

Cryogen Safety

PRS115

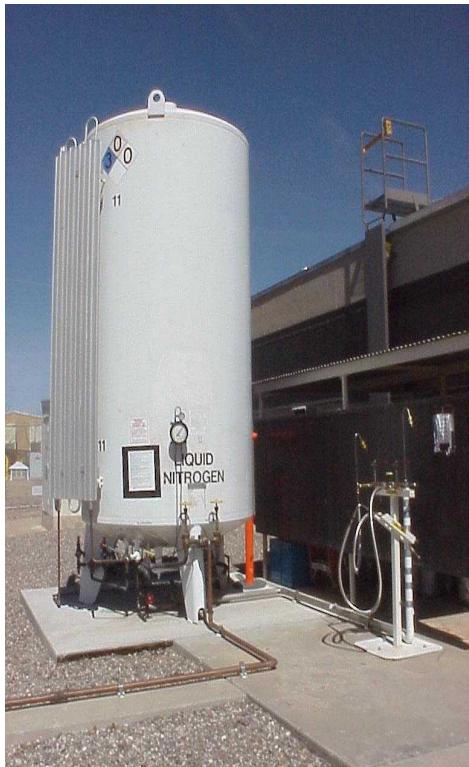
March, 2006

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Cryogen Safety - Theory and Safety Concerns {PRS115}

Course Objective:

Students will identify properties of cryogenic fluids, associated hazards, and safety practices unique to cryogenic pressure systems.



At the end of this course you should:

1. Know how cryogen safety relates to the SNL Pressure Safety Program
2. Recognize cryogenic fluid properties
3. Be aware of hazards associated with cryogenic systems and the recommended hazard mitigation techniques
4. Have an increased awareness of common accident scenarios

Pressure Safety Program

Goal is to provide a safe pressure environment

SNL Pressure Safety Program incorporates:

- DOE Pressure Safety Guidelines
- National Codes for Pressure Vessels, Systems, Hardware
- SNL Experience
- Sandia's Integrated Safeguards and Security Management (ISSM)

SNL Pressure Safety Program elements:

- Develop individual knowledge of a safe pressure environment
- Provide policy & procedures (Pressure Safety Manual)
- Provide advice & assistance (PSC and Pressure Advisors)
- Establish accountability through proper design, operation, documentation, and periodic inspections
- Provide hardware control (safe and rated for the application)



Cryogen Safety Information

Pressure Safety Program

ES&H Manual & Supplements:

- **Pressure Safety Manual**
cryo applications referenced
- **Safe Handling of Cryogenic Liquids**

Other SNL references

- **Facilities Administrative Procedure:**
(defines cryogen system ownership & responsibilities)

- **Homepage**
<http://psi.sandia.gov/>
subscribe to “Pressure Safety Issues”

PSI Program

Techweb | Safety Home

Home /

 SNL Pressure Safety Program

OUR GOAL IS TO PROVIDE A SAFE ENVIRONMENT FOR PRESSURE APPLICATIONS.

Hot Topics

Please refer to the PSC Bulletins for an important Safety Alert concerning accidents related to improper assembly of pressure hardware.

Please refer to Application Note #3 concerning pressure manifold design concepts, and Application Note #4 concerning common use of gas phase house nitrogen.



**must “subscribe”
to receive e-mail notifications**

* click on the SNL Subscription Notification Service icon on the Homepage

Content - Roger Shupuf
IMT Web Providers

Cryogen Safety Information

continued

- **Safety in the Handling of Cryogenic Fluids**

by F. J. Edeskuty and W. F. Stewart

1996 Plenum Press N.Y. {ISBN # 0-306-45161-1}

- **Cryogenics Safety Manual**

by the Safety Panel, British Cryogenics Council

1991 Butterworth-Heinemann Ltd. {ISBN # 0 7506 0225 2}

- **Cryogenic Process Engineering**

by K. D. Timmerhaus and T. M. Flynn

1989 Plenum Press N.Y. {ISBN # 0-306-43283-8}

- **Cryogenic Engineering & Cryogen Safety Courses**

CRYOCO 511 N. Adams Ave.

