Latent Heat of Vaporization

April 2023

The common liquefied gases are ammonia, propane, chlorine all have a vapor pressure that varies with temperature. Hydrogen chloride vapor pressure curve is as follows

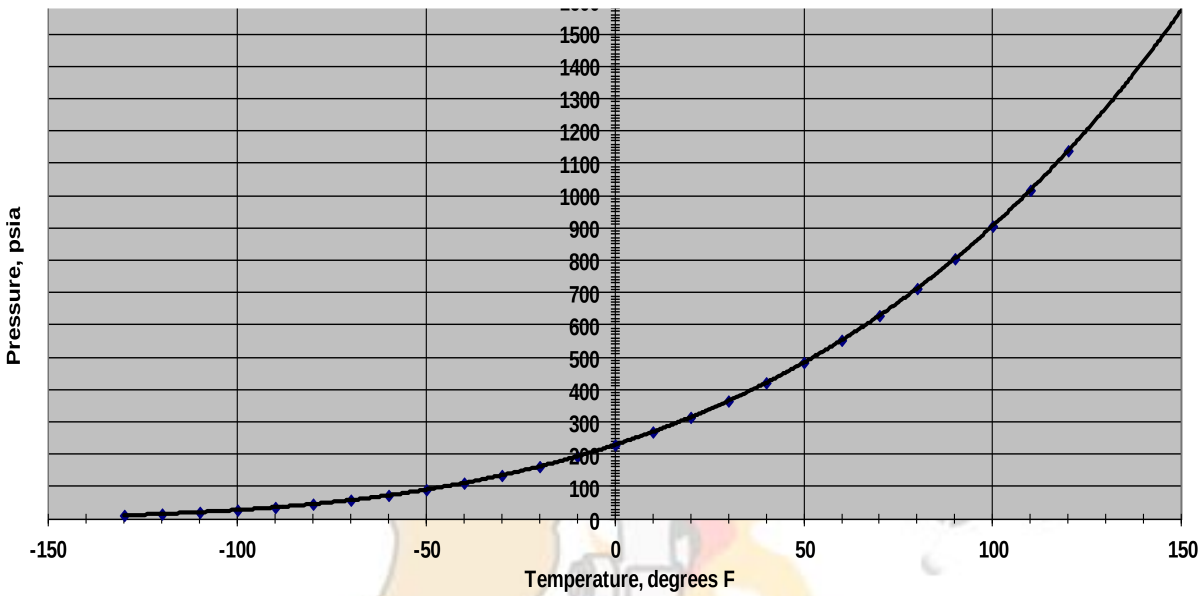


Fig. 1: Hydrogen chloride vapor pressure curve

The latent heat of vaporization (aka auto refrigeration) is the amount of heat required to vaporize the amount of liquid of the liquefied gas to replace the gas used as the vapor is withdrawn from the cylinder. The heat comes primarily from the remaining liquid and cylinder mass. As gas is withdrawn from a cylinder of liquefied gas the remaining liquid will cool due to this vaporization, which will lower the vapor pressure until it reaches the boiling point of the gas and a pressure of 0 psig. Common units used for heat are BTU/lb or cal/gm. This can be estimated by the following simplified equation.

Assumptions:

- Constant flow rate
- Constant gas density
- Constant heat transfer due to ventilation air of 70°F
- Ignores the constant enthalpy expansion at regulator

Simplified Equation is:

$$\text{Temp Liquid}_{\text{Time X}} = 70^{o}\text{F} - \frac{(\text{Y X Heat Vap}) + (\text{X Heat}_{\text{In}})}{(\text{Z} - \text{Y X})\,\text{Cp}_{\text{Liq}} + \text{Weight}_{\text{Cyl}}\,\text{Cp}_{\text{Cyl}}}$$

Where:

Y = Gas flow rate, lbs/min
X = Time, min
Z = Weight of Liquid at Time X, lbs
Cp = Heat Capacity, Btu/lb

If the compressed gas is vented as a liquid, this would not happen.

