

Material Safety Data Sheet for Phosphine (PH₃)

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Section 1: Chemical Product and Company Identification

Material Name:	Phosphine
Chemical Formula	: PH ₃
Synonyms:	Hydrogen phosphide, phosphoretted hydrogen, phosphorus trihydride, phosphorus hydride.
Manufacturer:	Voltaix, Inc.: Post Office Box 5357, North Branch, New Jersey 08876-5357, USA Voice: 908-231-9060 or 800-VOLTAIX, Facsimile: 908-231-9063

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Section 2: Composition/Information on Ingredients

Component	CAS Registry Number	Molar (volume) concentration	Exposure Guidelines
Phosphine	7803-51-2	100%	0.3 ppm TLV-TWA (ACGIH) 1 ppm TLV-STEL (ACGIH)

Section 3: Hazards Identification

Emergency Overview

Phosphine is a colorless gas with an odor that has been described, by various observers, as similar to that of garlic, rotting fish or stale urine. As exposure deadens the sense of smell, do not use smell to determine phosphine concentration. Phosphine's immediate health hazards are that it is a toxic gas and may cause thermal burns. It is a flammable gas that is *usually* pyrophoric (autoigniting in air). It may form mixtures with air that do not autoignite, but are flammable or explosive. Phosphine is reactive with oxidizers, halogens, and nitric acid.

NFPA 704 Rating (determined by Voltaix, Inc.):

Health 4, Fire 4, Reactivity 1, Special none *Note*: NFPA 49-1991 lists "Health 3" and "Reactivity 4", but these are not consistent with NFPA 704-1990.

In an emergency, Call CHEMTREC at 800-434-9300 or 703-527-3887.

Potential Health Effects

Routes of Exposure: At low concentrations, the primary route is inhalation. At high concentrations, phosphine autoignites, creating a thermal burn risk, but reducing the toxic hazard.

Lengths of Exposure: Phosphine has been found to be a severe respiratory irritant in short term human exposures. It has been found in animal studies to be toxic in acute (4 hour) tests and subacute (4 hours/day for two months) tests.

Severity of Effect: Depends on concentration and duration.

Target Organs: Respiratory and cardiovascular systems. Neurological and gastrointestinal effects have also been reported, as have renal and hepatic toxicity.

Type of Effect: Respiratory irritation and impairment, pulmonary edema, cardiovascular (including myocardial) injury, gastrointestinal irritation.

Signs and Symptoms of Exposure: Shortness of breath; chest tightness; headache; vertigo; weakness; fatigue; and nausea, vomiting, and diarrhea.

Medical Conditions that may be Aggravated by Exposure: None identified.

Reported Carcinogenic and Reproductive Effects: NTP has not reported genetic or long-term toxicology and carcinogenesis effects studies.

Section 4: First Aid Measures

Inhalation

This is the primary route of exposure.

- 1. Remove the affected person from the gas source or contaminated area. Note: Personal Protective Equipment (PPE), including positive pressure, self contained breathing apparatus, may be required to assure the safety of the rescuer.
- 2. If the affected person is not breathing spontaneously, administer rescue breathing.
- 3. If the affected person does not have a pulse, administer CPR.
- 4. If medical oxygen and appropriately trained personnel are available, administer 100% oxygen to the affected person.
- 5. Summon an emergency ambulance. If an ambulance is not available, contact a physician, hospital, or poison control center for instruction.
- 6. Keep the affected person warm, comfortable, and at rest while awaiting professional medical care. *Monitor the breathing and pulse continuously*. Administer rescue breathing or CPR if necessary.

Skin Contact

Flush with a copious stream of water while removing contaminated clothing. Continue flushing until the professional medical assistance arrives, but for no less than fifteen minutes. Assume the patient has also been exposed by inhalation and obtain professional medical assistance immediately. Treat thermal burns by assuring that affected area is cool by flushing with cool water, then apply dry sterile dressings. If the patient is burned on the face, neck, head, or chest, assume that the airway may also have been burned and obtain professional medical assistance immediately.

Eye Contact

Flush continuously with clean water until the professional medical assistance arrives, but for no less than thirty minutes. Continuation of flushing until patient is transferred to an ophthalmologist or emergency physician is recommended.

