Chemically Speaking LLC

Compressed Gas ER Fundamentals

Sept 2022

Compressed Gases Represent over 66% of RMP Chemicals. Chlorine and ammonia are at the top of the list based on a 2000 analysis

Chemical	Number of Processes	Percentage of Total
Ammonia (anhydrous)	8343	32.5
Chlorine	4682	18.3
Flammable Mixtures	2830	11.0
Propane	1707	6.7
Sulfur Dioxide	768	3.0
Ammonia (aqueous 20% or more conc.)	519	2.0
Butane	482	1.9
Formaldehyde	358	1.4
Isobutane	344	1.3
Hydrogen Fluoride	315	1.2
Pentane	272	1.1
Propylene	251	1.0
Methane	220	0.9
Hydrogen	205	0.8
Isopentane	201	0.8
All Others	4139	16.1

Both were also the top Toxic Inhalation Chemicals in transportation in 2013.
DHS concern with a terrorist incident involving ammonia or chlorine in transit. Jack Rabbit was a test program to study the actual dispersion in a worst case event. 2 ton releases conducted in 2010. 5 and 10 tons were just conducted Aug/Sept 2015 and 20 ton in 2016.

Jack Rabbit
DHS chlorine and ammonia release testing conducted at Dugway, UT. Jack Rabbit !! involved the emergency response community. Key questions were

1. Is it safe to shelter in place in emergency response vehicles?
2. What is the height at which a responder can survive (reliable vertical concentration)?
3. Is it possible/advisable to drive through the chlorine gas cloud?
4. Is the 1000 meter initial isolation zone in the current ERG valid?
5. What is the significance of various urban barriers?
6. What is the impact of long-term off-gassing?
7. What is the behavior of chlorine after a catastrophic release?
8. What is the behavior of the chlorine interacting with common urban materials?

The vehicles even after 5 exposures to high Cl_2 levels still ran. The turnout and SCBA were deonned and appeared to be unaffected. Concluded that a emergency responder would be protected and be able to escape a worse case Cl_2 release.

PHMSA's 2020 Emergency Response Guidebook provides first responders with a go-to manual to help deal with hazmat accidents during the critical first 30 minutes. DOT's goal is to place an ERG in every emergency service vehicle nationwide

Feel the Heat

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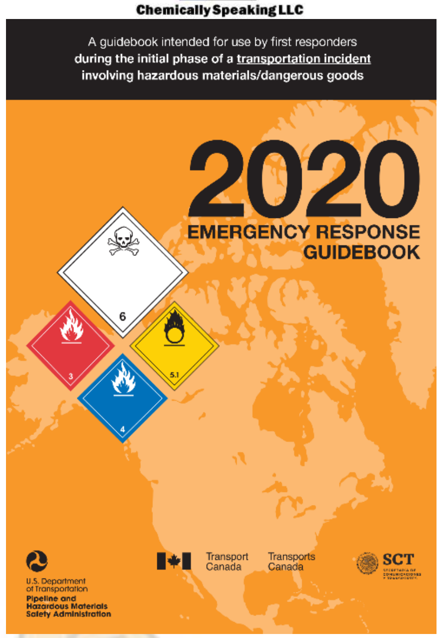