This effect can be significant in a worse case release incident.
For example, 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 at sea level.

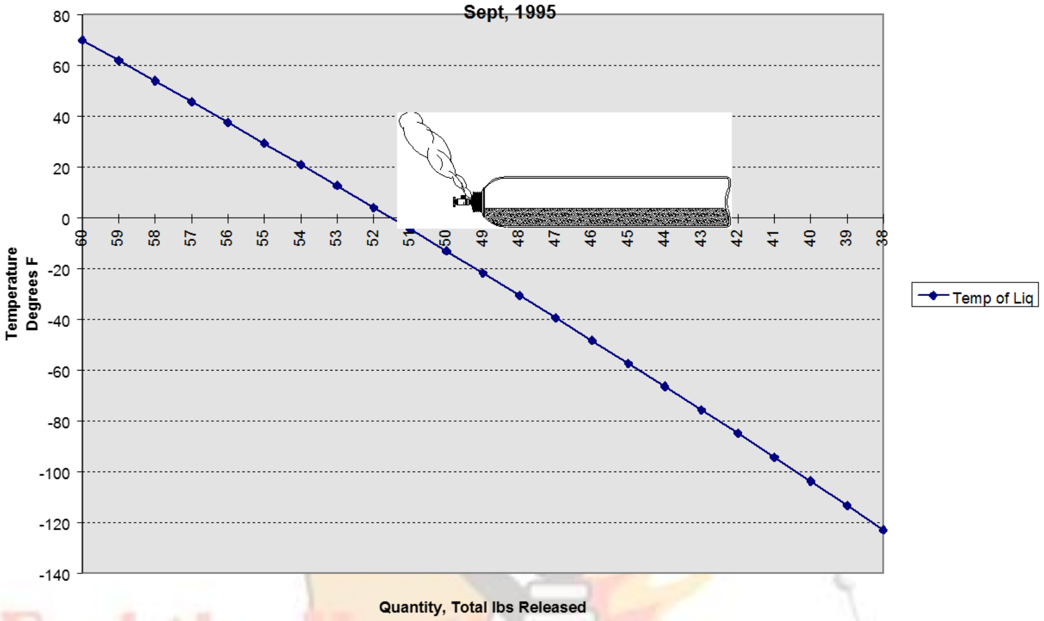
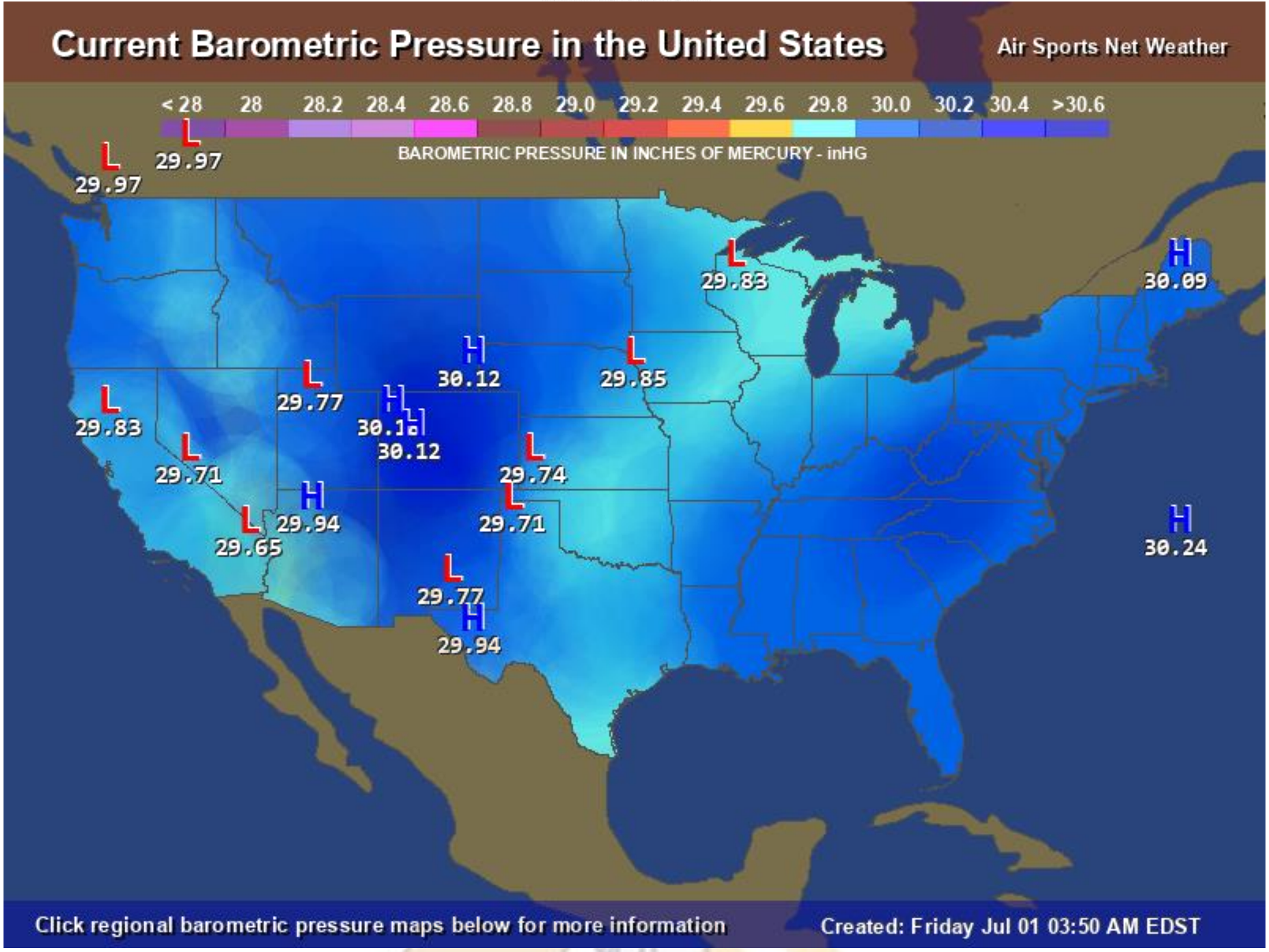