Ingestion

Ingestion is not an observed route of exposure to gaseous hazardous materials.

Chronic Effects

None is known to Voltaix, Inc.

Note to Physicians:

The reaction product of phosphine and moist air is phosphoric acid. Therefore, skin and eye burns should be treated as both thermal and chemical.

Section 5: Fire Fighting Measures

Flammability and Explosivity

Flash Point: Not applicable, this material is a gas.

Flammability Limits in Air: Unknown.

Autoignition Temperature: Approximately 38 deg. C (100 deg. F). Phosphine usually autoignites in moist air.

Flammability Classification (per 29 CFR 1910.1200): Flammable gas.

Known or Anticipated Hazardous Products of Combustion: Phosphorus oxide, which dissolves in water to form phosphoric acid.

Properties that may Initiate or Intensify Fire: Heating cylinder to the point of initiating decomposition of the phosphine or activating the pressure relief device.

Reactions that Release Flammable Gases: Thermal decomposition releases hydrogen.

Extinguishing Media

None.

<u>Fire Fighting Instructions</u>

The only safe way to extinguish a flammable gas fire is to stop the flow of gas. If the flow cannot be stopped, allow the entire contents of the cylinder to burn. Cool the cylinder and surroundings with water from a suitable distance. Extinguishing the fire without stopping the flow of gas may permit the formation of ignitable or explosive mixtures with air. These mixtures may propagate to a source of ignition.

Excessive pressure may develop in gas cylinders exposed to fire, which may result in explosion, regardless of the cylinder's content. Cylinders with pressure relief devices (PRD's) may release their contents through such devices if the cylinder is exposed to fire. Cylinders without PRD's have no provision for controlled release and are therefore more likely to explode if exposed to fire.

Positive pressure, self contained breathing apparatus is required for all fire fighting involving hazardous materials. Full structural fire fighting (bunker) gear is the *minimum* acceptable attire. The need for proximity, entry, and flashover protection and special protective clothing should be determined for each incident by a competent fire fighting safety professional.

Section 6: Accidental Release Measures

Containment

This material is a gas at atmospheric conditions. The only means of containment is the enclosure of the space into which the material is released. Such containment is described in <u>Section 7</u>.

<u>Clean Up</u>

Clean up consists of passing the entire gas volume of the enclosure through appropriate exhaust gas treatment equipment (EGTE). Purge the enclosure with a non-reactive gas, such as nitrogen, through the EGTE until an acceptably low level of contamination remains. Equipment contaminated by this material must then be cleaned or decommissioned appropriately.

Evacuation

If the release is not contained in an appropriate device or system, all personnel not appropriately protected (see <u>Section 8</u>) must evacuate the contaminated spaces. Consider evacuation of additional areas, as a precaution against the spread of the release or subsequent explosion or fire.

Special Instructions

Most, but not all, releases of phosphine into air will autoignite. As not all leaks will autoignite, consider the possible formation of ignitable or explosive mixtures with air.

Section 7: Handling and Storage

Handling

Handle this material only in sealed, purged systems. The design of handling systems for hazardous materials is beyond the scope of this MSDS, and should be performed by a competent, experienced professional. Consider the use of doubly-contained piping; diaphragm or bellows sealed, soft seat valves; backflow prevention devices; flash arrestors; and flow monitoring or limiting devices. Gas cabinets, with appropriate exhaust treatment, are recommended, as is automatic monitoring of the secondary enclosures and work areas for release.

Handle sealed gas cylinders in accordance with CGA P-1, Safe Handling of Compressed Gases in Containers.

Some material may have accumulated behind the outlet plug. Face the outlet away from you and wear appropriate protective

equipment when removing the plug to connect the cylinder to your system.

Never introduce any substance into a gas cylinder. If you believe your cylinder may have been contaminated, notify Voltaix, Inc. immediately. Provide as much information as possible on the nature and quantity of contamination.

Storage

Store cylinders in accordance with CGA P-1, *Safe Handling of Compressed Gases in Containers*, local building and fire codes and other relevant regulations. Materials should be segregated, by the hazards they comprise, for storage.

Protect the cylinders from direct sunlight, precipitation, mechanical damage, and temperatures above 55 deg. C (130 deg. F).

