Compressed Gases at UCSD

- A wide variety of compressed gases are used on campus
- For responsible and safe use, UCSD has formal guidelines on their use, storage and handling

UCSD Compressed Gas Guidelines

- Chemical Compatibility Guidelines
- Chemical Hazard Use Application (CHUA)
- Compressed Gas: Classification and Requirements Overview
- Compressed Gas: Toxic and Hazardous Gas Classifications
- Compressed Gas: Use and Storage Guidelines
- Compressed Gas: Safety Requirements by Hazard Class
What’s a Compressed Gas?

- Chemicals in a cylinder with the added hazards of pressure or low temperature

Compressed Gas Hazards

- Pressure
- Extreme Cold
- Health
- Toxicity
- Corrosivity
- Flammability
- Reactivity
- Oxidizing
- Water Reactive
- Asphyxiant
- Pyrophoric
- Explosive
- Self Reacting

Compressed Gases

- Gases
  - Over 200 gases are packaged in cylinders
- Gas mixtures
  - Infinite variety of mixtures varying from PPB to percent concentrations. Number of gases mixed together range from 2 to >50

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°F (>-90°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°F (-90°C) and 68°F (20°C) weight used to determine contents of cylinder.
**Acetylene is unique**

- It is a liquefied gas but because of its instability, it is packaged as a dissolved gas in a cylinder filled with a solid. The decomposition reaction of C₂H₂ is highly exothermic.
- Unsafe to use at pressures above 15 psig

**Gas Hazards, Physical & Chemical**

- Hazard is ability to injure or damage
- Almost all gases are classified as Hazardous Materials under the regulations
- Many have multiple hazards. For Transportation, the Primary and Subsidiary hazards are identified. For example Arsine will have a Toxic 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
- Gas pressures for liquefied gases can vary considerably due to temperature
- Extreme cold (Cryogenic Liquids)
  - Frostbite
  - Material Fracture

**Cryogenic Liquid Examples**

<table>
<thead>
<tr>
<th>Cryogenic Liquid</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon (LAR)</td>
<td>-302 °F (-186°C)</td>
</tr>
<tr>
<td>Helium (LHe)</td>
<td>-452 °F (-269°C)</td>
</tr>
<tr>
<td>Hydrogen (LHY)</td>
<td>-423 °F (-253°C)</td>
</tr>
<tr>
<td>Nitrogen (LIN)</td>
<td>-320 °F (-196°C)</td>
</tr>
<tr>
<td>Oxygen (LOX)</td>
<td>-297 °F (-183°C)</td>
</tr>
</tbody>
</table>
Physical Properties of Cryogenic Liquids

<table>
<thead>
<tr>
<th>Name</th>
<th>BP Temp @ 1 atm</th>
<th>Liquid Density @ BP</th>
<th>Gas Density @ BP</th>
<th>Latent Heat of Vaporize</th>
<th>Gas Density @ 70F (21C)</th>
<th>Gas from Liquid</th>
<th>vol/vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>-218</td>
<td>45.6</td>
<td>575</td>
<td>86.3</td>
<td>0.075</td>
<td>1.20</td>
<td>726</td>
</tr>
<tr>
<td>Argon</td>
<td>-296</td>
<td>87.9</td>
<td>1393</td>
<td>5.7</td>
<td>4.132</td>
<td>1.65</td>
<td>842</td>
</tr>
<tr>
<td>Carbon</td>
<td>-313</td>
<td>81.1</td>
<td>919</td>
<td>92.8</td>
<td>0.073</td>
<td>1.17</td>
<td>766</td>
</tr>
<tr>
<td>Fluorine</td>
<td>-207</td>
<td>64.1</td>
<td>1037</td>
<td>6.8</td>
<td>4.088</td>
<td>1.37</td>
<td>661</td>
</tr>
<tr>
<td>Helium</td>
<td>-205</td>
<td>7.8</td>
<td>125</td>
<td>1.7</td>
<td>0.010</td>
<td>0.16</td>
<td>754</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-202</td>
<td>4.4</td>
<td>71</td>
<td>1.4</td>
<td>0.005</td>
<td>0.06</td>
<td>650</td>
</tr>
<tr>
<td>Methane</td>
<td>-259</td>
<td>26.5</td>
<td>424</td>
<td>1.8</td>
<td>0.040</td>
<td>0.67</td>
<td>636</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-205</td>
<td>50.3</td>
<td>908</td>
<td>4.6</td>
<td>0.072</td>
<td>1.15</td>
<td>666</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-207</td>
<td>71.3</td>
<td>1142</td>
<td>4.7</td>
<td>0.063</td>
<td>1.33</td>
<td>661</td>
</tr>
</tbody>
</table>