Fig. 2: HCl Vent versus Temperature

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

At sea level atmospheric barometric pressure is 29.92 in Hg (760 mm/Hg). At Denver which is 5,000 ft above sea level barometric pressure is 24.9 in Hg. (632 mm/Hg). This changes the boiling point of water to 203°F (95°C).



At that point, if we apply the Ngai ER rule of thumb, there will be a heat transfer of 200-400 BTUs per hour from the air into the cylinder, therefore the remaining liquid will vaporize over a period of 19-38 hrs. Application of water to the cylinder exterior due to a knockdown water spray will heat it faster since hydrant water is typically about 50°F.

Fig. 3: Subcooled nitrous oxide

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

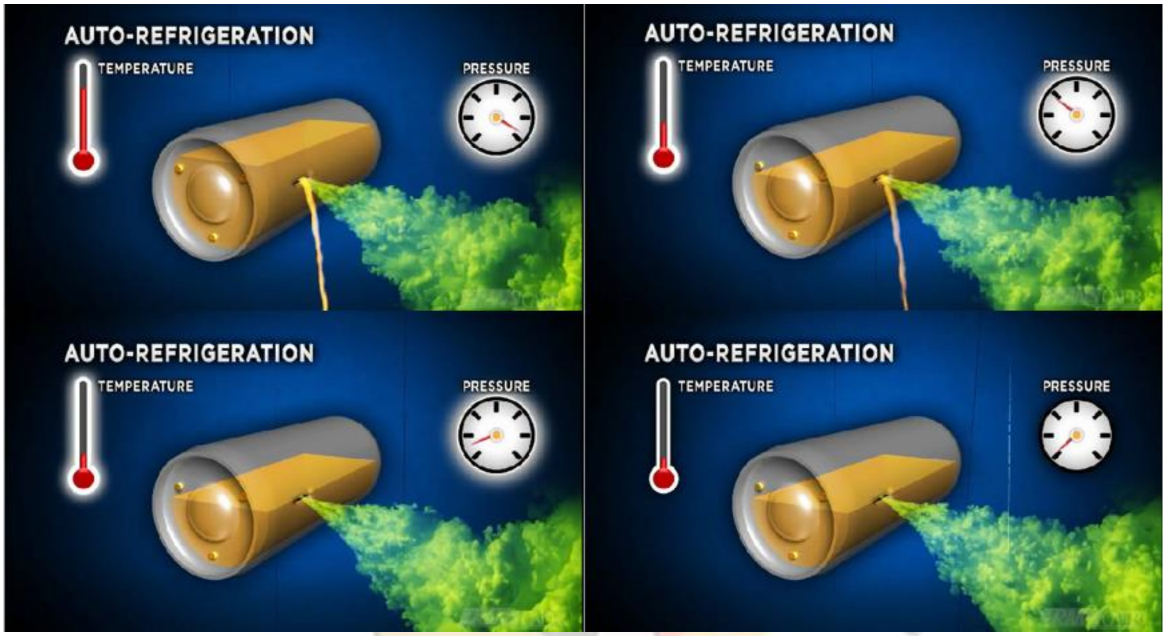


Fig. 4: Chlorine Institute Auto refrigeration Video

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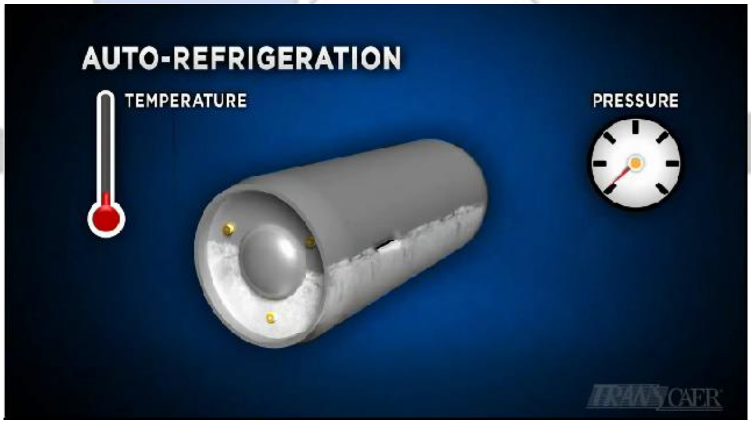


Fig. 5: Liquid chlorine has reached the boiling point and pressure drops to 0 psig

Fig 6: “Empty” chlorine ton cylinder crushed at junk yard

Actual Testing Results

Ammonia

To demonstrate this at an ammonia training class in 2010, the packed valve on a full 100 lb cylinder was opened fully. The cylinder was on a scale and a thermocouple was placed on the surface to measure temperature.

Fig 7: Venting 100 lb ammonia cylinder

Vented 19 lbs in 8 minutes 10 secs when the temperature reached -28°F (-33.4°C) the boiling point of ammonia when the venting slowed considerably. The remaining 81 lbs would take over a day to vent.

The powerful effect of the latent heat of vaporization was evident after the fatal silane incident in 2005. Several full ammonia cylinders in the gas room started to vent due to the intense fire activating the pressure relief devices. As they vented the cold temperatures caused the sprinkler water around the cylinder to freeze. Sixteen hours after the fire the Taiwan EPA HazMat team had to physically break the cylinders from the ice to remove them.

Fig 8: Removing ammonia cylinders frozen to ground

Arsine

In 1995 as part of the Solkatronic Risk Management Planning it was determined that a full 60 lb arsine cylinder release would be the worst case event for the facility. While a valve shear is extremely unlikely it was assumed to be the case.