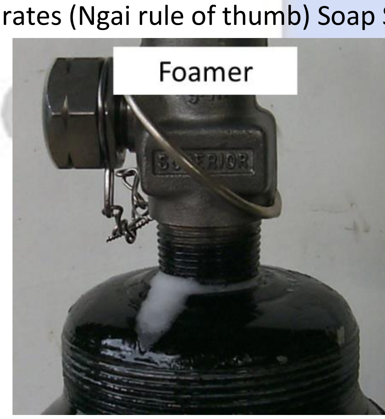
Was used to validate and update

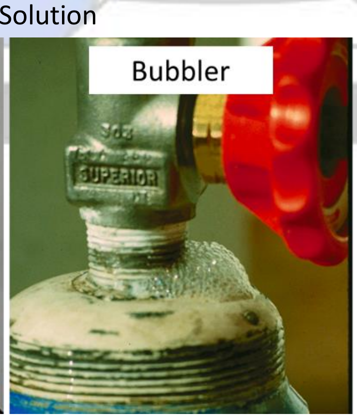
TRANSPORT CONTAINER	UN1017 Chlorine: Large Spills											
Rail tank car	1000	(3000)	10.1	(6.3)	6.8	(4.2)	5.3	(3.3)	11+	(7+)	9.2	(5.7)	6.9	(4.3)
Highway tank truck or trailer	600	(2000)	5.8	(3.6)	3.4	(2.1)	2.9	(1.8)	6.7	(4.3)	5.0	(3.1)	4.1	(2.5)
Multiple ton cylinders	300	(1000)	2.1	(1.3)	1.3	(0.8)	1.0	(0.6)	4.0	(2.5)	2.4	(1.5)	1.3	(0.8)
Multiple small cylinders or single ton cylinder	150	(500)	1.5	(0.9)	0.8	(0.5)	0.5	(0.3)	2.9	(1.8)	1.3	(0.8)	0.6	(0.4)

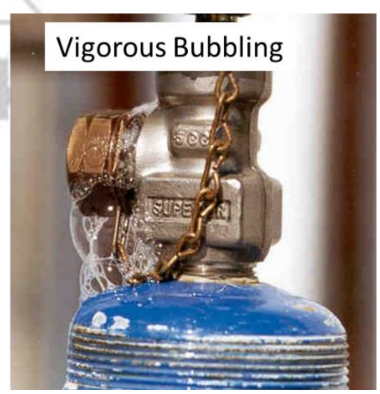
How bad is the leak?

Soap is a universal leak detection method

Leak rates (Ngai rule of thumb) Soap Solution







Foamer <0.1 cc/min, very small bubbles looks like foam

Bubbler 0.5-10 cc/min clear bubbles 1 cm in dia

Vigorous bubbler 10-50 cc/min large bubbles

Whistler >50 cc/min can hear the leak

A small leak of a corrosive gas will not suddenly cause a cylinder failure. It can take months for corrosion to compromise the valve

A full 150 lb cylinder contains 150 lbs of liquefied Chlorine Gas
The gas specific volume of Cl_2 at 70°F is 5.39 ft^3/lb
5.39 ft^3/lb x 150 lbs = 808.5 ft^3 of gas
808.5 ft^3 x 28,315 cc/^{ft3} = 22,892,677 cc
At a leak rate of 50 cc/min this will leak for 457,854 minutes (318 days)!

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 gas that has a critical temperature at ambient temperatures is Hexafluoroethane (F-116) of 67.5°F (19.7°C). Other gases include Silicon Tetrafluoride and Boron Trifluoride

At temperatures below this, it will behave as a liquefied gas. Rapid use/release will subcool the remaining product, dropping the pressure in the cylinder

At temperatures above this, it will behave as a compressed gas and no subcooling will occur during use

Gas Density

The density of the gas is the weight of the gas in a fixed volume, temperature and pressure, typically at 70°F (21°C) and 1 atm (0 psig)

Common units are lb/ft^3 or gm/liter

Gas density will change with temperature, increasing as it gets colder and decreasing as it warms

Extremes

Hydrogen	0.005 lb/ft^3 (0.090 g/l)

Tungsten Hexafluoride 0.795 lb/ft^3 (12.73 g/l)

Vapor Specific Gravity

Vapor Specific Gravity (Vapor density) is the gas density relative to air density at 70^{o}F (21^{o}C) and 1 atm (0 psig)

Vapor SG less than 1 means it's lighter than air and will float if released into air.

Vapor SG greater than 1 means it heavier than air and will sink if released into air.

Extremes are

Hydrogen	0.07
Tungsten Hexafluoride	10.28

Cl_2 has vapor specific gravity of 2.45

4H MEDIC ANNA – Gases lighter than air

- H - Hydrogen
- H - Helium
- H - Hydrogen Cyanide
- H - Hydrogen Fluoride
- M - Methane
- E - Ethylene
- D - Diborane
- I - Illuminating Gases
- C - Carbon Monoxide
- A - Acetylene
- N - Neon
- N - Nitrogen
- A - Ammonia

Cooling a gas will increase Vapor Specific Gravity

Ammonia at 70^{o}F it has a Vapor SG of 0.59 so it will go up. Ammonia is also very water soluble. It will react with the moisture in the air forming ammonium hydroxide droplets which are heavier than air.

