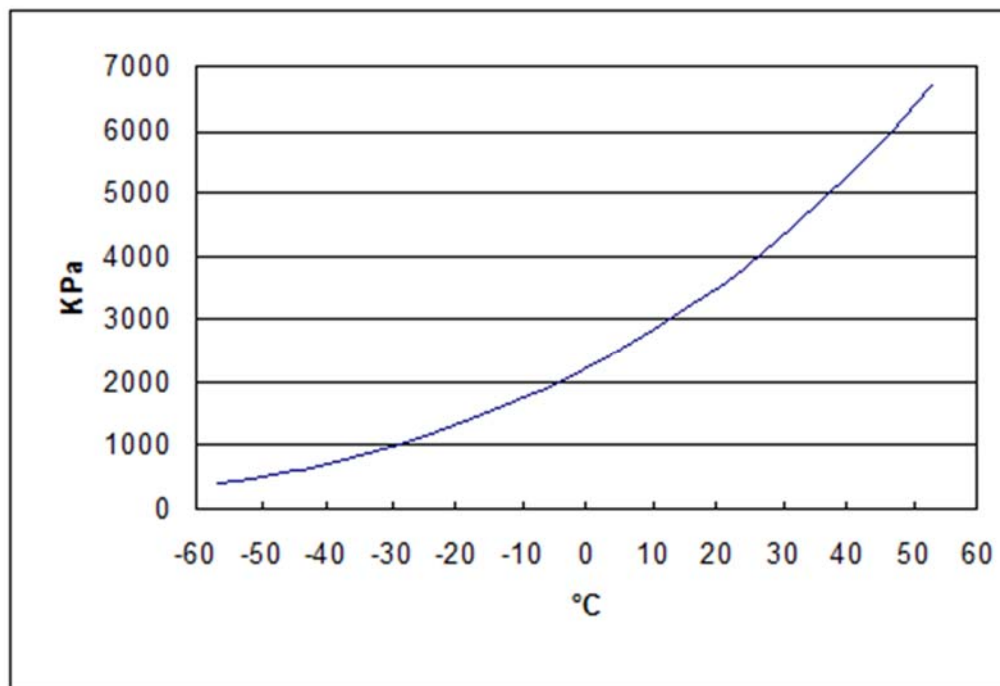


Figure 1—Phosphine vapor pressure curve (SI Units)

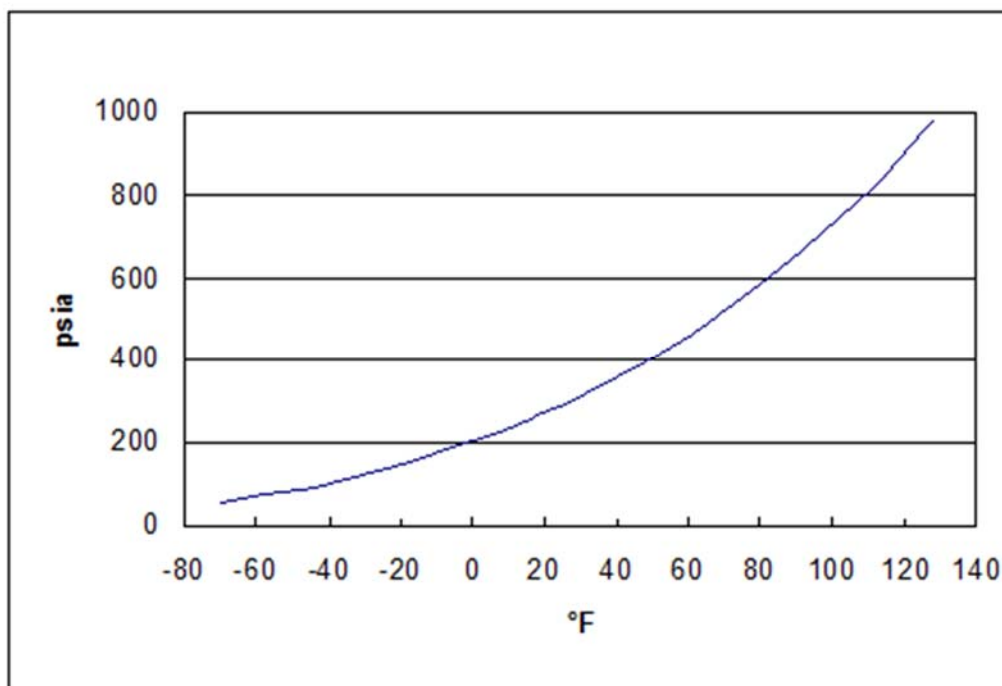


Figure 2—Phosphine vapor pressure curve (U.S. Units)

4.6 Environmental properties

With controls, phosphine releases can be minimized and pose no threat to human life and the environment.

Phosphine released into the atmosphere reacts principally with the hydroxyl ion (OH^-) radical to form hydroxy phosphide ion (OHP^-). The eventual products will be water and phosphorus oxyacids. Phosphine is also removed from air by soils and oxidized to orthophosphate. Many countries have regulations with measurable action to be taken if a release occurs. The users of phosphine shall review application regulations.

