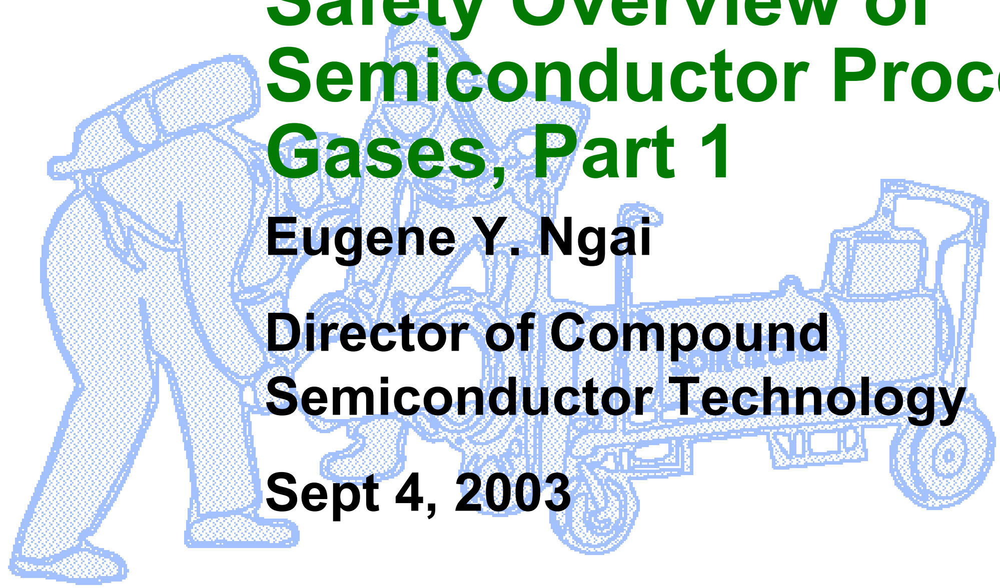
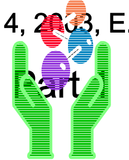
Safety Overview of Semiconductor Process Gases, Part 1

Eugene Y. Ngai

Director of Compound Semiconductor Technology

Sept 4, 2003



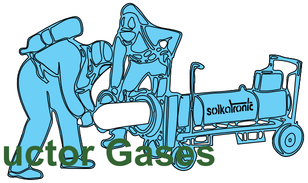


Semiconductor Gases

The Semiconductor Industry uses a variety of gases which have a wide range of Chemical and Physical Properties

- Ammonia
- Argon
- Arsine
- Boron Trichloride
- Boron Trifluoride
- Carbon Dioxide
- Carbon Tetrafluoride
- Chlorine
- Chlorine Trifluoride
- Diborane
- Dichlorosilane
- Disilane
- Fluorine
- Halocarbon 23, 32, 116
- Helium
- Hydrogen
- Hydrogen Bromide
- Hydrogen Chloride
- Hydrogen Fluoride
- Hydrogen Iodide
- Hydrogen Selenide
- Methyl Fluoride
- Methyltrichlorosilane
- Nitrogen
- Nitrogen Trifluoride
- Nitrous Oxide
- Octafluorocyclobutane
- Oxygen
- Perfluoropropane
- Phosphine
- Phosphorus Pentafluoride
- Silane
- Silicon Tetrachloride
- Silicon Tetrafluoride
- Sulfur Hexafluoride
- Sulfur Tetrafluoride
- Tetrafluoromethane
- Trichlorosilane
- Trimethylsilane
- Tungsten Hexafluoride
- Xenon

There are many new gases being evaluated for use, Carbon Monoxide, Nitric Oxide



Packages

- These are packaged in an assortment of cylinder sizes. Small lecture bottles to bulk tankers.
- In the US, Compressed Gases must be packaged in DOT Specification cylinders

Gas Physical State

Gases in cylinders and containers are packaged and shipped in a variety of physical states.

Compressed gas (nitrogen, hydrogen).

- **Gas with a critical temperature below ambient. Will always remain a gas regardless of pressure. Defined as any gas with boiling point >-130^{0}F (>-90^{0}C) pressure used to determine contents of cylinder. Gases that are highly compressible such as Silane, Boron Trifluoride and Carbon Tetrafluoride (F-14) are typically weighed for accuracy.**

Liquefied gas (propane, carbon dioxide).

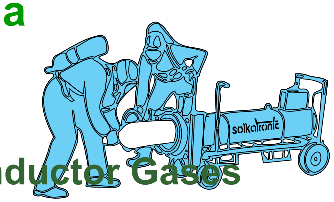
- **Gas with a critical temperature above ambient. Will liquefy at its' vapor pressure. Defined as any gas with boiling point between -130^{0}F (-90^{0}C) and 68^{0}F (20^{0}C) weight used to determine contents of cylinder.**

Dissolved gas (acetylene).

Cryogenic liquid (liquid nitrogen, liquid oxygen).

Liquids with gas padding (Silicon Tetrachloride, Trichlorosilane).

- **Chemicals with vapor pressure at 68^{0}F (20^{0}C) of < 1atm. Not a compressed gas by definition.**



Chlorine Gas Property Information CGA Handbook

PHYSICAL CONSTANTS [1]

