Gas Mixture Toxicity

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Classification of a gas mixture containing a toxic gas has always been a matter for debate. On one side is science while the other is based on emotions. People have a natural fear of toxic compounds, they believe that they can never be made non toxic just by dilution. The science of toxicology is based on exposure of a group of tests animal to a diluted mixture of a toxic compound in air and time (dose). For gases it is by inhalation.

A toxic material can have an acute (short term exposure) and/or a chronic (long term exposure) affect. For Emergency Response acute exposure is the most critical limit.

Toxic Classification

In transportation the authorities are concerned with acute exposures that can occur due to a motor vehicle or handling accident, therefore they base the classification on LC_{50} values. This is representative of a high level single dose exposure of a short duration. The LC_{50} is Lethal Concentration 50%. For gases the test method is defined as 10 (5 male and 5 female) white albino rats exposed for 1 hour to a specific concentration. They are then observed for 14 days. If 50% die in this time period, the concentration used is the LC_{50} value. GHS (Globally Harmonized System) uses a 4 hr exposure which is equal to ½ of the 1 hr value.

Gases and their mixtures are classified as Toxic when their LC_{50} value is <5000 ppm. They are Highly Toxic if their LC_{50} value is <200 ppm. In the US this is further broken down into 4 levels

Zone A – 0-200 ppm
Zone B – 201-1000 ppm
Zone C – 1001-3000 ppm
Zone D – 3001-5000 ppm

The ISO standard 10298 *Gas cylinders — Gases and gas mixtures — Determination of toxicity for the selection of cylinder valve outlets* summarizes gas LC_{50} values based on validated toxicity studies for pure gases or an estimated value based on studies that may not be the same (different animal, time, number of animals, etc) as the method described above. Phosphine has a LC_{50} of 20 ppm based on mouse data, the rat studies were inconsistent. ISO 10298 also contains calculation rules for estimating gas mixture toxicity of the gases listed assuming no synergistic affects from the gases mixed together. Using this method a phosphine mixture is no longer classified as toxic by the transportation regulations at a concentration of 4000 ppm.

The NFPA 704 Health hazard classification for gases is based primarily on their LC_{50} values with 4 being the most toxic (<1000 ppm) Zone A & B gases, 3 is Zone C (1001-3000 ppm) and 2 is Zone D (3001-5000 ppm). GHS has also established a Harmful classification for gases between 5001-10,000 ppm this would mean Phosphine mixtures at concentrations of 2000 – 4000 ppm would be classified as harmful.

LC_{50} values are much higher than worker exposure levels (PEL/TLV) which are low level chronic exposures over a long period of time. The phosphine PEL and ACGIH TLV is 0.3 ppm (0.42 mg/m^3). This is the concentration a worker can be continuously exposed to for 8 hrs per day for 30 years without a chronic affect. The ACGIH Short Term Exposure Limit (STEL) is 1 ppm (1.4 mg/ m^3). This is a concentration a worker can be exposed to 4 times per 8 hrs without an affect. The NIOSH Immediately Dangerous to Life or Health (IDLH) is 50 ppm.

Phosphine at a concentration of 1000 ppm is considered to be fatal after a few breaths and 500 ppm is considered to be lethal in 30 minutes. Serious affects have also been reported from exposure to a 5-10 ppm level for several hours. Gastrointestinal, cardiac, respiratory and neurological effects have been observed in humans. Longer periods of exposure also produce kidney and liver effects. Symptoms of phosphine poisoning include pulmonary irritation, shortness of breath, cough, headache, dizziness, fatigue, nausea, loss of appetite, indigestion, jaundice, numbness, paresthesia, ataxia, double vision, tremors, pulmonary edema, tonic convulsions and death.

Currently the hazard labeling used by the gas supplier is primarily to meet the transportation regulations and as noted above a phosphine mixture is not toxic when the concentration is <4000 ppm. This classification method has been adopted by the UN under the Global Harmonization System (GHS), by the International Fire Code and CGA P-1. Under the GHS regulations the label will also contain worker safety information. Some companies however have taken the conservative approach, classifying all concentrations of phosphine as being toxic, even 1 ppm.