Cryogenic Liquids

- To maintain cold temperature, liquid must be vaporized constantly. Cylinder is dewar
- Cold temperature
  - Material embrittlement
  - Frostbite
  - Increases vapor density
- Liquid can be
  - Asphyxiating (N₂, He)
  - Flammable (H₂)
  - Oxidizer (F₂, O₂)
  - Toxic (F₂, CO)

Gas Chemical Hazards

- Toxicity
- Reactivity
- Corrosivity
- Routes of Entry
  - Inhalation - Primary
  - Dermal - Very Few Gases (HF) however, injection is possible. Gases that react in air to form water soluble compounds (NH₃, HCl, etc.) will require corrosion resistant PPE
  - Ingestion - Not Likely

Gas Toxicity Definition

- Transportation, Worker Safety and Fire Codes based on LC₅₀
- Acute single dose exposure (classification system does not address chronic toxicity)
- Lethal concentration LC₅₀
  - Concentration of a gas (or a gas mixture) in air administered by a single exposure during a short period of time (24 h or less) to a group of young adult albino rats (males and females) which leads to the death of half of the animals in at least 14 days.
  - The accepted exposure time for gases is 1 hour and a population of 10 white albino rats
- GHS uses a 4 hour exposure which is 50% of a 1 hour
Gas Toxic Definition Transportation

- Toxicity (International)
  - LC50 <5000 ppm is toxic
  - LC50 <200 ppm is highly toxic
  - GHS also defines Harmful as 5000-20,000 ppm
- US DOT further breaks down the categories
  - LC50 0-200 ppm Zone A
  - LC50 201-1000 ppm Zone B
  - LC50 1001-3000 ppm Zone C
  - LC50 3001-5000 ppm Zone D
which they use to define further requirements for the package. For example all Zone A&B gases must meet the requirements of 49CFR173.40 which mandates additional packaging requirements.

Inhalation Hazard Label Used only in US

Toxic Gas

- ISO 10298 summarizes and validates key toxicity studies for the pure gases or provides an estimate. It also contains calculation rules for estimating gas mixture toxicity of the gases listed.
- Toxic gases under OSHA and the Fire Codes is <2000 ppm LC50.

Toxic Gas Exposure

TOXIC
The capacity of a material to produce injury or harm. Toxic gases damage or interfere with the metabolism of living tissue thereby producing personal injury, illness, and, in some cases, death. Toxicity can be acute or chronic, with damage as a result of repeated or long-term exposure; sometimes damage may be manifested after a period of latency.

ACUTE
Acute short-term, high-concentration, immediate results. The exposure occurs quickly and can result in immediate damage to the body. For example, inhaling high concentrations of Carbon Monoxide or Arsine gas will produce acute poisoning.

Metal Hydride Gases

- B2H6
- SiH4
- Si2H6
- GeH4

<table>
<thead>
<tr>
<th>Metal</th>
<th>Hydride</th>
<th>Periodic Table Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>B2H6</td>
<td>B, C, N, O</td>
</tr>
<tr>
<td>Si</td>
<td>SiH4</td>
<td>Si, Ge, As, Se</td>
</tr>
<tr>
<td>Si</td>
<td>Si2H6</td>
<td>Si, Sn, Sb, Te</td>
</tr>
<tr>
<td>Ge</td>
<td>GeH4</td>
<td>Ge, Sn, Sb, Te</td>
</tr>
</tbody>
</table>

- H2S
- PH3
- H2Se
- AsH3
Metal Hydride Gas Hazards

- With the exception of silane and disilane all are toxic, inhalation is the major route of entry
- Dermal route of entry with the unreacted gas is not likely
- In a fire however, the combustion byproducts (oxides) can become a dermal problem
- Chemical scrubbing can form hydrogen as a byproduct