	U.S. Units	SI Units
Chemical formula	Cl_2	Cl_2
Atomic weight	35.453	35.453
Molecular weight	70.906	70.906
Vapor pressure		
at 0°F (–17.8°C)	28.533 psia	196.74 kPa, abs
at 20°F (–6.7°C)	42.730 psia	294.62 kPa, abs
at 40°F (–4.4°C)	61.767 psia	425.88 kPa, abs
at 80°F (26.7°C)	118.16 psia	814.71 kPa, abs
at 120°F (48.9°C)	205.70 psia	1418.3 kPa, abs
Density of the gas		
at 32°F (0°C) and 1 atm	0.20057 lb/ft³	3.2127 kg/m³
Specific gravity of the gas		
at 32°F (0°C)and 1 atm (air =1)	2.485	2.485
Specific volume of the gas		
at 70°F (21.1°C) and 1 atm	5.3882 ft³/lb	0.33638 m³/kg
Density of saturated liquid		
at 32°F (0°C)	91.563 lb/ft³	1466.7 kg/m³
at 60°F (15.6°C)	88.765 lb/ft³	1421.9 kg/m³
at 80°F (26.7°C)	86.674 lb/ft³	1388.4 kg/m³
at 120°F (48.9°C)	82.208 lb/ft³	1316.8 kg/m³
at 160°F (71.1°C)	77.231 lb/ft³	1237.1 kg/m³
at 200°F (93.3°C)	71.461 lb/ft³	1144.7 kg/m³
Boiling point at 1 atm	–29.15°F	–33.97°C
Melting point at 1 atm	–149.76°F	–100.98°C
Critical temperature	290.75°F	143.75°C
Critical pressure	1157.0 psia	7977.5 kPa, abs
Critical density	35.8 lb/ft³	573 kg/m³
Triple point	0.20226 psig at –149.76°F	1.3946 kPa, abs at –100.98°C
Latent heat of vaporization at boiling point	123.85 Btu/lb	288.08 kJ/kg
Latent heat of fusion at melting point	38.836 Btu/lb	90.331 kJ/kg
Specific heat of dry gas (C_p)		
at 0°C, 1 atm	0.11565 Btu/(lb)(°F)	0.48422 kJ/(kg)(°C)
at 30°C, 101.5 psig (699.8 kPa)	0.13108 Btu/(lb)(°F)	0.5488 kJ/(kg)(°C)
Ratio of specific heats (C_p, C_v)		
at 0°C, 1 atm	1.3473	1.3473
at 30°C, 1 atm	1.3352	1.3352
at 30°C, 101.5 psig (699.8 kPa)	1.4240	1.4240
Viscosity at 68°F (20.0°C) and 1 atm		
Liquid	0.346 cP	0.346 mPa•s
Gas	0.0134 cP	0.0134 mPa•s
Weight of the liquid at 70°F (21.1°C)	11.728 lb/gal	1405.3 kg/m³
Specific gravity of saturated liquid		
at 32°F and 53.507 psia (0°C and 368.93 kPa, abs	1.4667	1.4667

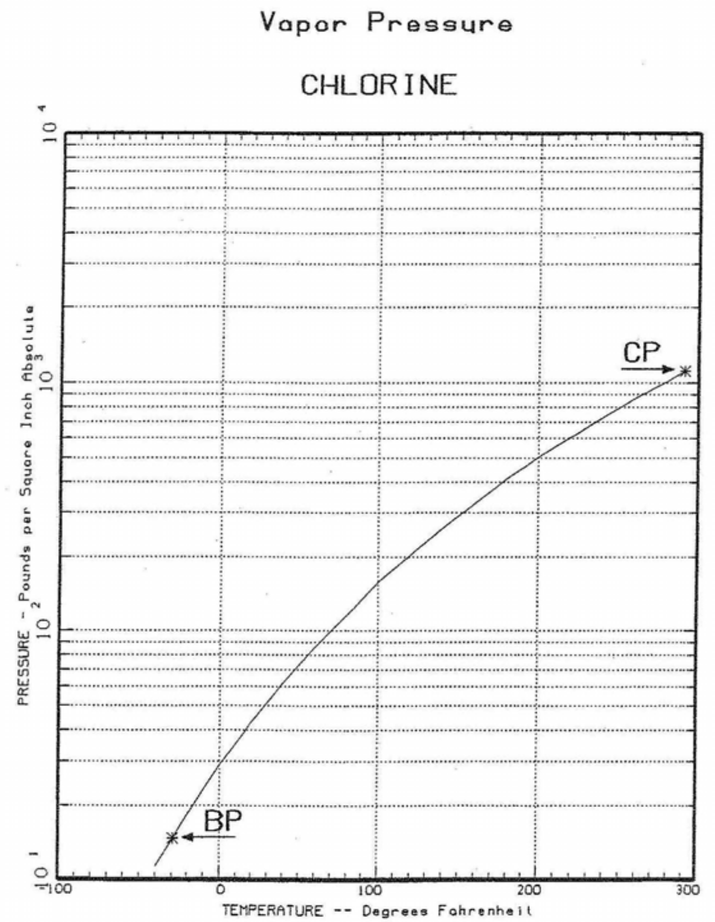
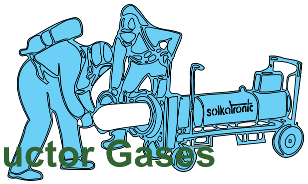
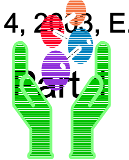


Fig. 1 Vapor pressure curve for chlorine.

Key Physical Properties of Compressed Gases

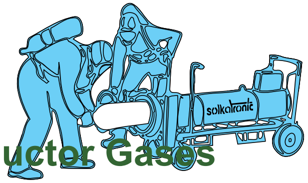
- Critical Temperature
- Gas Density
- Vapor Density
- Liquid Density
- Flammability Limits
- Boiling Point
- Vapor Pressure
- Latent Heat of Vaporization





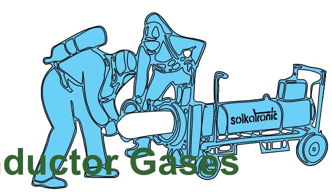
Critical Temperature

- **The critical temperature of a chemical is the point when it can no longer exist as a liquid or solid. It behaves as a gas regardless of the pressure at temperatures above this.**
- **Common Semiconductor gas that has a critical temperature at ambient temperatures is Hexafluoroethane (F-116) of 67.5^{0}F (19.7^{0}C). Other gases include Silicon Tetrafluoride and Boron Trifluoride**
  - **At temperatures below this, it will behave as a liquefied gas. Rapid use will subcool the remaining product, dropping the pressure**
  - **At temperatures above this, it will behave as a compressed gas and no subcooling will occur**



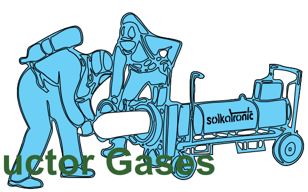
Gas Density

- The density of the gas typically at 70^{0}F (21^{0}C) and 1 atm
- Common units are ft^3/lb or gm/liter
- Most users use gas
- Gas density will change with temperature and will affect the mass flow from the cylinder.
- Extremes are
  - Hydrogen 0.005 lb/ft^3 (0.090 g/l)
  - Tungsten Hexafluoride 0.795 lb/ft^3 (12.73 g/l)