It is impossible for anyone to be exposed to the full concentration of the gas mixture in a cylinder unless they put on a breathing mask and pipe it directly into it. In the case of the 50 ppm mixture, one would be asphyxiated well before it will have a toxic affect. If the cylinder should leak it will mix with the room air a person close by will be exposed to a diluted concentration. For a person to be exposed to 25 ppm, the mixture would be diluted by 50%. This would mean that the person is breathing a air mixture containing

Phosphine	25 ppm
Hydrogen	49.9975%
Oxygen	10.45%
Nitrogen	39.50%

Which is asphyxiating since oxygen concentration below 18.5% is considered dangerous by OSHA.

An interesting fact that you should also be aware of is with acetylene which is classified as a flammable gas. The characteristic odor of acetylene is due to the phosphine impurity. Most welders use grade C

Limiting Characteristics	Maxima for Gaseous Acetylene [1]		
	A	C	H
Acetylene, Min. % Assay	95	98	99.6
Phosphine & arsine [2]		500	25
Hydrogen sulfide [2]		500	25

Acetylene for welding is typically produced by reacting calcium carbide with water. Most calcium carbides have varying amounts of calcium phosphide as an impurity. This will also react with the water to form phosphine. Typical levels of over 300 ppm are common. Acetylene suppliers try to reduce this below 200 ppm as levels above this can have a significant effect on its flammability.

The IFC requires a facility handling toxic gases to have medical treatment protocols available and a medical facility trained on treatment. Very often users use SDS for this purpose, which are poorly written medical guidelines. If available, the US Health Dept ATSDR Medical Treatment Guidelines should be used.

These are comprehensive medical treatment protocols developed by Medical Doctors primarily for EMTs, paramedics and medical doctors to diagnose and treat acute chemical exposures. It focuses on concerns of Emergency Responders on key Hazardous Materials response issues such as the following for diborane.

Prehospital Management

- **Rescue personnel are at low risk of secondary contamination from victims who have been exposed to diborane gas. However, rescuers entering areas with potential high concentrations should wear appropriate equipment to avoid self-exposure to diborane. An air concentration of 15 ppm is considered "immediately dangerous to life or health".**
- **Acute exposure to diborane gas causes chest tightness, coughing, skin, eye and nose irritation, and lacrimation. Respiratory impairment and noncardiogenic pulmonary edema may occur.**
- **There is no specific antidote for diborane poisoning. Treatment is supportive.**

Hot Zone	Rescuers should be trained and appropriately attired before entering the Hot Zone. If the proper equipment is not available, or if rescuers have not been trained in its use, assistance should be obtained from a local or regional HAZMAT team or other properly equipped response organization.

These are much better than an SDS since it focuses on issues that a responder or medical professional would be concerned with such as secondary exposure.

The following are available for compressed gases

1. Ammonia
2. Arsine
3. Chlorine
4. Diborane
5. Ethylene Oxide
6. Hydrogen Chloride
7. Hydrogen Cyanide
8. Hydrogen Fluoride
9. Hydrogen Sulfide
10. Methyl Bromide
11. Methyl Mercaptan
12. Nitrogen Oxides
13. Phosgene
14. Phosphine
15. Selenium Hexafluoride
16. Sulfur Dioxide
17. Vinyl Chloride

These guidelines are so valuable that the author had them translated into Simplified Chinese, Traditional Chinese and Korean and for use in Asia.

Medical treatment for the highly toxic metal hydride gases

1. Arsine, germane and hydrogen selenide - Curry, S., Warpinski, G., Ngai, E.Y., "Tox and Hound – Fellow Friday – Metal Hydrides I", May 29, 2021, https://toxandhound.com/toxhound/ff-metal-hydrides/
2. Phosphine - Curry, S., Makar, G., Ngai, E.Y., "Tox and Hound – Fellow Friday – Metal Hydrides II – Phosphine (PH3)", Nov. 19, 2021 https://toxandhound.com/toxhound/ff-phosphine/
3. Diborane and pentaborane - Curry, S., Ngai, E.Y., Gold, J., "Tox and Hound – Fellow Friday – Metal Hydrides III – Boron Hydrides", May 26, 2022 https://toxandhound.com/?s=Boranes

Eugene Ngai

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