- Phosphine is considered a hazardous air pollutant (HAP). It is known or suspected to cause serious health effects and/or adverse environmental effects;
- Phosphine 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 can require that the person or organization responsible for phosphine use notify the government when the amount on-site reaches a predetermined limit;
- Guidance documents should be obtained from the local government agency to offer direction in following regulations and control emissions; and
- Risks to human health and the environment vary considerably depending upon the type and extent of exposure. Phosphine users are strongly encouraged to characterize risk on the basis of locally measured or predicted exposure scenarios.

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 risks. 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 major hazards

5.1 Fire and explosion hazards [21, 22, 23, 24, 25]

Phosphine is flammable and explosive in air and can autoignite at ambient temperatures.

The lower flammability limit (LFL) is reported to be 1.6% to 1.8% by volume in air [11, 12, 13]. The upper flammable limit (UFL) is 98% [14, 15]. When phosphine burns, it produces a dense white cloud of phosphorus pentoxide (P_2O_5) fumes. These fumes are a severe respiratory tract irritant due to the rapid formation of orthophosphoric acid (H_3PO_4) on contact with moisture (water) in human lungs.

Therefore, personnel shall wear protective clothing and self-contained breathing apparatus (SCBA) when fighting phosphine fires. Only trained personnel should respond to phosphine fires.

As in the case of a fire of any flammable gas, the flow should be stopped if it is safe and practical to do so. Normally, this can be accomplished by shutting off the cylinder valve if safe to do so.

Flammable gases shall not be used near open flames, sources of heat, or adjacent to oxidizers and non-explosion proof electrical systems. Transportation, storage, and use of phosphine should be in well-ventilated areas.

In order for a phosphine ignition to occur, two conditions need to occur simultaneously:

- concentration of phosphine is within its flammable limits; and
- sufficient air or an alternate oxidizing source is present.

Since phosphine is a pyrophoric gas, no source of ignition is required.

Phosphine can begin to slowly decompose into its elements of phosphine and hydrogen at temperatures of 375 °C (707 °F) [5].

The presence of impurities, particularly diphosphine ($\text{PH}_2\text{-PH}_2$), often causes phosphine to ignite spontaneously at room temperature and can form explosive mixtures with air as low as 1.6% [11]. However, it should be noted that phosphine can diffuse into the atmosphere without autoignition when a fume hood, cabinet, or other ventilated area exhaust velocity is high.

If the flow of phosphine cannot be stopped, let it burn until the fire stops naturally, keeping adjacent cylinders and equipment cool. If a phosphine fire is extinguished and the flow of phosphine is not stopped, a hazardous combustible mixture can continue to form. It is possible that the mixture can then be auto-ignited even under low oxygen concentration and any unburned phosphine can ignite violently, explode, cause more damage, and restart the fire. Measures shall be taken to protect persons from cylinder rupture in the case of cylinder failure or piping failure.

Although a phosphine fire shall not be extinguished until the flow of phosphine is stopped, water sprays should be used to extinguish any secondary fire and to prevent the spread of fires. The phosphine containing equipment can be kept cool by water sprays to decrease the rate of phosphine release or to prevent further damage. This is best done at a distance. A controlled water spray can help knock down and minimize the dispersion of phosphine and phosphine by-products in the gas cloud. Water used in firefighting can become contaminated when in contact with the oxidized phosphine by-products (phosphorus oxides and/or oxyacids), so there should be measures in place to contain and possibly treat such contaminated water.

Remote controlled water spray equipment is preferable to the use of hoses in cooling equipment and to reduce the spread of fire. Should the use of hoses become necessary, operating personnel should remain behind protective structures, upwind of the fire, and wear protective clothing and SCBA.

Firefighting or other emergency personnel should communicate and cooperate with personnel who are familiar with the physical and toxicological properties of phosphine. They should also communicate and cooperate with personnel who are familiar with materials in the area of the emergency. Unexpected conditions may require special actions.

If a cylinder of phosphine or supply piping system is ruptured so that quantities of phosphine are released and ignited, hazardous conditions can exist:

- Flame effects—The major concern is that the flames can impinge on surrounding valves and piping thus weakening these structures potentially leading to failure. Fire balls or jet fires can be present. Wind velocity and direction can change the shape of the fire ball or jet to an elliptical shape and push it further downwind of the release;
- Radiation effects—The major concern is that radiation effects from the fire can result in the excessive heating of adjacent equipment and process lines; and
- Reaction by-products—Oxidation of phosphine yields water and phosphorus oxides and oxyacids.

A thorough process hazard analysis (PHA) with identified sufficient safeguards shall be in place to minimize the risk of a potential incident.

5.2 Toxicology

5.2.1 Phosphine exposure

Phosphine is highly toxic to the human respiratory system and organs. Phosphine has an odor of decaying fish or welding grade acetylene. The odor of phosphine depends on the impurities it contains and the environment into which it is released.

The main hazard to humans is the possibility of unrecognized occupational exposure to phosphine causing acute poisoning. Neither smell nor sensory irritation can be relied upon for warning of toxic concentrations, especially in the presence of other fumes, gases, or vapors. Approximately 20% to 50% of persons can detect the odor threshold value of 0.03 ppm to 3 ppm [9, 10].