A 29 liter aluminum crude Arsine cylinder with 60 pounds (cylinder #CC68085) was connected to the Arsine disposal manifold and placed on a mixing room scale with a 1 gram accuracy. A second empty 29 liter aluminum cylinder (#CC64161) was placed in a dewar filled with liquid Nitrogen. While this system probably creates a higher initial flow rate due to the vacuum caused by the cylinder immersed in liquid Nitrogen, it was more desirable than releasing this high flow rate of Arsine into a scrubbing system.

The pressure of the cylinder was monitored by a high accuracy pressure gauge on the residual manifold.

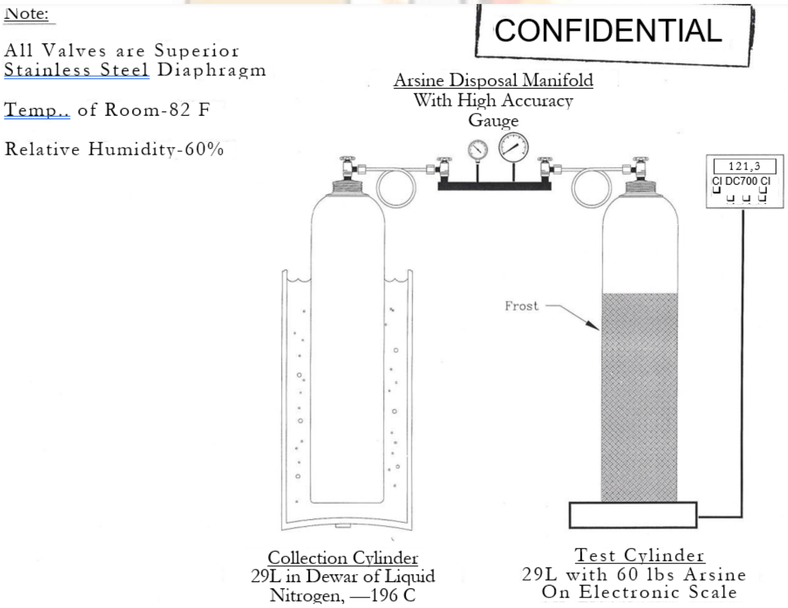


Fig: 9: Test System

After 10 minutes there was ice formation on 60% of the cylinder that was venting.

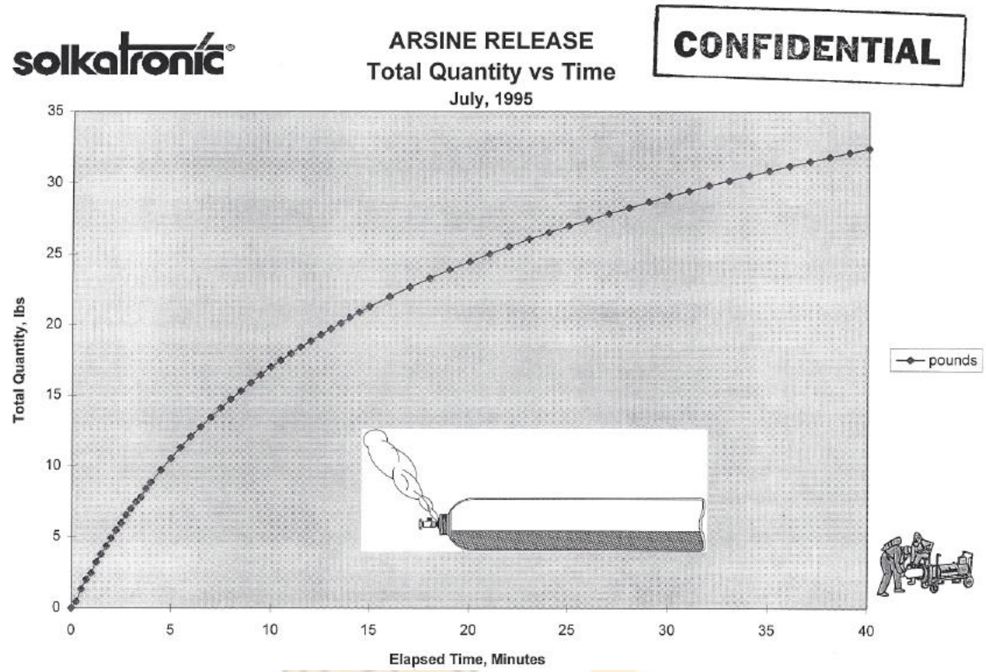


Fig 10: Quantity Release versus Time

Theoretically under ideal flow conditions where flow is not limited and the system is truly adiabatic, it would take vaporization of 33 pounds of arsine to chill the liquid to its boiling point of -80°F 0 psig. This assumes:

- Latent heat of vaporization remains constant at 92 BTU/lb.
- Heat capacity of liquid Arsine remains constant at 0.2125 BTU/lb.
- Heat capacity of the aluminum remains constant at 0.374 BTU/lb.

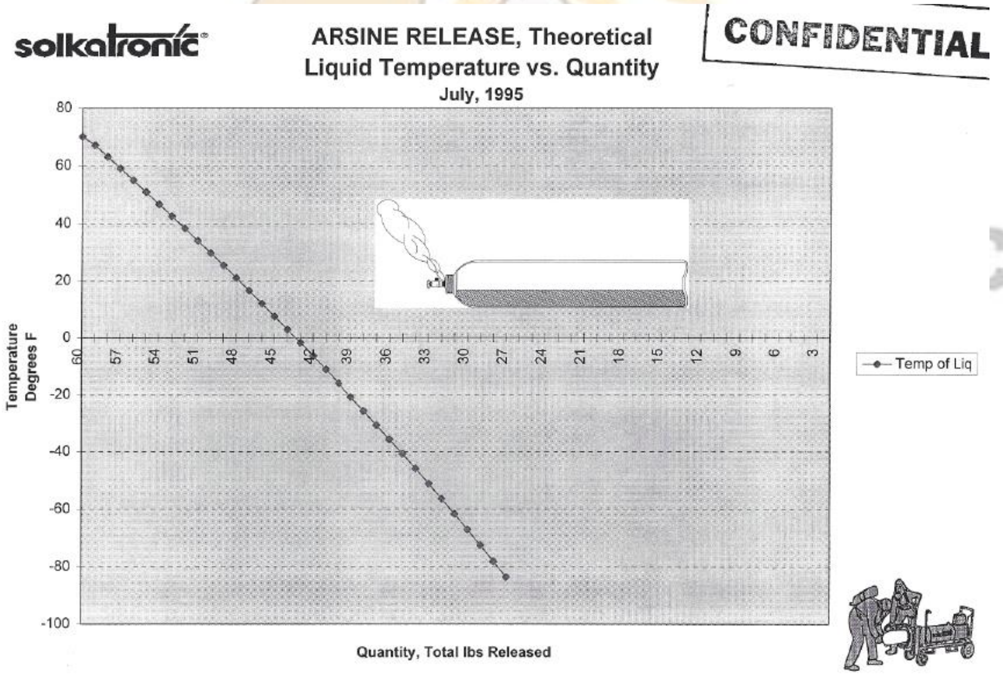


Fig: 11: Temperature of Remaining Liquid Versus Time

Comparison of the actual flow versus theoretical reveals that at 40 minutes into the test, 32.5 pounds of Arsine has been released and the pressure has been reduced to 5.5 psig. At this pressure, the liquid Arsine would be chilled to -50°F which theoretically would require 27 pounds of vaporization. The difference of 5.5 pounds is 506 BTU's transferred from the environment during this period of time. The condensation and freezing of moisture in the air contributes significantly to this and it is estimated that <0.27 pounds is on the surface of the cylinder (assuming latent heats of vaporization and fusion = 1865 BTU/lb.)