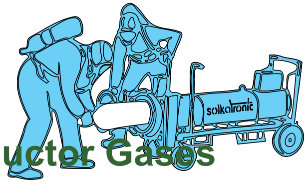
Vapor Density

- **Vapor Density is the gas density relative to air density at 70^0F (21^0C) and 1 atm**
- **A vapor density less than 1 means it's lighter than air and will float if released into air.**
- **A vapor density greater than 1 means it heavier than air and will sink if released into air.**
- **Extremes are**
  - **Hydrogen 0.07**
  - **Tungsten Hexafluoride 10.28**



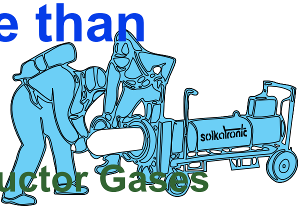
Liquid Density

- The density of the liquid typically at 70^0F (21^0C) and at saturation pressure (vapor pressure) in the cylinder
- Common units are ft^3/lb or gm/liter
- The liquid density of a liquefied gas will determine how much can safely be packaged in a cylinder.
- Extremes are
  - Ammonia 38.55 lb/ft^3 (0.618 kg/l)
  - Tungsten Hexafluoride 212.6 lb/ft^3 (3.41 kg/l)



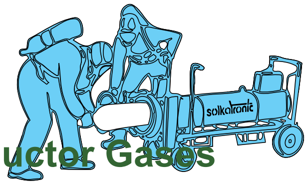
Flammability Limits

- **Basic Conditions (Fire Triangle) for a gas to burn**
  - Concentration is within flammability limits
  - Oxidizing medium such as Air or Oxygen is present
  - Ignition source
- **Flammability Range**
  - Lower Flammability Limit (LFL) - Lowest concentration of gas in air at STP that will burn upon ignition
  - Upper Flammability Limit (UFL) - Highest concentration of gas in air at STP that will burn upon ignition
  - Flammability & Explosive are normally interchanged (LFL & LEL and UFL & UEL) but have different meanings. The Explosive Range in air is only for certain gases and have a much narrower range than Flammability



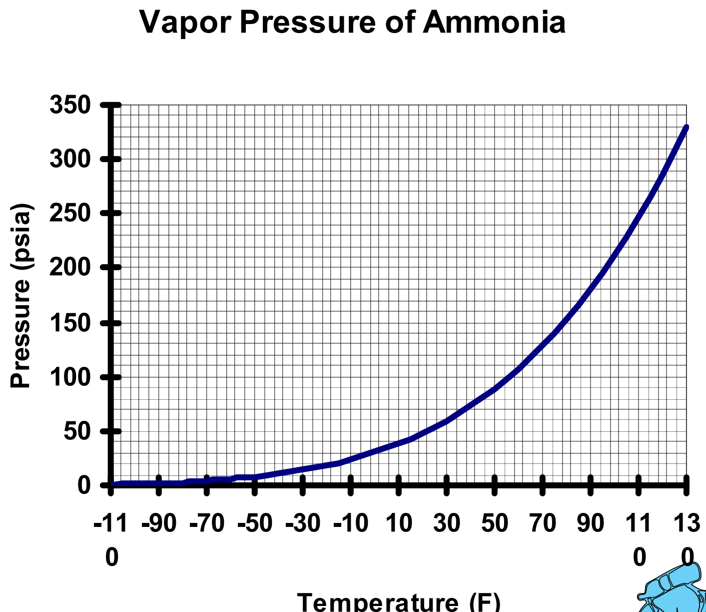
Boiling Point

- **The boiling point of a chemical is defined as the point at which the vapor pressure is at 1 atmosphere**
- **Gases which have a Boiling Point close to ambient temperatures can cause use problems**
  - Boron Trichloride 55^{0}F (12.8^{0}C)
  - Chlorine Trifluoride 53^{0}F (11.7^{0}C)
  - Dichlorosilane 47^{0}F (8.3^{0}C)
- **If the temperature falls below the boiling point, the cylinder will be in a vacuum**
- **May need to heat trace**
  - Tubing
  - Cylinder



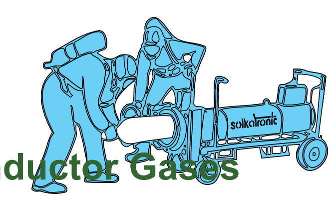
Vapor Pressure

- For liquefied gases the vapor pressure is the saturated vapor pressure above the liquid at temperatures below it's critical temperature.
- It can vary considerably due to temperature changes. For example Ammonia
  - 45 psig at 30⁰F
  - 114 psig at 70⁰F
  - 197 psig at 100⁰F



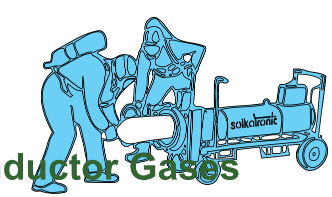
Latent Heat of Vaporization

- **The amount of heat required to vaporize the liquid to replace the gas used**
- **Common units used are BTU/lb, cal/gm**
- **Heat comes from the remaining liquid and cylinder masses**



Temperature Affect On Physical Property Of Gases

- Temperature can have a significant affect on the physical property of gases
  - Pressure
  - Subcooling
  - Liquid Expansion
  - Product Migration