Liquid Density

The density of the liquid typically at 70°F (21°C) and at saturation pressure (vapor pressure) in the cylinder

Common units are lb/ft^3 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)

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

A flammable gas in transportation is flammable in concentrations of <13% in air or has a flammability range wider than 12% regardless of lower flammability concentration. Ammonia with a range of 16-25% does not meet this definition therefore it is

Gases that do not meet this definition such as Ammonia are classified nonflammable gases. A release in confinement can easily reach the LEL

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°F (12.8°C)
- Chlorine Trifluoride 53°F (11.7°C)
- Dichlorosilane 47°F (8.3°C)

If the temperature falls below the boiling point, the cylinder will be in a vacuum. This could suck in air and moisture.

Change in barometric pressure changes the boiling point

Vapor Pressure

For liquefied gases the vapor pressure is the saturated vapor pressure above the liquid at temperatures below its critical temperature.

It can vary considerably due to temperature changes. For example Ammonia

- 45 psig at 30°F
- 114 psig at 70°F
- 197 psig at 100°F

Common Toxic Low VP Liquefied Gases

	Chemical Symbol	VP, psig	Boiling Point	Freezing Point
Boron Trichloride	BCl_3	4.4	54.5°F (12.5°C)	-161.1°F (-107.3°C)
Chlorine Trifluoride	ClF_3	6.8	53.2°F (11.75°C)	-105.4°F (-76.3°C)
Cyanogen Chloride	CClN	19.7	55°F (12.9°C)	20.3°F (-6.5°C)
Dichlorosilane	$SiCl_2H_2$	9.1	46.7°F (8.2°C)	-187.6°F (-122.0°C)
Ethylene Oxide	C_2H_4O	6.4	50.7°F (10.4°C)	-170.7°F (-112.6°C)
Hydrogen Fluoride	HF	0.8	67.1°F (19.5°C)	-118.4°F (-83.6°C)
Methyl Bromide	CH_3Br	27.5	38.4°F (3.6°C)	-137°F (-94°C)
Methyl Mercaptan	CH_3SH	15.0	42.7°F (6.0°C)	-189°F (-123°C)
Monomethylamine	CH_3NH_2	28.8	20.5°F (-6.3°C)	-136°F (-93.5°C)
Nitrogen Dioxide	NO_2	0.0	70°F (21°C)	11.8°F (-11.2°C)
Phosgene	$COCl_2$	9.1	46.8°F (8.2°C)	-198°F (-127.8°C)
Tungsten Hexafluoride	WF_6	2.7	35.6°F (2°C)	383.7°F (195.4°C)

Temperature can have a significant affect on the physical property of gases and must be considered during an ER