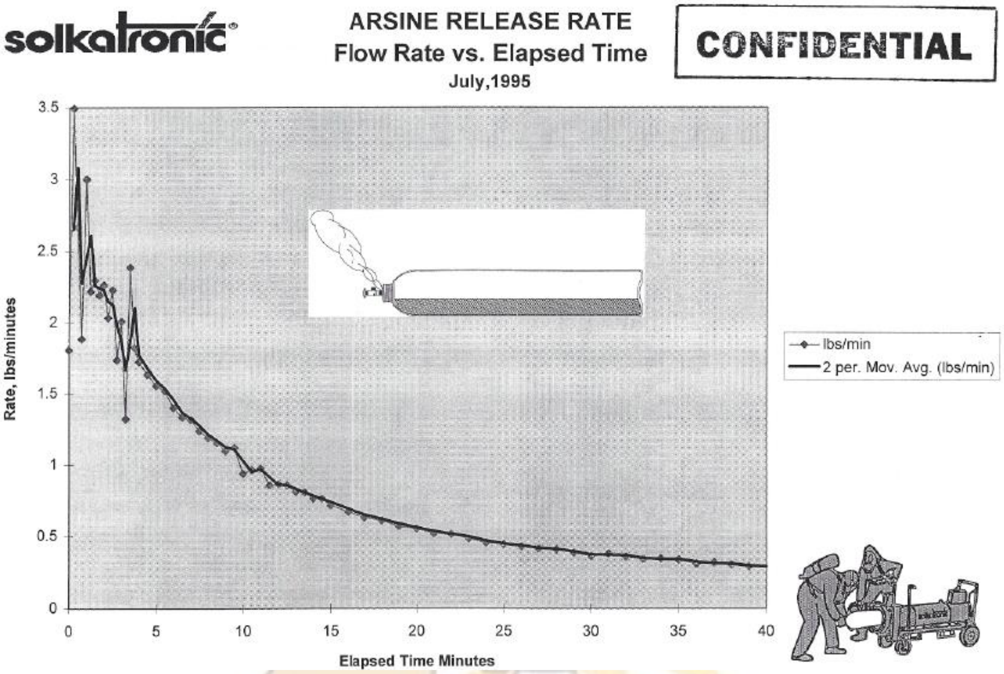


Fig: 12: Release Rates

If one assumes that the heat is transferred over 30 minutes this would translate into 17 BTU/min. At 40 minutes the flow rate has been reduced to 1.45 cfm and continues to decline. It can be concluded that an equilibrium would be established between the heat transfer (17 BTU/min), and the Arsine vaporized (92 BTU/lb) which is estimated to be a flow of 0.92 cfm. At this rate the remaining 27.5 lbs would be released over an 149 minute period (2.5 hours).

An interesting note is that the highest release rates achieved were 17.5 cfm which occurred in the first minute which is significantly less than that theoretically estimated in many publications of 38.2 cfm.

The boiling point will change as the elevation above sea level changes.

For the more commonly used liquefied gases, propane, ammonia, chlorine ice would be formed on the cylinder surface since their boiling points are much less than 32°F.

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

1. Gases which have a boiling point of less than 10°F will develop a frost line at the liquid level. High vapor pressure
2. Gases which have a boiling point between 10°F and 40°F will have water condensation. Medium vapor pressure