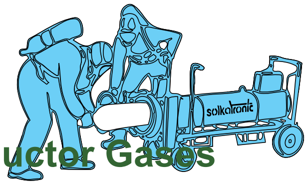


Temperature Affect On Gas Pressure

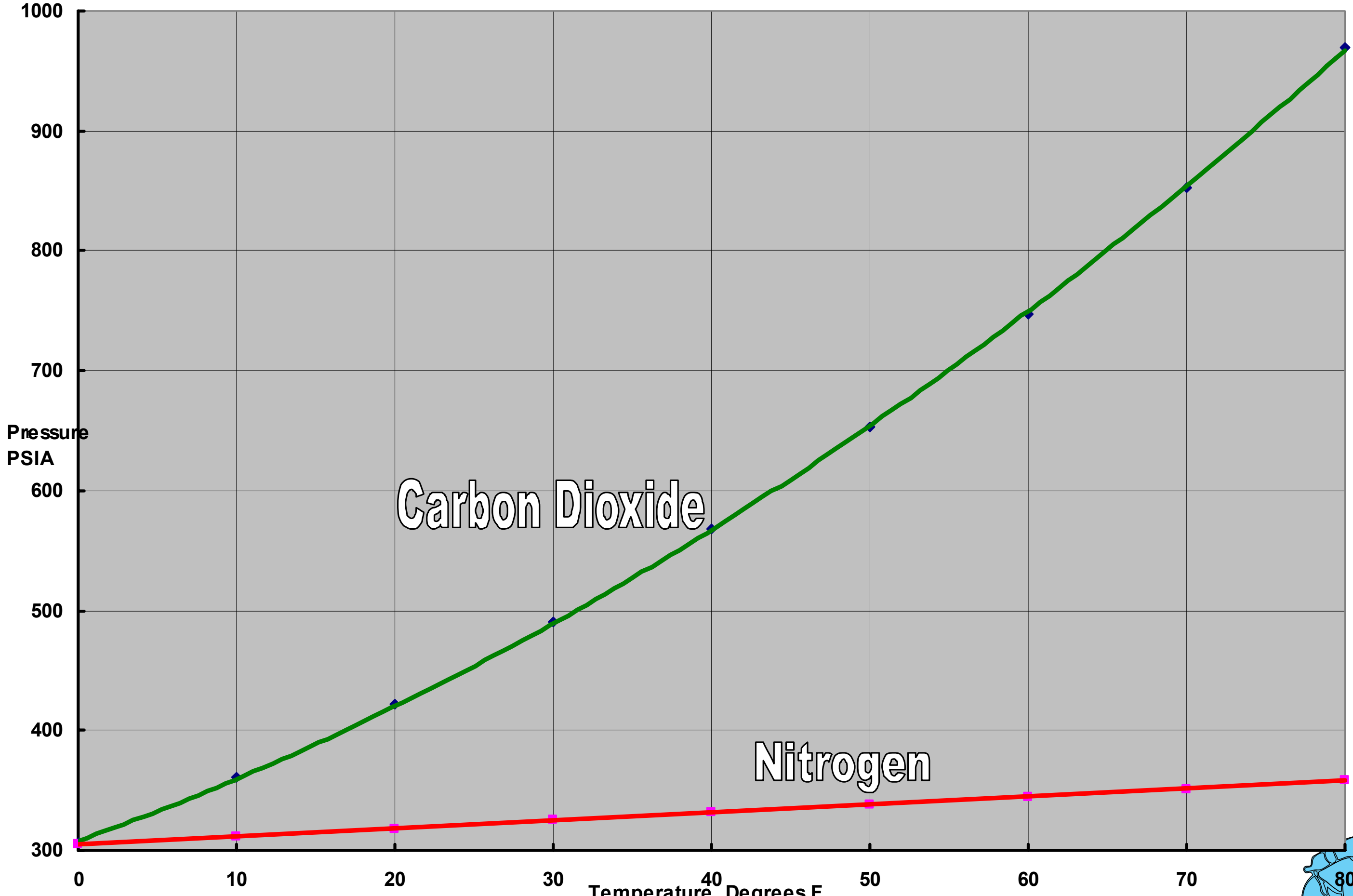
- For a Compress Gas, temperature changes will have a minor affect on pressure. The gas will expand or contract as a function of

$$P_2 = P_1 \, T_2/T_1$$

- For a Liquefied Gas, temperature changes will have a significant affect on pressure due to the vapor pressure



Temperature Affect
Compress Gas vs. Liquefied



AIR PRODUCTS

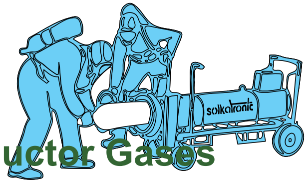
Electronics Division

Temperature Affect As Gas Is Withdrawn From A Liquefied Gas Cylinder

As gas is withdrawn from the cylinder, the liquid is vaporized to make up for the loss. The vaporization energy required is supplied by the liquid (latent heat of vaporization) and the mass of the cylinder. This will cool the liquid and cylinder lowering the vapor pressure.

Once the Vapor Pressure reaches 0 psig the gas vaporized will be a function of the heat transferred in from the environment. Typically 200-400 BTUs per hour.

High humidity, temperature or immersion of cylinder in water will improve the heat transfer rate.



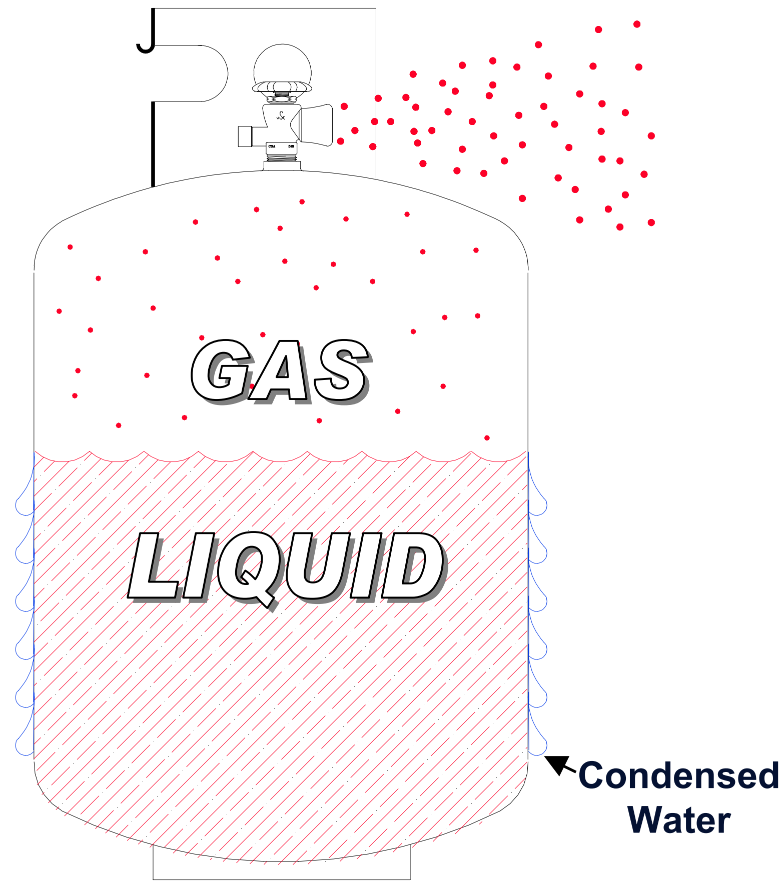
Cooling of Typical 20 lb Propane Cylinder