Louisville, CO. 80027 (303) 665-8302

- **Vendor info / OEM manuals**

- video tape from Chart (formerly MVE) on LN₂ dewars

- detailed dewar filling instructions

Personnel Involved with Pressure Systems

- should be identified by job task & responsibilities

Pressure Advisors (PRS160)

- oversight and consultant functions

*There should be a
“game plan” for every
pressure system.*

Pressure System Installers (PRS150 & PRS250)

- design, modify, and operate systems without supervision

Pressure System Operators (PRS150)

- hazard awareness, familiarity with system assembly and requirements, and know of available assistance

Operators - for cryogen applications (PRS115)

- cryogen safety is now addressed separately
- where other pressure or vacuum responsibilities exist, both training courses may be applicable



Personnel Involved with Pressure Systems should be:

- identified according to job task
- aware of system hazards, requirements, and available assistance

Pressure Operator = PRS150 + **Hardware Training ?** + OJT

Pressure Installer = PRS150 + PRS250 + **Hardware Training** + OJT

Pressure Advisor = PRS150 + PRS250 + **Hardware Training** + PRS160

NOTE: add PRS115 for any cryogenic applications

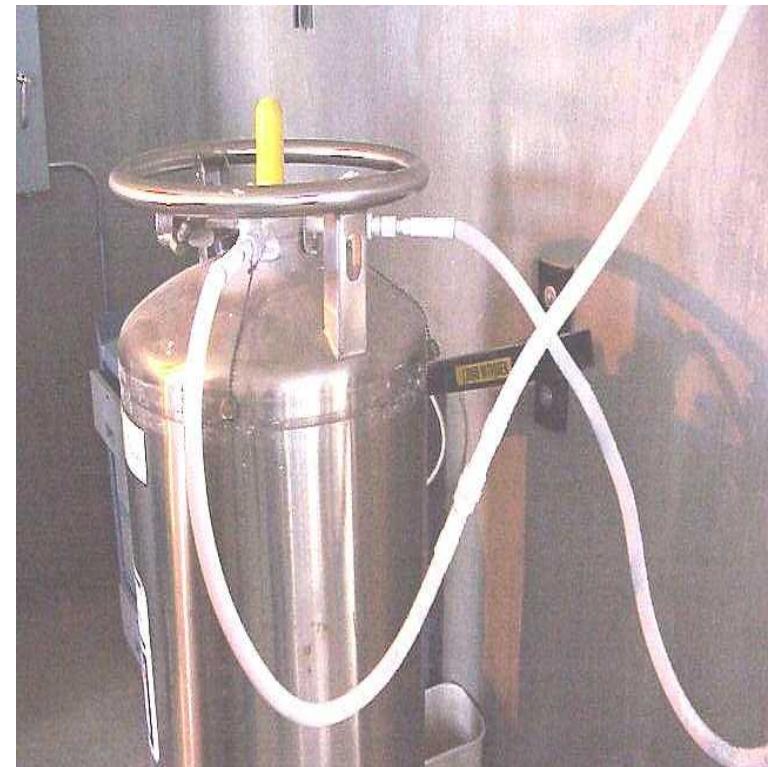
Qualification forms - in PSM Chapter 2

- 1) matches personnel to their application(s)
- 2) documents training (including OJT)
- 3) qualification recommended and approved

Cryogen Safety

Cryogenic Liquids:

Cryogenic liquids are **gases that have been transformed into extremely cold liquids** which are stored at low pressures in specially constructed, multi-walled, vacuum-insulated containers. Although - 160°F is frequently cited, for safety considerations, we use - 100°F which will include liquid carbon-dioxide (CO₂) and liquid ammonia (NH₃) in this classification.