Metal Hydride Gas Hazard Characteristics

- With the exception of Silane these are all liquefied gases that are classified as toxic or highly toxic gases under the transportation regulations
- All of these are also supplied as gas mixtures in concentrations from ppm to %

### Metal Hydride Gas Vapor Pressure

- Arsine (AsH$_3$) 217 psig (1.496 mPa)
- Germane (GeH$_4$) 569 psig (3.923 mPa)
- Hydrogen Selenide (H$_2$Se) 123 psig (0.848 mPa) 68°F (20°C)
- Phosphine (PH$_3$) 513 psig (3.537 mPa)
- Diborane (B$_2$H$_6$) 522 psig (3.599 mPa) @ 60°F (15.6°C), Critical temperature of 62°F (16.7°C)
- Silane (SiH$_4$) Critical temperature of 20°F (-7°C)

### Metal Hydride Gas Flammability

- Extremely wide range, considerably higher than hydrocarbons
  - Arsine (AsH$_3$) 4.5 – 78%
  - Diborane B$_2$H$_6$ 0.8 – 98%
  - Germane (GeH$_4$) 2.8 – 98%
  - Hydrogen Selenide (H$_2$Se) 4.5 – 68%
  - Phosphine (PH$_3$) 1.6 – 98%
  - Silane (SiH$_4$) 1.4 – 96%
Pyrophoric Gas

- Pyrophoric gases are flammable gases which have autoignition temperatures that are below 130°F (54.4°C). The autoignition temperature (AIT) of a flammable material is that in which spontaneous ignition will occur at 1 atm in air. It is strongly influenced by concentration and the test method used to measure it.
- Pyrophoric gases require oxidizers to burn.
- Of all the Pyrophoric Gases, Silane is the most unpredictable. When released into air, Silane will react in one of the following manners:
  - Delayed Ignition (Explosion)
  - No Ignition
  - Immediate Ignition

Of these the latter is only safe condition. Temperature, humidity, flow rate, will influence the ignition. Disilane and Phosphine in laboratory tests have exhibited the same behavior.

Autoignition Temperature Of Common Gases

<table>
<thead>
<tr>
<th>Autoignition Temperature</th>
<th>Autoignition Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>°F</td>
<td>°C</td>
</tr>
<tr>
<td>Silane</td>
<td>&lt;146</td>
</tr>
<tr>
<td>Acetylene</td>
<td>581</td>
</tr>
<tr>
<td>Disilane</td>
<td>-100</td>
</tr>
<tr>
<td>Diethyl Amine</td>
<td>594</td>
</tr>
<tr>
<td>Monochlorosilane</td>
<td>-22</td>
</tr>
<tr>
<td>Butylene</td>
<td>722</td>
</tr>
<tr>
<td>Phosphine</td>
<td>&lt;32</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>752</td>
</tr>
<tr>
<td>Nickel Carbonyl</td>
<td>68</td>
</tr>
<tr>
<td>1,3 Butadiene</td>
<td>788</td>
</tr>
<tr>
<td>Diborane</td>
<td>44</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>804</td>
</tr>
<tr>
<td>Dichlorosilane</td>
<td>136</td>
</tr>
<tr>
<td>Propane</td>
<td>842</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>320</td>
</tr>
<tr>
<td>Ethylene</td>
<td>842</td>
</tr>
<tr>
<td>Germane</td>
<td>343</td>
</tr>
<tr>
<td>Propylene</td>
<td>851</td>
</tr>
<tr>
<td>Trichlorosilane</td>
<td>360</td>
</tr>
<tr>
<td>Vinyl Chloride</td>
<td>882</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>500</td>
</tr>
<tr>
<td>Ethane</td>
<td>882</td>
</tr>
<tr>
<td>Arsine</td>
<td>545</td>
</tr>
<tr>
<td>Ammonia</td>
<td>929</td>
</tr>
<tr>
<td>Butane</td>
<td>550</td>
</tr>
<tr>
<td>Methane</td>
<td>897</td>
</tr>
</tbody>
</table>