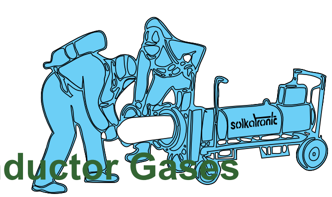
As the grill consumes the Propane Gas the liquid will vaporize to gas to makeup for the loss in pressure

The remaining liquid will subcool and after a period of time, droplets of water will appear on the sidewall where the liquid contacts the cylinder wall

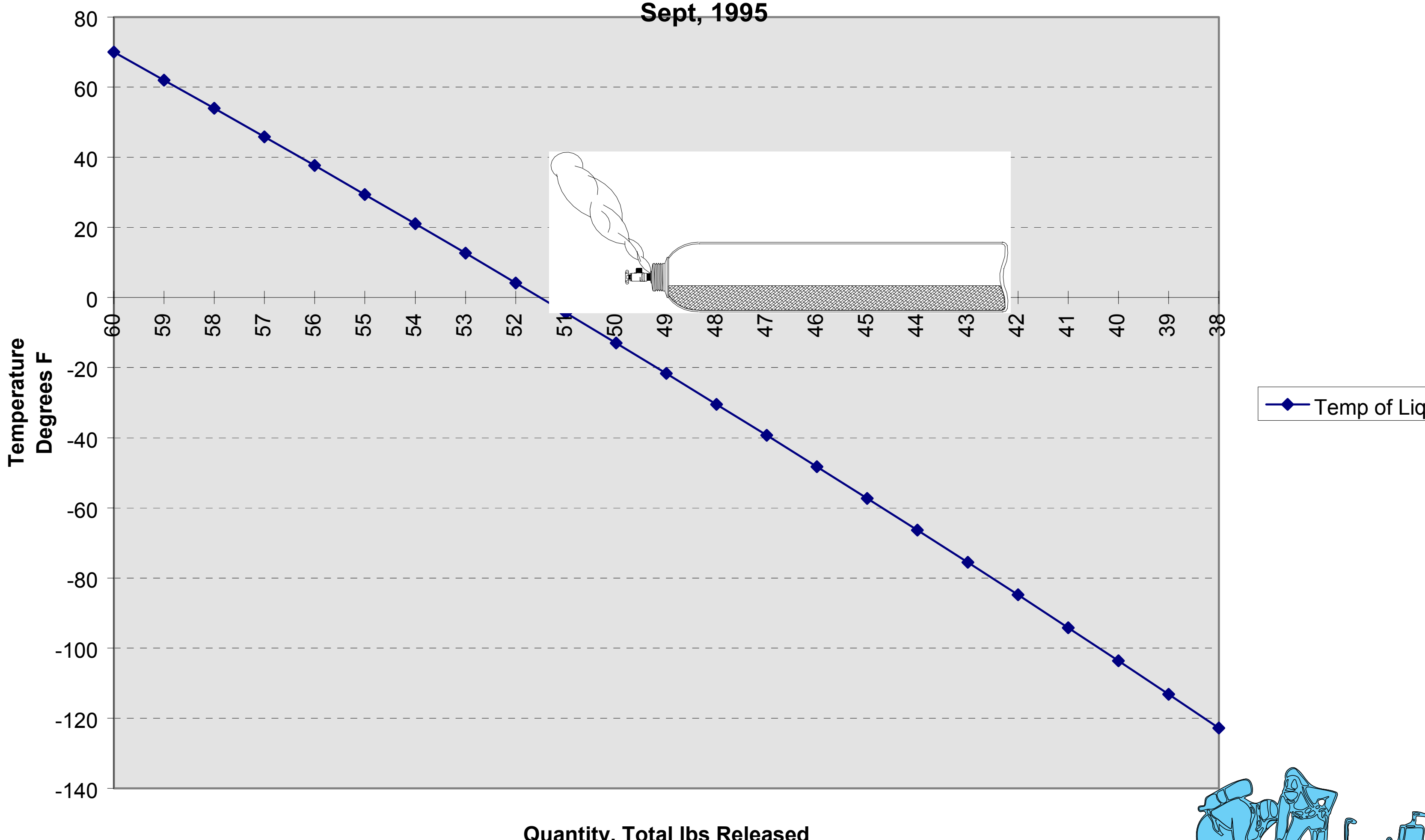
If use rate is high and for an extended period the water will freeze

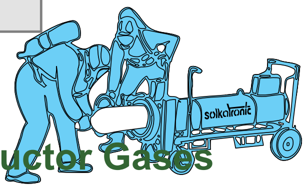
Large grill rated at 44,000 BTU/hr will consume 2.03 lbs of Propane. With a full cylinder at 20 lbs this will cool the remaining 18 lbs to 45^0F in the hour assuming a normal heat transfer rate of 200 BTU/hr from the Air. A half full cylinder will cool faster since there is less mass to cool. The 8 lbs will cool to 15^0F, freezing the condensed water





Temperature of a 60 lb Hydrogen Chloride cylinder at maximum gas flow though the valve versus lbs remaining



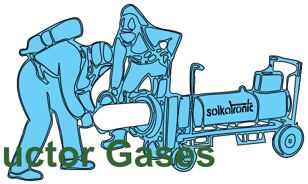


Subcooled Cylinder

- Liquefied Contents of Cylinder subcool if the gas is quickly withdrawn, freezing moisture from air at liquid level if the boiling point of the gas is less than 32^0F
- Temperature will reach boiling point of liquefied gas.
- Typically the level of the frost is at the liquid level of gas in cylinder
- In unusual cases, it can reach the brittle temperature of the cylinder and cause failure if physically impacted