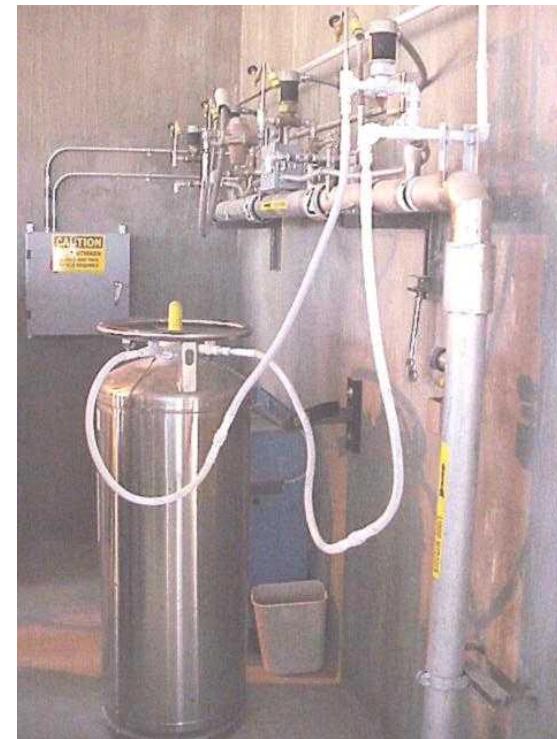
Why Cryogenics in a Pressure Safety Program?

Pressure Safety Manual requirements apply to cryogenic applications
- special considerations for cryogenic fluid properties

Knowledge of cryogen types, characteristics, and hazards will heighten safety awareness

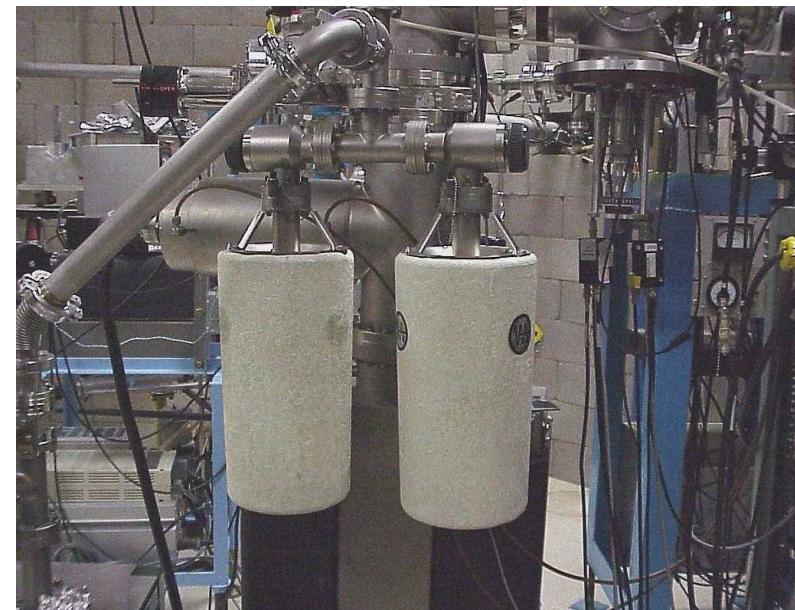
Common cryogen hazards:

- Thermal (Freezing)
- PPE concerns (includes noise)
- Ice build-up
- Back strain / lifting
- **Pressure Build-up**
- Brittle Materials
- **Asphyxiation / O₂ deficiency**
- Oxygen Enrichment



Cryogen Applications

- 1) Vacuum - cold traps & sorption pumps
- 2) Provide a source of gas
 - {high volume / high purity}
- 3) Super conductor research
- 4) Low temperature materials research
- 5) Cryo-aerosol cleaning applications
- 6) Rocketry - space shuttle, etc.
- 7) Low volume storage and shipping
- 8) Refrigeration - food transport, etc.
- 9) Medical uses
- 10) Misc.