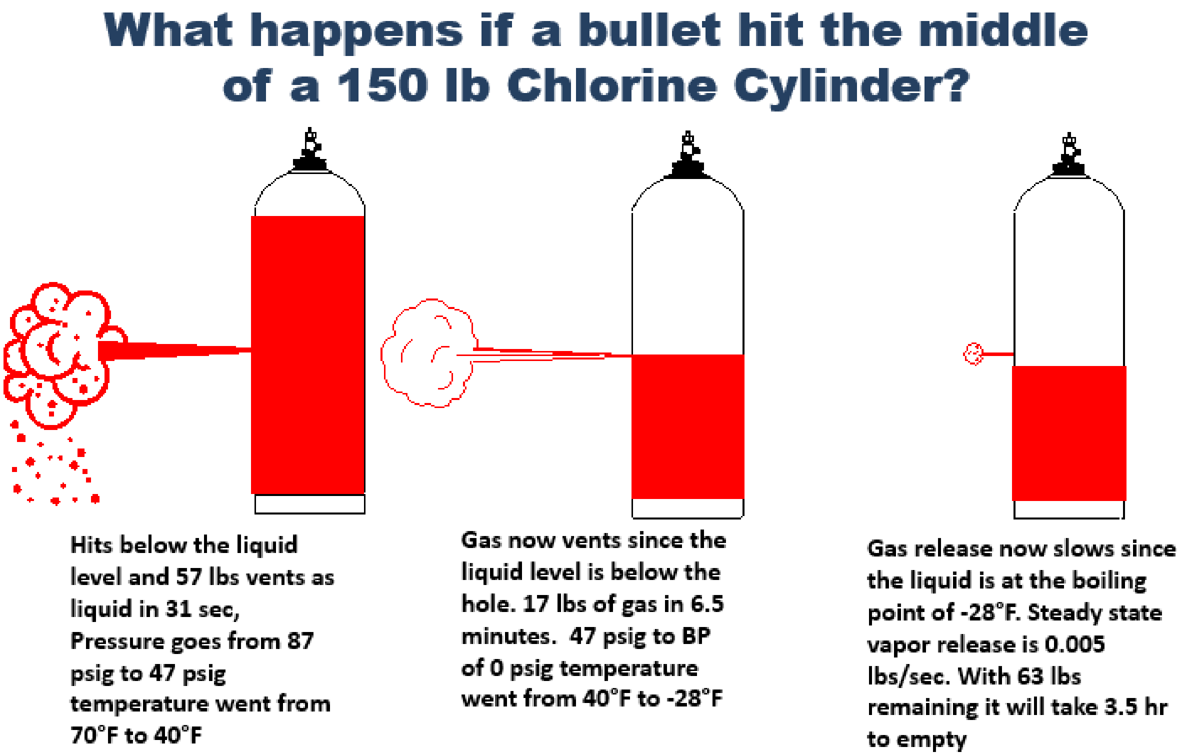
3. Gases which have a boiling point between 40°F and 100°F will have minimal or no cooling. The following low vapor pressure gases will not condense water on the cylinder surface since the boiling point is well above freezing.

	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)

Table 1.: Low Vapor Pressure Liquefied Gases

People have mistakenly assumed a cylinder was close to empty when the release rate slowed down considerably. In one case the HazMat team installed a Cl_2 A Cap on a leaking HCl cylinder. It successfully contained the leak until the cylinder warmed up and the HCl vapor pressure built up beyond the 120 psig it would normally contain. In another incident the waste disposal workers thought the arsine cylinder they vented was empty. They removed the cylinder valve and poured in some chemical neutralizer, it immediately vaporized the subcooled arsine and acutely exposed 2 workers. One died a few days later and the other suffered permanent injuries.

If a terrorist shoots a Cl_2 cylinder, what can happen? It depends on where the bullet hit.



What happens if a bullet hit the middle of a 150 lb Chlorine Cylinder?

Hits below the liquid level and 57 lbs vents as liquid in 31 sec, Pressure goes from 87 psig to 47 psig temperature went from 70°F to 40°F

Gas now vents since the liquid level is below the hole. 17 lbs of gas in 6.5 minutes. 47 psig to BP of 0 psig temperature went from 40°F to -28°F

Gas release now slows since the liquid is at the boiling point of -28°F. Steady state vapor release is 0.005 lbs/sec. With 63 lbs remaining it will take 3.5 hr to empty

Fig. 13: Bullet Penetrating 150 lb Cl_2 Cylinder In the Middle

In one of the 2016 Jack Rabbit tests, the vapor was released through a 6 inch diameter opening of a 20 ton tanker. 6 tons was quickly released with violent boiling likely propelling a significant amount of liquid out. The remaining liquid subcooled to the boiling point of -29°F.

Figs. 14 & 15: Vapor Venting from 20 Ton Chlorine Tanker

Latent heat of vaporization of a liquefied gas has a pronounced effect on gas release rates and liquid temperatures.

Eugene Ngai