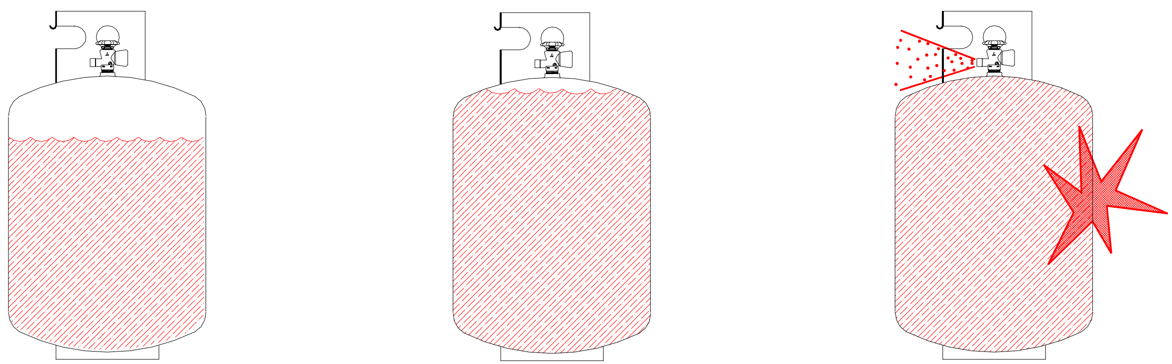
Liquid Expansion

- Liquid will expand with temperature increase.
- A liquefied gas could expand to fill the contents of a cylinder (“Liquid Full”)
- Liquefied gas is incompressible and can create significant pressure if confined
- In a fire a liquefied gas cylinder could expand faster than the pressure relief device can relieve



Propane 20 lb Cylinder Liquid Volumes at 70^{0}F, 130^{0}F and Liquid Full

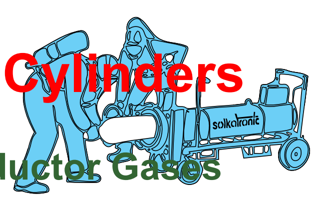
Cylinder volume will vary between 47.1 - 47.8 lbs water capacity



70^{0}F (21^{0}C)	130^{0}F (54.4^{0}C)	152^{0}F (66.7^{0}C)
83.6% Full	94% Full	100% Full
110 psig (8.5 atm)	258 psig (18.6 atm)	350 psig (24.8 atm)
		Once this Temp. is exceeded, the pressure will increase dramatically

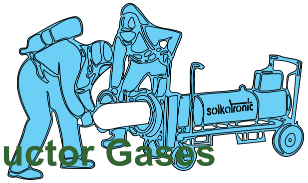
A Car Trunk Reaches 180^{0}F (82^{0}C)! (Taxi?)

See CGA Position Paper PS-7 on Safe Transport of Cylinders



Maximum Fill Density

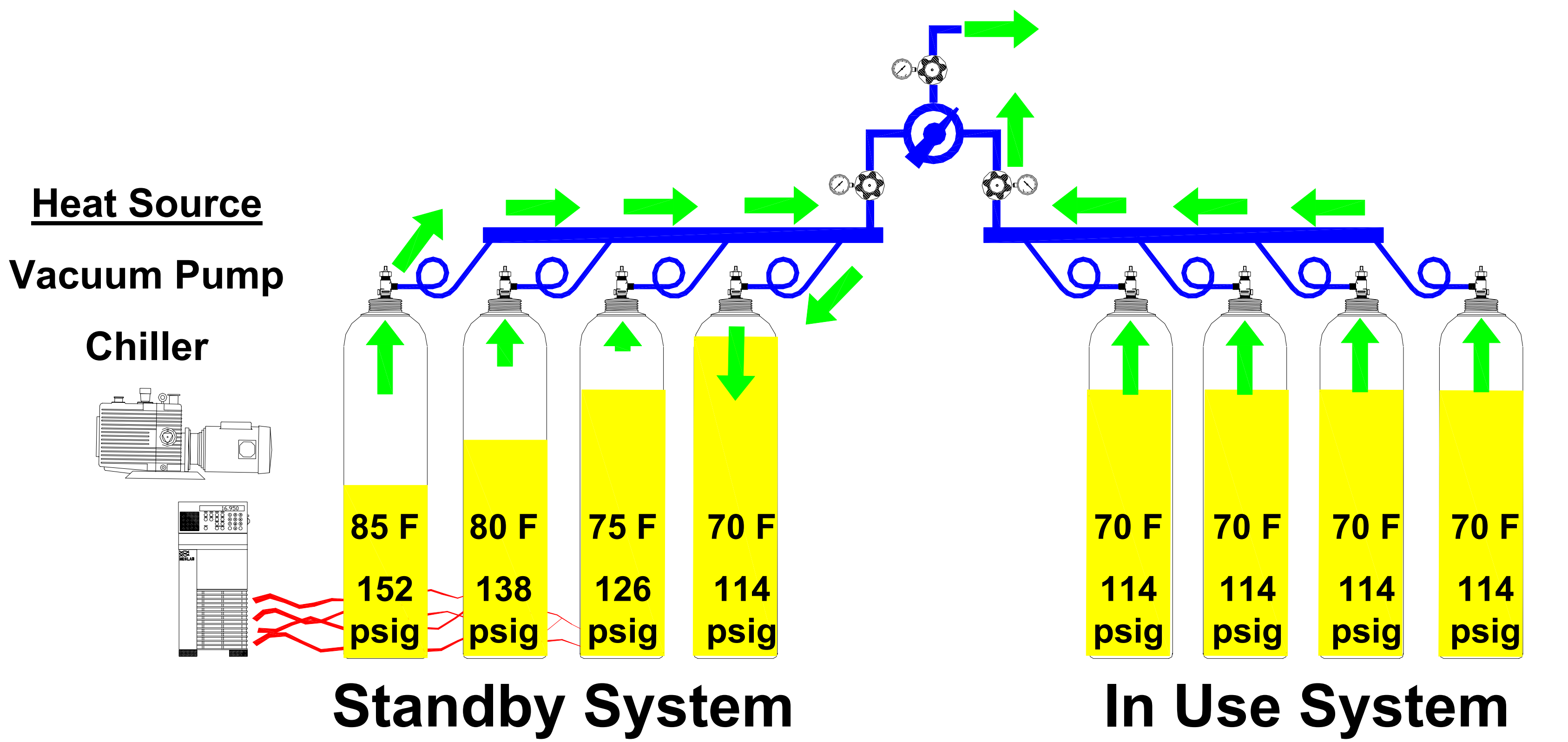
- 49 CFR 173.304(B) "The liquid portion of a liquefied gas must not completely fill the package up to 130^0 F" (54.4^{0}C)
- United Nation's ST/SG/AC.10/C.3/34 allows liquefied to be filled up to a weight where the pressure at 149^{0}F (55^{0}C) cannot exceed the test pressure of the cylinder