Flammable Gas Definition

- Transportation
  - Is Flammable in concentrations of <13% in air or has a flammability range wider than 12% regardless of lower flammability concentration. May not identify some gases which are flammable under certain conditions
  - Ammonia (16-25%)
  - HCFC’s e.g. 134b

Gas Flammability

- 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 &UEL 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
### Flammable Gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Autoignition Temp</th>
<th>Flammable Range %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>581°F (305°C)</td>
<td>2.5-80%</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>1128°F (609°C)</td>
<td>12.5-74.0%</td>
</tr>
<tr>
<td>Deuterium</td>
<td>1060°F (571°C)</td>
<td>5-75%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>914°F (490°C)</td>
<td>2.7-36%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1050°F (566°C)</td>
<td>4-76%</td>
</tr>
<tr>
<td>Methane</td>
<td>1004°F (540°C)</td>
<td>5-15%</td>
</tr>
<tr>
<td>Methyl Fluoride</td>
<td>5.6-22.2</td>
<td></td>
</tr>
<tr>
<td>Methylsilane</td>
<td>320°F (160°C)</td>
<td>1.3-88.9</td>
</tr>
<tr>
<td>Trimethylsilane</td>
<td>473°F (245°C)</td>
<td>1.38-51.25</td>
</tr>
</tbody>
</table>

### Oxidizer Gas, Characteristics

- Oxidizer gases are the opposite of flammable gases
- Oxidizer gases will promote and accelerate combustion of flammable materials
- Under certain conditions a oxidizer system can react or explode due to
  - Poor Design
  - System Cleanliness
  - Materials of Construction
  - System Operation

### Oxidizer Gases

- The key oxidizer gases are
  - Chlorine
  - Chlorine Trifluoride
  - Fluorine
  - Oxygen
  - Nitrous Oxide
  - Nitrogen Trifluoride
- Once an oxidizer gas starts to react with a fuel, the only safe mitigation technique is to shut off the gas flow, fire extinguishers will not put out the fire.
- Under certain conditions it will ignite metal and it is dangerous to put water onto these fires

### Key Oxidizer Gases and their Hazard Characteristics

<table>
<thead>
<tr>
<th>Name</th>
<th>Hazards</th>
<th>Safeguards</th>
<th>Physical State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td></td>
<td>Compressed</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl₂</td>
<td>Toxic &amp; Corrosive</td>
<td>Liquefied Gas</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>N₂O</td>
<td>Inert &amp; Can Autodecompose</td>
<td>Liquefied Gas</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>Highly Toxic &amp; Corrosive</td>
<td>Fill Limit</td>
</tr>
<tr>
<td>Nitrogen Trifluoride</td>
<td>NF₃</td>
<td>Inert &amp; Under Certain Conditions React</td>
<td>Maximum Fill Pressure</td>
</tr>
<tr>
<td>Chlorine Trifluoride</td>
<td>CIF₃</td>
<td>Toxic and Corrosive</td>
<td>Liquefied Gas</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td>Toxic</td>
<td>Not Shipped</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F₂</td>
<td>Highly Toxic &amp; Corrosive</td>
<td>Fill Limit</td>
</tr>
</tbody>
</table>
Oxidizer Systems

- Systems must be properly designed and maintained to prevent reaction
  - Cleaned
  - Slow opening valves
- Nitrogen trifluoride fill pressures have been limited to 1450 psig to decrease the potential
- At high pressures, the nitrogen trifluoride will start to decompose into fluorine which will react with the system

Oxidizer Fluoride Gas Systems

- Most be designed for oxygen service and fluorine passivated
- Fluoride Gases
  - Bromine trifluoride
  - Chlorine trifluoride
  - Fluorine
  - Tetrafluorohydrazine
  - Tungsten hexafluoride

Corrosive Gas

- Acid and Alkaline
- Non corrosive when very pure
- Most are highly water soluble. Small leaks will attract water from the air forming highly corrosive liquids which drip down the cylinder
- Large leaks will form white cloud due to the droplets of liquid acid/base that is formed
- The corrosive liquids will corrode most metals and are a severe irritant to the skin.
- The gas will be a severe irritant to the respiratory system and eyes