Ship and store cylinders with the outlet plug and valve protective cap in place.

Section 8: Exposure Control/Personal Protection

Engineering Controls

Local exhaust is required. Secondary containment, with appropriate exhaust gas treatment, is strongly encouraged and is required in some jurisdictions.

Monitor the work area and the secondary containment continuously for release of the material. Automatic alerting of personnel and automatic shutdown of flow are appropriate in most applications and are required in some jurisdictions.

Purge all primary containment systems with a nonreactive gas, such as nitrogen, before introducing phosphine.

Personal Protective Equipment (PPE)

Respiratory Protection: Positive pressure, full face, air supplied breathing apparatus should be used for work within the secondary containment equipment if a leak is suspected or the primary containment is to be opened, *e.g.*, for a cylinder change. Air supplied breathing apparatus is required for response to demonstrated or suspected releases from the primary containment.

Eye/Face Protection: When using respiratory protection as described above, use a face mask that provides splash and impact protection for the face and eyes. For handling sealed cylinders, wear safety glasses.

Skin Protection: Wear appropriate gloves when handling sealed cylinders. Use gloves and other skin protection, as assigned by a competent safety professional, when working within the secondary enclosure with the primary enclosure compromised, *e.g.*, cylinder changing, to protect both from exposure to the material and from fire that may result from its release to the air.

Other Protection: Wear appropriate protective footwear when moving cylinders.

Exposure Guidelines

TLV-TWA: 0.3 ppm (ACGIH).

TLV-STEL: 1 ppm (ACGIH).

PEL- TWA: 0.3 ppm (0.4 mg/m³) (OSHA).

PEL-STEL: 1 ppm (1 mg/m³) (OSHA).

REL-TWA (10 hour): 0.3 ppm (NIOSH).

REL-STEL: 1 ppm (NIOSH).

IDLH: 200 ppm (Reported by ACGIH to have been established by NIOSH).

Note: This is approximately ten times the value ACGIH claims as the one hour LC_{50} . Its validity as an IDLH is therefore suspect.

Section 9: Physical and Chemical Properties

Notes:

- 1. "N/A" means not applicable.
- 2. Unless otherwise specified, properties are reported at 0 deg. C (32 deg. F) and 1 atmosphere (1.0 bar, 14.7 psia).

Property	Phosphine	
Appearance	colorless	
Odor	garlic, decomposing fish, stale urine	
Physical state at atmospheric conditions	gas	
pH	N/A	
Vapor Pressure	35.6 bar (517 psia) at -20 deg. C (68 deg. F)	
Vapor Density	1.53 g/L	
Boiling point (at 1 atm)	-87.7 deg. C (-125 deg. F)	
Melting point	-1338 deg. C (-208 deg. F)	
Solubility in water (v/v, at 20 deg. C)	0.27	
Specific gravity of liquid (water = 1)	0.74 at-87.7 deg. C (-125 deg. F)	
Molecular weight	34.00	

Section 10: Stability and Reactivity

Chemical Stability: Phosphine is stable at room temperature. At elevated temperature (above 150 deg. C), phosphine decomposes to phosphorus and hydrogen. Diphosphine may also result from thermal decomposition.

Conditions to Avoid: Temperatures above 55 deg. C, sources of ignition, exposure to air.

Incompatibility with Other Materials: Oxidizers, halogens, nitric acid.

Hazardous Decomposition, Reaction and Oxidation (other than burning) Products: Phosphorus oxide, phosphorus, hydrogen, diphosphine.

Hazardous Polymerization: Not reported to occur.

Section 11: Toxicological Information

Acute Data (by route): Exposure by inhalation: LC_{50} , 4-hour, rat is reported both as 11 ppm and 57 ppm. The other data, summarized in the table below, are more consistent with the higher of these two values. The primary effect is respiratory irritation and pulmonary edema. Reaction with air may produce irritation or thermal burns to skin, eyes and mucous membranes.