Liquid Full Cylinder

- Under some unusual conditions at a user location, a cylinder can be accidentally overfilled with liquid causing an unsafe condition
- If it exceeds the maximum fill density and the cylinder valve is closed, it could catastrophically rupture

Manifolded Ammonia System Example



Examples of Conditions Which can Cause Temperature Variances

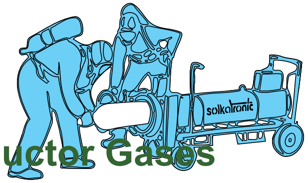
LIN Vapors Drawn Into Gas Bunker

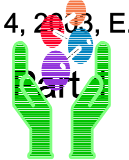
Sunlight Onto Gas Cabinets

Chiller/Heater Compressor Vent

Liquid Expansion Safety

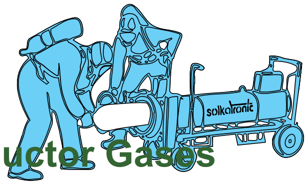
- When using liquid, never trap it between two valves without a pressure relief device
- Never heat a cylinder beyond 125^0F (51.7^0C). A cylinder full of liquefied gas will become liquid full at temperatures above this.
- Weigh a cylinder to determine its contents





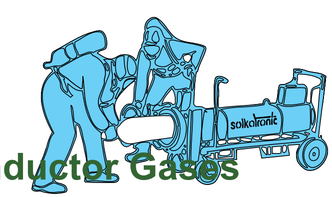
Gas Hazards
Physical & Chemical

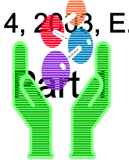
- Hazard is ability to injure or damage
- Almost all gases are classified as Hazardous Materials under DOT, OSHA , EPA, or Fire Codes
- Many have multiple hazards. Under DOT Primary and Subsidiary identified. For example Arsine will have a Poison Gas and Flammable Gas Label



Physical Hazards

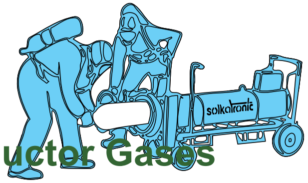
- **The most common hazard of compressed gases is pressure**
  - **A gas with a pressure >25 psig is Classified as Hazardous under DOT**
- **Extreme cold**
  - **Frostbite**
  - **Material Fracture**
- **Asphyxiating**





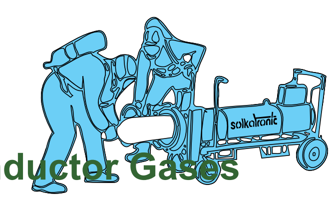
Pressure Hazard

- Gas pressures for liquefied gases can vary considerably due to temperature
- Users should reduce the pressure to a safer level using a regulator
- All components used for the piping system must be capable of withstanding the expected pressure.



Pressure Hazards

- Some liquefied gases stored for extended periods of time > 2 years can develop pressures well above their vapor pressures due to the reaction of moisture and the carbon steel forming Hydrogen
  - Hydrogen Fluoride
  - Hydrogen Bromide
- High concentration Diborane mixtures can also develop significant pressures from the thermal decomposition

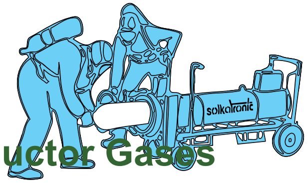


Aerosol Can Rupture, UK 2003

Pictured is a pressurized can that exploded in a vehicle and imbedded itself in the back seat of the car. The metal backing in the seat back stopped it from penetrating the seat completely. The driver had a lucky escape; the can could have shot off in any direction. The temperature outside of the vehicle was about 100 degrees F and the can had directions on it about not being stored at temperatures above 140 degrees F

Gas Chemical Hazards

- Toxicity
- Reactivity
- Corrosivity
- Routes of Entry
  - Inhalation - Primary
  - Dermal - Very Few Gases (HF) however, injection is possible. Gases that react with the moisture in air to form their corresponding acids (DCS, HCl, etc.) will deposit on your skin
  - Ingestion - Not Likely

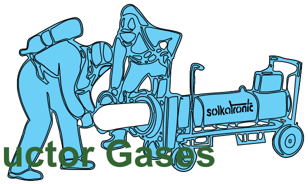


Poison

All Substances are Poisons. There is none which is not a Poison

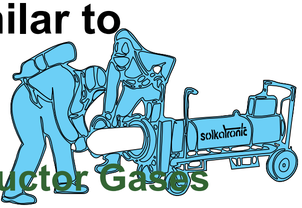
The Dose Makes The Poison

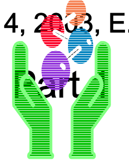
Paracelsus, 1493-1541



Toxicity Measurements

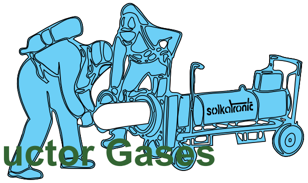
- TLV-TWA : ACGIH established Time Weighted Average to which a person may be exposed day after day for a 40 hr workweek without adverse effect. These are recommended values
- TLV-STEL : ACGIH established Short Term Exposure Limit which a person may be exposed to to 15 minutes without irritation, tissue change or debilitating narcosis. Maximum of 4 times per 8 hrs with 60 minutes in between each period
- TLV-C : ACGIH established value which should never be exceeded
- IDLH : NIOSH/OSHA established value which poses an immediate threat to health. It is a level in which a healthy adult male would not suffer any irreversible effect. Typically 30 minute value is used as escape period
- LC_{50} : Lethal concentration where exposure for 1 hr causes 50% of test population to die within 14 days. DOT is white albino rats 5 male and 5 female
- PEL : Permissible exposure limit established by OSHA which is similar to TLV-TWA but are also the regulatory guidelines in the US