Corrosive Acids

- Liquefied gases with a wide range of vapor pressures. Highly soluble in water forming a acid solution

<table>
<thead>
<tr>
<th>Vapor Press, psig</th>
<th>Hydrolyzes to inorganic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Bromide</td>
<td>Hydrobromic</td>
</tr>
<tr>
<td>Hydrogen Chloride</td>
<td>Hydrochloric</td>
</tr>
<tr>
<td>Hydrogen Fluoride</td>
<td>Hydrofluoric</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>Sulfuric</td>
</tr>
<tr>
<td>Tungsten Hexafluoride</td>
<td>Hydrofluoric</td>
</tr>
</tbody>
</table>
Corrosive Alkaline

- Liquefied gases with a wide range of vapor pressures. Very soluble in water forming a corrosive alkaline solution

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vapor Press, psig @70 F</th>
<th>Hydrolyzes to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>114</td>
<td>Ammonium Hydroxide</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>11</td>
<td>Ammonium Hydroxide</td>
</tr>
<tr>
<td>Monomethylamine</td>
<td>29</td>
<td>Ammonium Hydroxide</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>13</td>
<td>Ammonium Hydroxide</td>
</tr>
</tbody>
</table>

Gas Cylinders

- In US are made to DOT (Department of Transportation) and/or TC (Transport Canada) Specifications
- Material of Construction
  - Carbon Steel
    - Chrome/Molybdenum Alloy (3AA)
    - Light weight - high strength (HC series)
    - Open Hearth, electric or basic oxygen process steel (low pressure welded)
  - Aluminum
  - Fiber Wrapped Aluminum
  - Stainless Steel
  - Specialty Alloy (Nickel or Monel)

Gas Cylinders

- **Types**
  - Returnable
  - Disposable (Nonrefillable)
- **Construction**
  - Seamless
    - Forged
    - Spun or Plug
  - Welded
  - Fiberwound
- **Sizes**
  - Variety of sizes available

Typical Cylinders

- **High Pressure (1800-6000 psig)**
  - Seamless cylinders typically used for Nitrogen, Hydrogen, etc. Narrow shoulder, concave bottom
- **Medium Pressure (150-500 psig)**
  - Welded cylinders typically used for liquefied gases such as Hydrocarbons. Footring, broad shoulder
- **Disposable (260 -500 psig)**
  - DOT 39 - Welded, used for Freon, Propane, etc.
  - DOT 2P - Aerosol can
Cryogenic liquid container (dewar)

- A pressurized, double-walled, insulated container used to hold either a cryogenic liquefied gas or refrigerated liquefied gas. (large thermos bottle)
- Commonly used to hold a compressed gas that has been liquefied by cooling it to very cold temperatures:
  - Liquid Argon: -303°F
  - Liquid Carbon Dioxide: -109°F
  - Liquid Nitrogen: -320°F
  - Liquid Oxygen: -297°F

ESG Cylinder and Valve

Valve Protection

Cylinders containing Toxic, Flammable or Corrosive gas must have a valve protection device in place during transportation. This can be a cylinder cap, a valve guard or the cylinder is overpacked in a crate/box.

- The most common device is a cylinder cap made of carbon steel which threads onto the cylinder collar.
- Attachment:
  - Coarse Thread
  - Fine Thread
  - Bayonet

Locking Type (caution)
Cylinder Cap

- Toxic Gas Zone A & B cylinders must have caps that have been performance tested with a 7’ drop test and not leak.
- CGA V-9 describes the requirements
- Must be made of ductile metal for Oxidizer Gases a fire resistant non-metal maybe used.
- Must always be on during movement to protect valve.

Removing Cylinder Caps

- Use gloved hands to remove
- If difficult to do so, never stick wrench or screwdriver into the vent hole to remove. Use special wrench or strap wrench.