Effect	Species	Time	Concentration (ppm)	Concentration, adjusted to one hour
LC ₅₀	Rat	4 hour	11	22
LC ₅₀	Rat	4 hour	57	114
LCLO	Human	5 minutes	1000	289
LCLO	Mouse	2 hour	271	383
LCLO	Cat	2 hour	50	71
LCLO	Rabbit	20 minutes	2500	1443
LCLO	Guinea Pig	4 hour	100	200
LCLO	Mammal	5 minutes	1000	289

Chronic and Subchronic Data: Rats exposed to 4 ppm, 4 hr for 9 of 12 days exhibited reduced weight gain and some respiratory irritation, but returned to normal during 2 week recovery. Exposure of unspecified animals to 5 ppm for 4 hours per day for 2 months did not produce fatalities, similarly exposure to 10 ppm for seven days did, but to what fraction of the exposed population was not reported. Phosphine is listed in the *Registry of Toxic Effects of Chemical Substances* (RTECS), but no information on its carcinogenicity is available.

Phosphine is suspected as the cause in an acetylene generator operator death; the exposure was estimated to be 8 ppm, for 1 to 2 hours per day. Other, more toxic, hydrides, *e.g.*, arsine and hydrogen selenide, may have been present in that case.

Autopsy findings on humans believed to have died from phosphine exposure include pulmonary edema, diffuse cardiovascular injury, and focal myocardial necrosis.

Diarrhea, nausea and vomiting, chest tightness, cough, headache, dizziness have been reported in intermittent human exposure up to 35 ppm, averaging 10 ppm. No cumulative effects were observed.

Special Studies: None known to Voltaix, Inc.

Section 12: Ecological Information

Ecotoxicity: None known to Voltaix, Inc.

Environmental Fate: None known to Voltaix, Inc.

Section 13: Disposal Considerations

Classification under RCRA, 40 CFR 261: Phosphine has been assigned the Hazardous Waste Number P096. It meets the criteria for an "acute hazardous waste".

US EPA waste number and descriptions: P096 (Phosphine).

Special Instructions and Limitations: Treat process and other exhaust streams appropriately before release to the atmosphere.

Notice: The information above is derived from Voltaix, Inc.'s interpretation of the US federal laws, regulations and policies concerning the material, as shipped by Voltaix, Inc., at the time this MSDS was prepared. Federal controls are subject to change and state and local controls may also apply. Proper waste disposal is the responsibility of the owner of the waste. The user is encouraged to consult with appropriate experts in developing a disposal plan.

Section 14: Transport Information

Basic Description: Phosphine, Division 2.3 (Poison Gas, Flammable Gas), UN 2199 Poison - Inhalation Hazard, Inhalation Hazard Zone A.

Additional Information for shipment by water. IMDG Page Number 2172.

Additional Information for shipment by air: Transportation by air is not

Section 15: Regulatory Information

TSCA Status: This material is listed in the index of chemical substances.

CERCLA Reportable Quantity (40CFR302.4): This material is listed; the Final Rule Reportable Quantity (RQ) is 45.4 kg (100 lb).

SARA Title III Status (Section 302 (40CFR355), Section 311/312, Section 313 (40CFR372)): 40CFR355 lists phosphine as an Extremely Hazardous Substance with a Threshold Planning Quantity (TPQ) of 227 kg (500 lbs.) and a Reportable Quantity (RQ) of 45.4 kg (100 lb). Phosphine is not listed in 40CFR372.

Note: State and local requirements may be more stringent.

Section 16: Other Information

<u>References</u>

Book of SEMI Standards, Facilities Standards and Safety Guidelines. Mountain View, CA: Semiconductor Equipment and Materials International, 1993.

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Documentation of TLV's and BEI's. Cincinatti, Ohio: American Conference of Government Industrial Hygienists, 1992.

Effects of Exposure to Toxic Gases: First Aid and Treatment. Lyndhurst, NJ: Matheson Gas Products, 1977.

Fire Protection Guide on Hazardous Materials. Quincy, MA: National Fire Protection Association, 1991.

Safe Handling of Compressed Gases in Containers (Pamphlet P-1). Arlington, VA: Compressed Gas Association, Inc., 1991.

Revision Indication

This MSDS was completely rewritten for this release.

Disclaimer

Voltaix, Inc. cannot guarantee that these are the only hazards that exist. Users are solely responsible for the safe storage, handling, use and disposal of this material, and for compliance with the applicable laws, regulations and accepted practices.

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