Pressure

Subcooling

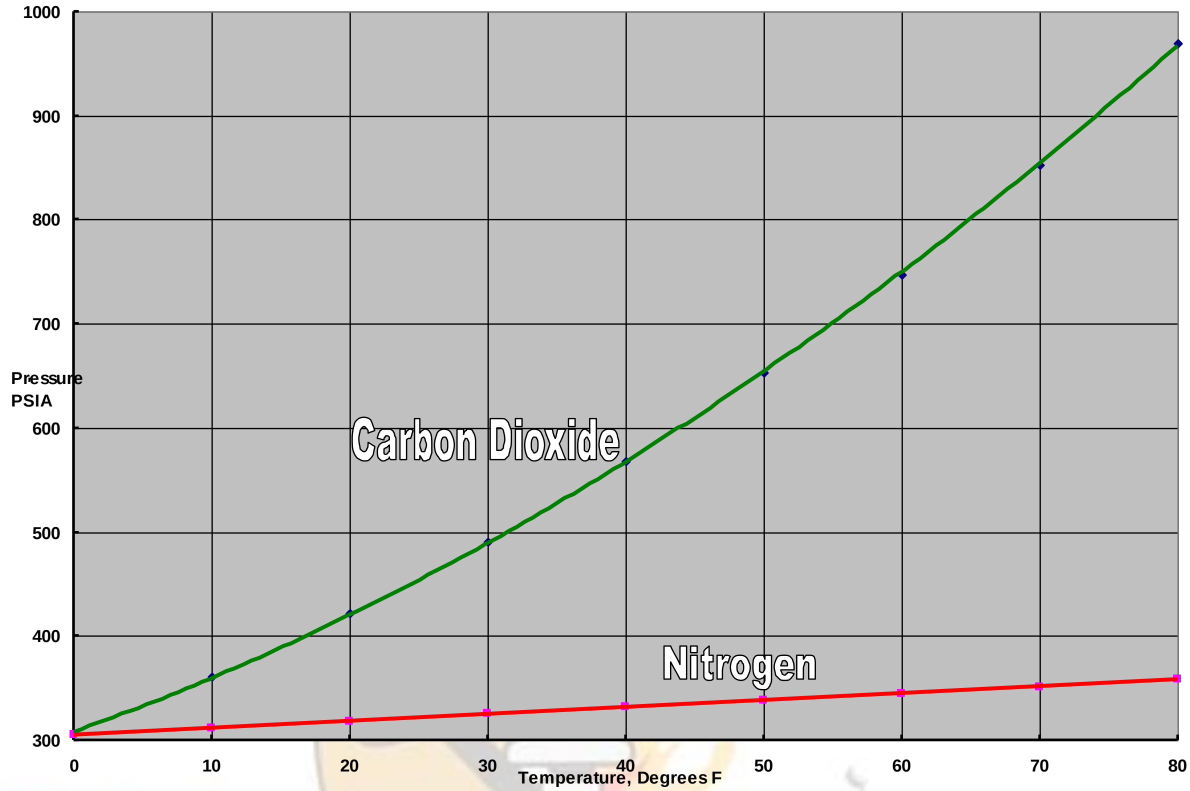
Liquid Expansion

Product Migration

Temperature

For a Non liquefied Gas, temperature changes will have a minor effect on pressure. (Nitrogen)

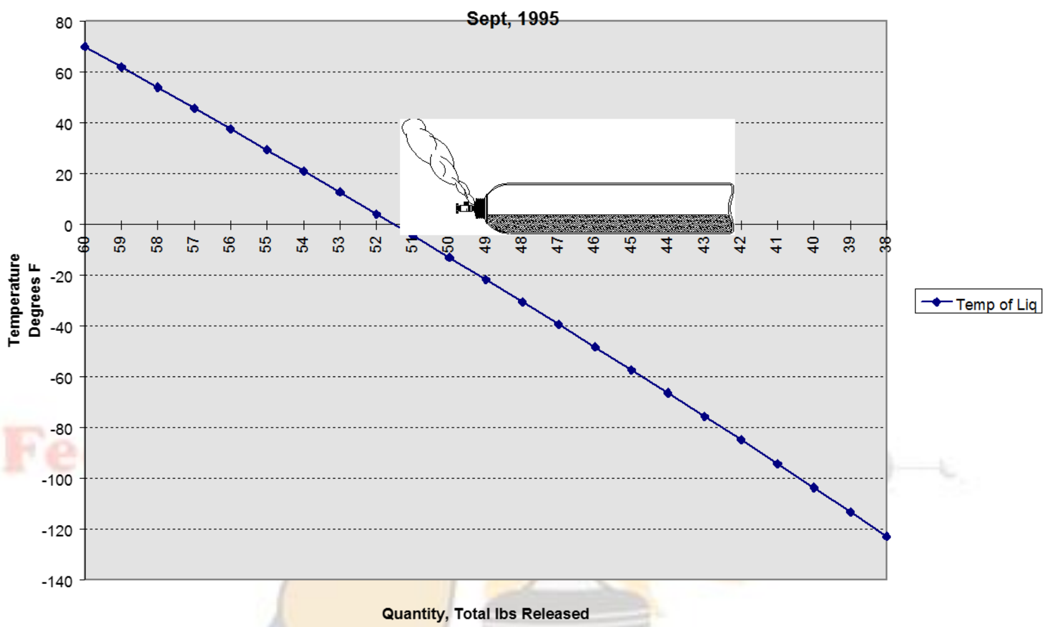
For a Liquefied Gas, temperature changes will have a significant effect on pressure due to vapor pressure (Carbon Dioxide)


Pressure
PSIA
1000
900
800
700
600
500
400
300
Carbon Dioxide
Nitrogen
0
10
20
30
40
50
60
70
80
Temperature, Degrees F

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
In a vapor release of a liquefied gas, the heat comes from the remaining liquid and cylinder masses
This will cool the cylinder and liquid, lowering the vapor pressure
Once it reaches the boiling point of the liquefied gas, the release rate will slow to the amount of heat into the cylinder. (Ngai rule of thumb) 200-400 BTUs per hour.