Cylinder Collar

- Collar is not machined into cylinder
- A separate piece that is attached by a thin rolled or peened section of metal
- Dangerous to lift cylinder by the Cap
- Can be a leak path
- Can trap water in deadspace

Valve Protection Shrouds/Caps
Cylinder Valves

- Pressure Seal
- Metal Diaphragm
- Packed

Liquid/Vapor Valve

- Valve that allows gas or liquid to be dispensed
- Dip tube on liquid

Wrench Operated Valve

- Packed Valve
- Open by holding locking nut and turning valve stem counterclockwise
- Used primarily on Lecture Bottles

Cylinder Pressure Relief Devices (PRD)

- Used to protect cylinders from catastrophic failure in fire and in certain cases overpressurization (Not effective for liquid full cylinders)
- In US and Canada required for most cylinders. Exceptions:
  - Prohibited on Poison Gas, Zone A
  - Optional for Ammonia and Amines < 165 lbs
  - Optional for Lecture Bottle or small cylinders (less than 12” long x 4.5” dia)
- Device Selection CGA Pamphlet S1.1 (49CFR173.34(d))
- Use varies around the world, e.g.:
  - Europe is prohibited for most gases except flammable
  - Japan & Korea required for all
- Exemptions for Silane and Nitrogen Trifluoride.
Rupture Disk, CG-1

- A frangible metal disk typically designed to fail at 5/3 of cylinder working pressure.

Fusible Plug, CG-2, CG-3

- A thermally activated metal device which will activate at 165°F or 212°F releasing contents.

Combination Device, CG-4 & CG-5

Frangible Disk & Fusible Plug

- A Device which combines the Frangible Disk and Fusible Plug which will fail only under both high temperature and pressure conditions.

Spring Loaded Relief, CG-7

- A spring loaded device with a soft valve seat which will relieve excess pressure caused by fire and reseat to minimize quantity of liquefied flammable gas released into fire.
Cylinder Valve Outlet Connections
United States

- Standards established by CGA
- Types:
  - Industrial
  - Medical
  - Semiconductor
- Prevent connection of incompatible or excessive pressure gases
- Required under 29CFR1910.101(b) which references CGA P-1 for user in US
- Summarized in CGA Pamphlets V-1 for pure gases and V-7 for Mixtures

Industrial Cylinder Valve Outlet Connections

- Primary task of CGA over 75 years ago
- All gases are grouped based on chemical and physical properties
- Over 54 connections have been established which cannot interconnect with each other to form a gas tight seal
- Unique connections are formed by using various combinations of:
  - Male/Female Threads
  - Different Diameters
  - Nipple Shapes
  - Right/Left Handed Threads
- Sealing is from:
  - Nipple Deformation
  - Flat Gasket
  - Tapered Thread

CGA Industrial Outlet Connection

- Basic rule is left handed thread for Flammable and Right handed for Oxidizer (Exception is new OPD propane connection)
- Middle number is even for right handed and odd for left handed (Exception is DISS Connections)
- Notch on nut to indicate left hand thread
- Adapters shall never be used to prevent connection of incompatible gases or excessive pressure
- Replacement of gaskets after every use
- Visual inspection of nipple after every use for damage
- Teflon tape shall not be used for threads

CGA Fittings
Bullet and Gasket Types

- Bullet: Seal by deformation of Nipple, e.g. CGA 350, 510
- Flat Gasket: Seal with replaceable soft gasket, e.g. CGA 330, 660 & 670
Typical CGA Outlet Connections

- Lecture Bottle has a universal CGA 150 or 170 connection and a valve without a PRD
- 7X has the assigned Outlet connection and a PRD

Valve Outlet Connection

- Never use Teflon tape on the connection threads
- Connection adapters shall not be used

Difference Between a 7X Cylinder and a Lecture Bottle

- Lecture Bottle has a universal CGA 150 or 170 connection and a valve without a PRD
- 7X has the assigned Outlet connection and a PRD

Semiconductor Cylinder Valve Outlet Connections (DISS)

- Diameter Index Safety System (DISS)
- To provide high integrity connection via use of replaceable metal gasket between two polished beaded surfaces, $10^{-5}$ (VCR type)
- Cleaner connection by eliminating virtual leaks
- For user safety right handed threads
- Rotational damage of beaded surfaces. Antirotation fingers added to prevent
- Will not fit under standard cylinder cap
- Adopted by ISO 10692 as International Standard
Restrictive Flow Orifices (RFO)

- To reduce the hazard of Silane and the Highly Toxic Gases, the US Fire Codes and Insurance standards are requiring the use of a Restrictive Flow Orifice (RFO) to limit the gas flow from a cylinder.