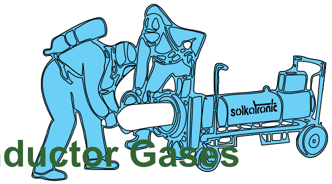
Toxic Affect Of Gases

- Exposure to a Toxic gas can have an Acute or Chronic affect . In the Semiconductor Fabs, the compressed gases are handled in sealed systems for purity and safety reasons. There should be limited low level exposures
- Acute
  - Immediate affect of short term high level exposure
- Chronic
  - Long Term affect to continuous low level exposure
    Carcinogenic
    Mutagenic



Toxic

- The user will see a variety of methods used to identify Toxic Hazards. The user must become familiar with the systems
- Poison and Toxic are used interchangeably in the US.
- Internationally, only Toxic is used since Poison in French means fish

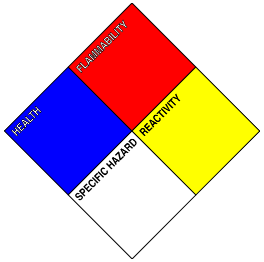


Toxic Labels (United States)

A number of labels are used to identify gas toxicity. In all cases it focuses on the Acute hazard

The Hazard Diamond on a cylinder is used to convey hazard information to transportation workers and emergency responders. Under International Transportation regulations all gases with LC_{50} < 5000 ppm are classified as a Toxic Gas with further classification by DOT into 4 hazard zones: (49CFR173.116) based on 1 hour rat exposures

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

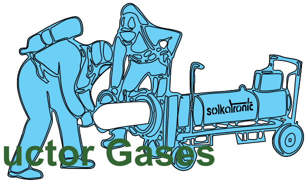


The National Fire Protection Association 704 system is used to convey hazard information to emergency responders. It uses a variety of exposure information to rate the Health value. For inhalation, 1 hour rat exposures is used

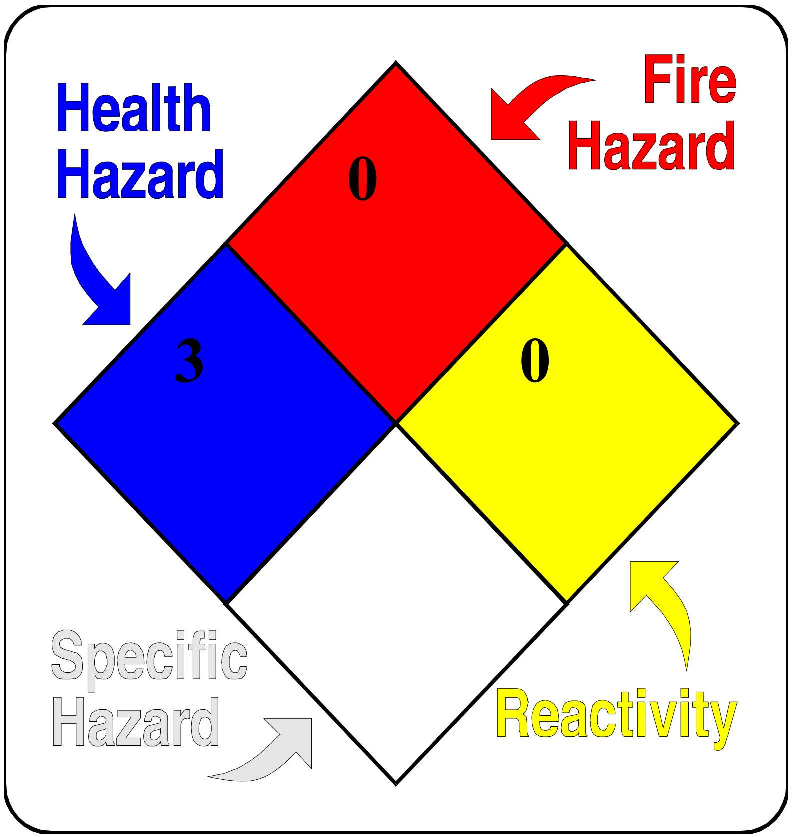
4	0-1000 ppm
3	1000 – 3000 ppm
2	3000 – 5000 ppm
1	5000 – 10,000 ppm

The Hazardous Materials Identification System (HMIS) is used to convey Hazard information to the user. It uses a variety of exposure data to rate the Health value. For Inhalation, 4 hour rat exposures is used

4	<0.05 mg/l
3	0.05 – 0.5 mg/l
2	0.5 - 2 mg/l
1	2 – 20 mg/l



NFPA 704 Sign

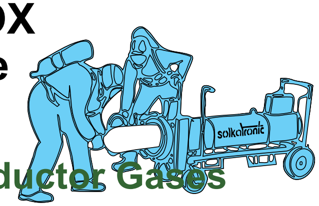


- Developed to provide Emergency Response personnel information. Many Fire Codes require use by entrance to rooms and outside of buildings
- Blue -Health

  Red - Fire

  Yellow - Reactivity

  White - Other Hazards
- Higher the number, greater the danger
- Criteria is different from HMIS which is for employee awareness
- For gases some symbols include ~~W~~ (Water Reactive(, OX (Oxidizer), SA (Simple Asphyxiant)



Hydrogen Chloride Example

- Hydrogen Chloride has a LC_{50} value of 3120 ppm is classified as follows:
  - DOT — Poison Gas, Zone C
  - Fire Codes — Corrosive Gas
  - NFPA — 3 Health Hazard
  - HMIS — 3 Health Hazard
  - Toxic Gas Ordinance — Class 3
- In some countries, Toxicity is also based on PEL values. In Taiwan or Japan a gas with a PEL < 200 ppm is classified as a Toxic
  - Silane
  - Nitrogen Trifluoride