A 60 lb Hydrogen Chloride cylinder with the valve cutoff will quickly vaporize 22 lbs which would cool the remaining liquid to the boiling point of -121°F at 0 psig.



Applying the Ngai rule of thumb, heat transfer of 200-400 BTUs per hour, the remaining liquid will vaporize over a period of 19-38 hrs. Application of water to the cylinder will heat it faster.

Subcooled cylinder will typically have water or ice condensed on the surface

Liquefied gas cylinders should not be heated above 130°F due to 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

US 49 CFR 173.300

1. Pressure in the cylinder at 70°F less than or equal to the rated pressure of the cylinder. Reference 173.301.
2. The cylinder not to be liquid full at any temperature up to 131°F. Ref. 173.304(b).
3. The pressure in the cylinder at 131°F less than 5/4 the cylinder's rated pressure. Ref. 173.301 (a) 8

ADR & United Nation ST/SG/AC.10/C.3/34

1. 95% of the liquid density under its own vapor pressure at 50°C (122°F) Ref.: Packing Instructions P-200
2. 100% of the liquid density under its own vapor pressure at 60°C (140°F) Ref.: Packing Instructions P-200
3. The density such that the pressure at 65°C (149°F) is at the cylinder's test pressure. Ref.: Packing Instructions P-200

Gas	DOT kg/l (lbs/liter)	ADR kg/l (lbs/liter)	Japan kg/l (lbs/liter)	UN kg/l (lbs/liter)
Arsine	1.269	1.10	0.416	1.10
Phosphine	0.418	0.45	0.207	0.45
Hydrogen Selenide	1.71 (3.67)	1.60 (3.60)	0.244 (0.54)	1.60 (3.60)

July 1, 2014 Food Truck propane cylinder rupture and deflagration in Philadelphia. The pressure relief device was illegally plugged and the cylinder was overheated by the grill that was adjacent to the storage cabinet

Overfilled or over heated cylinders will rupture and stay in one piece

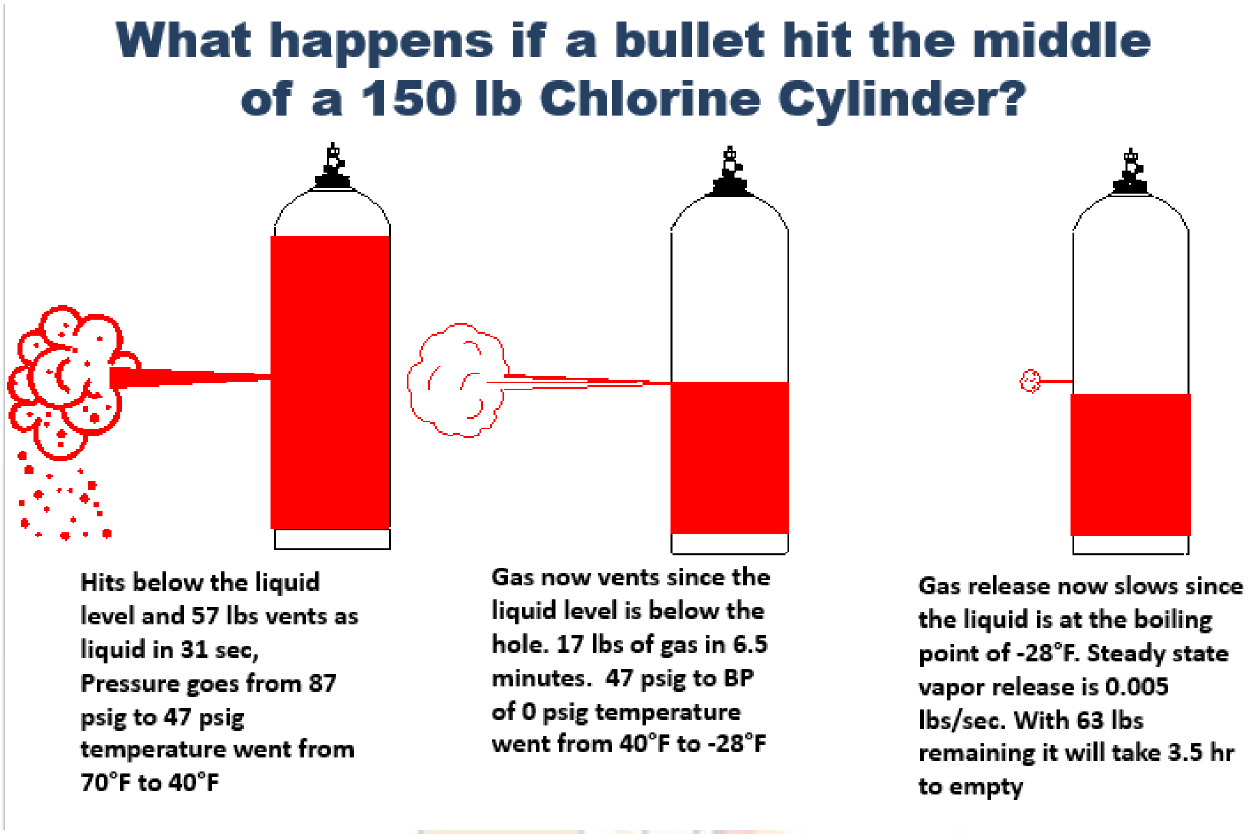
How hard is it to Puncture a Cylinder?