Cryogenic Outlet Fitting Lock

- A number of fatalities have occurred as a result of outlet connections being removed from dewars and replaced with one that "fit" the system. For example, a Nitrogen dewar was placed onto a nursing home Oxygen system. To prevent this from happening, outlet are silver brazed or mechanically locked.

Cylinder Colors

- Gas cylinder colors differ from one manufacturer or supplier to another.
- A universal color code does NOT exist except for a few medical and diving gases in the US.
- It is essential that a gas be identified by the name stenciled and the label on the cylinder, not by the color of the cylinder.

Cylinder & Container Marking & Labeling

- Many markings and labels are required by DOT or OSHA for shipment and use. These are:
  A. DOT
     - Shipping Name
     - UN or NA #
     - Reportable Quantity
     - Inhalation Hazard (if required)
     - Hazard Zone or Packing Group (if required)
     - Technical Name (if not same as Shipping Name)
     - Name and Address of Shipper
   B. DOT Hazard Labels
   - All stenciling must be in contrasting color
Cylinder & Container Marking & Labeling (cont)

B. OSHA
Warning Label with
Name of Product
Appropriate Warnings
Physical and Health Hazards
Name and Address of supplier

C. MISCELLANEOUS
In some cases, the following information will also be included:
- "Flow Restrictor Equipped" stenciled on cylinder.
- "Dip Tube" stenciled or labeled on cylinder.
- "DOT Exemption #" stenciled on package. This is required when an exemption has been obtained for the packaging, i.e., Dichlorosilane in an overpack drum.
- "Inside Package meets Prescribed DOT Specifications". This is required whenever the outermost package is not the prescribed package for the gas contained. For example, small cylinders are packaged in cardboard or wooden cartons to stabilize them and to prevent damage during shipment. The outside package must also contain all of the required DOT markings and labels.

Hazardous Materials Labels and Markings

- Global Harmonization
  - Transportation
  - Worker Safety

Hazardous Materials Warning Labels

- Symbol Mandatory
- Background Color Mandatory
- Text Optional
- Class Number Mandatory

In US TOXIC can be interchanged with Poison. Internationally if text is used must be Toxic. US has new Inhalation Hazard Label.

Cylinder Shoulder Labels

- Used around the world for all gases
- In US was for formerly only permitted for Flammable and Non Flammable Gases that are delivered in Company Owned vehicles. Now authorized for all materials
- When cylinders are nested, the label can still be seen
- When used, do not need the DOT 4" diamond
Cylinder Carts

- Cylinders are to be moved only via approved hand carts.
- Cylinder carts shall be ergonomically suited for handling the cylinder to be moved.
- Cylinder carts shall have a physical restraint to secure the cylinder during movement.
- Dragging, rolling or lifting by the cylinder cap is not approved. They shall not be dropped or struck against each other or other surfaces.

Cylinder Transport

- All cylinders shall be transported with the cylinder cap on.
- All cylinders shall be leak tested prior to removal from storage or use area.
- Cylinders are not to be left unattended during transportation.
- Transport only at approved times.
- Transport only through approved routes.
- Lifting magnets, cylinder caps or slings shall not be used to move cylinders with a crane or hoist - cylinders must be in specially designed cages or cradles.
- Cylinders shall only be moved in skids/cradles designed for forklift movement.

Cylinder Storage

- Cylinders shall be stored in dedicated areas conforming to local/national regulations.
- Storage areas shall have adequate natural or mechanical ventilation.
- The area shall be protected from the weather.
- The area shall be free of standing water.
- Cylinders shall be secured at 2 points using noncombustible straps or chains at the midsection of the cylinder.
- Cylinders shall be grouped into compatible groups based on their hazards.