High pressure seamless cylinders are designed to withstand a bullet penetration without shattering (non shatterable)

High pressure seamless cylinders (3AA) are designed to withstand bullet penetration without catastrophic failure even when pressurized to the working pressure
Difficult to penetrate high pressure seamless cylinders using normal bullets. Need armor piercing and must hit square to the curvature
Low pressure welded cylinders are easier to penetrate

What happens when you shoot a full oxygen cylinder?
Oxygen hole is caused by oxygen reacting with the carbon steel

Bullet penetration of a full 150 lb Cl_2 cylinder will vent as follows



Hydrogen chloride has a critical temperature of 124.5°F (51.4°C). An HCl cylinder cooking in the sun when shot will vent its contents in minutes because it is no longer liquefied

Liquefied Gas Subcooling assuming 70°F (Ngai Rule of thumb)

- Gases which have a boiling point of less than 0°F will develop a frost line. High vapor pressure
- Gases which have a boiling point between 0°F and 40°F will have water condensation. Medium vapor pressure
- Gases which have a boiling point between 40°F and 100°F will have minimal or no cooling. Low vapor pressure

Gas	Boiling Point °F
Ammonia	-28
Arsine	-81
Butane	31
Chlorine	-29
Cyanogen Chloride	55
Hydrogen Chloride	-121
Hydrogen Cyanide	78
Hydrogen Fluoride	67
Hydrogen Sulfide	-77
Nitrogen Dioxide	70
Phosgene	47
Phosphine	-126
Sulfur Dioxide	14

Worst case venting of liquefied gas cylinders (Ngai rule of thumb)

Assumes:

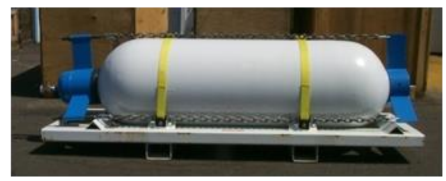
- Outside temperature is 70°F
- Release from full cylinder
- Release is from vapor space
- No additional heat into cylinder

High vapor pressure (e.g. Ammonia, Hydrogen Chloride) 30-50% vents in minutes
Medium vapor pressure (e.g. Butane, Sulfur Dioxide) 10-30% vents in minutes
Low vapor pressure (e.g. Cyanogen Chloride, Chlorine Trifluoride) <10% vents in minutes

5502 ERCV (Emergency Response Contianment Vessel)
ASME Pressure Vessel, Section 8, Div 1
Working Pressure - 1100 psig
Quick Opening Flange
Double O Ring (Buna N and Viton)
Cylinders Up To 50 liters
Volume of 34.6 gallons (131 liters)
Empty Weight - 945 lbs
Normally On Disk Brakes
Pneumatic Foam filled Tires, Optional Solid
Chain To Hold Cylinder In Place
Slide Rails

Scrubbers

5502 ERCV



Y Containment Cap

Ion Implant Carriers

Cascade System

Cold Coil