Cylinder Storage

- Incompatible groups shall be separated by a fire partition or distance.
- Segregate full and "empty" cylinders.
- Storage Areas shall be adequately marked.
- Storage areas shall be secured from unauthorized entry.
- Cylinders should not be stored for extended periods of time. In general 5 years is the maximum.
- Cylinders of Hydrogen Fluoride and Hydrogen Bromide should be returned to the supplier within 2 years. Over time they can pressurize due to hydrogen formation.
Cylinder Storage

- Cylinder storage areas shall be free of flammable materials
- Easy access to the cylinders shall be provided

Compressed Gas Use Requirements

- Outlined in “Compressed Gas: Safety Requirements by Hazard Class”
- Based on Hazard Class
- Requirements for exhausted enclosures/cabinets, gas detection, etc

Potential Leak Points

- Toxic or corrosive gas cylinders should be tested for leaks at the following locations

Compressed Gas Cylinder General Safety Guidelines

- Cylinders shall not be stored or used if the contents are not properly identified. Never use color as the identifier
- Labels and markings on the cylinder shall not be covered, defaced or removed
- Never refill cylinders without the owners permission
- Compressed gas cylinders shall be used and stored only in designated locations
- Proper PPE shall be worn at all times
- Compressed gases shall be used only by trained and qualified personnel.
- Compressed gas cylinders shall be transported only by trained and qualified personnel.
Gas System Safety

- Gas systems set up for one gas service shall not be used for other services.
- All compressed gas cylinders in use, except low vapor pressure gases such as Boron Trichloride, shall have a pressure regulator to lower the pressure.
- “Buddy System” for Highly Toxic and Pyrophoric gas cylinders.
- Highly toxic or high pressure pyrophoric cylinder valve shall have a RFO installed (Restrictive Flow Orifice)
- Only systems designed and cleaned for oxygen service shall be used for oxygen and other oxidizer gases
- Strong fluorine gases (ClF₃, F₂, NF₃, etc) shall only be used in systems that have been oxygen cleaned and fluorine passivated

Use Safety

- All cylinders are to be placed into the final use area/cabinet and immediately restrained using cylinder straps or chains, prior to removal of the cylinder cap.
- Cylinders are not be subjected to temperatures outside of the following range: -20°F (-29°C) to 125°F (52°C).
- Cylinders heated using electrical devices must have adequate safeguards to prevent overheating, resistance heaters can short circuit on the cylinder metal or the control thermocouple may not be properly installed. An independent overtemperature alarm circuit must be installed.
- Valve outlet adapters to change the valve outlet connection to match the gas cabinet pigtail are prohibited.

Regulators

- Mechanical device to reduce gas pressure in cylinder to safe levels
- Single and 2 stage
- Before a regulator is removed from a cylinder, the cylinder valve shall be closed and the regulator relieved of gas pressure

Use Safety

- Connection to the valve outlet shall be smooth and not forced
- Tools such as wrenches shall not be used to open or close valves unless they are designed for wrench operation, in this case a short wrench 6” (15 cm) shall be used
- Gas systems shall be properly marked or labelled
- Checkvalves shall be used to prevent backflow
Gas Cabinets

- Metal enclosures that are used to isolate hazardous gas cylinders
- Gas cabinets are used to protect the operator and the surrounding environment from the hazards of the cylinder (toxicity, corrosive, flammable, etc)
  - Confines a leak
  - Exhaust ventilation to capture/dilute the leak
- It is also used to isolate the cylinder from the hazards of the external environment
  - Fire
  - Incompatible gases or chemicals
  - Secures cylinder from tampering/theft
- Allows incompatible gases to be located in the same area

Typical Single Cylinder Gas Cabinet

- Gas cabinet material is metal having a minimum of 12 gauge (2.5 mm) thickness

Continuous Gas Detection Hazard Class I & II Compressed Gases

- Methods of Detection
  - Thermal Conductivity
  - Electrochemical
  - Flame Emission Spectrometry
  - Infrared Spectrometry
  - Mass Spectrometry
  - Paper Tape
  - Solid State Sensor
  - Gas Chromatography

- Sampling Methods
  - Diffusion
  - Extractive

Cylinder Return

- Users must return cylinder with all of the safety devices that it came with.
- Make sure the cylinder valve is closed tightly and the vaportight cap is on wrenchtight before the cylinder valve protection cap is placed on the cylinder.
- No stickers should be placed over the vent holes of the cylinder valve protection cap
- Status tag shall indicate “empty” or residue
- Treat cylinder as if it was full
- All labels and markings on the cylinder must be legible