Cryogen Properties

Temperature {Normal Boiling Point at 1 atm}

| { Kelvins } | { °F } | { °C } | Cryogen {Temp. @ 1 atm.} | Liquid to Gas Expansion Ratio | Pressure build-up of trapped liquid warmed to room temp. |
|-------------|--------|--------|---|----------------------------------|---|
| 273 | 32 | 0 | {ice melts} | | |
| 194.6 | -109 | -78.3 | carbon dioxide $\text{CO}_2 \approx 840 \text{ psig} @ 70^\circ \text{ F}$ | {CO ₂ } | $\approx 1 \text{ lb} : 8.5 \text{ ft}^3$ |
| 111.6 | -258 | -161.4 | liquid methane | {LCH ₄ } | 1 : 578 |
| 90.2 | -297 | -182.7 | liquid oxygen | {LOx} | 1 : 860 |
| 87.3 | -302 | -185.5 | liquid argon | {LAr} | 1 : 847 |
| 77.4 | -320 | -195.6 | liquid nitrogen | {LN ₂ } | 1 : 696 43,000 psig |
| 20.3 | -423 | -252.7 | liquid hydrogen | {LH ₂ } | 1 : 851 28,000 psig |
| 4.2 | -452 | -268.8 | liquid helium | {LHe} | 1 : 757 18,000 psig |

Notes:

- Air can be condensed to an oxygen enriched liquid at LN₂ temperatures
- Argon, nitrogen, and oxygen can be condensed to solids at LH₂ or LHe temperatures
- All of the above substances are condensed to solid at LHe temperatures

(except helium itself)

Thermal (freezing) Hazards

- Cryogens and cold boil-off gases can freeze tissue
- Cold metal parts will freeze tissue
 - skin moisture freezes and sticks to the surface



Recommended PPE for Cryogenic Applications

(PPE = Personnel Protective Equipment)

1) Consider engineering controls first

- **safe design of equipment / fill stations**
{hands / face away from point of discharge}
- **insulation / valve design {rated for service}**
{vacuum jacketed or insulated transfer lines}

2) Procedural – open valves slowly (hose whipping)

- **slow transfers to minimize splashing**
(also, minimize generation of asphyxiant boil-off gases)
- **assure system shut down {valve is closed!}**

3) Wear PPE appropriate for the application

- **minimum of safety glasses with side shields**
for open handling of liquids, dewar filling, breaking
connections, etc...



Recommended PPE for Cryogenic Applications {continued}

4) Additional protection

- loose fitting gloves / sleeves / apron
- safety shoes / hearing protection

5) Other clothing concerns

- wear cuffless trousers over boots
- some clothing {sandals, shorts, etc.}
can increase the risk of exposure



Ice Buildup - The Most Common Atmospheric Effect of Cryogen Systems...Often a Hazard

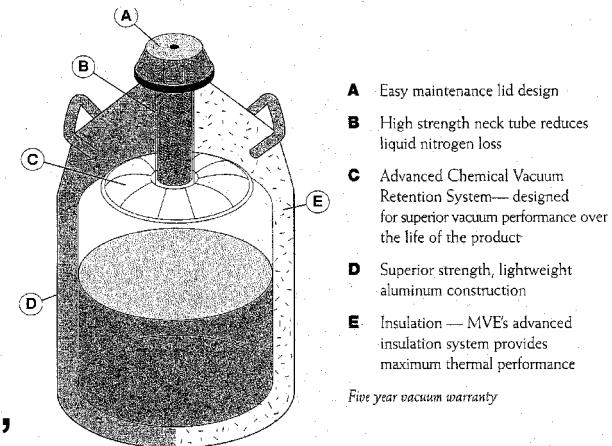
1) Cold surfaces gather atmospheric moisture.

2) Critical elements (pressure reliefs, valves, etc.) must be maintained above water freezing point.

3) Most common solution is extended length of poor conducting material {stainless steel}

4) Critical vents should be covered, or pointed down, i.e....dewar necks or vent tubes, pressure reliefs, etc...

5) Frost on dewars may indicate a problem?
loss of vacuum? or
normal operation? {evaporators - to generate gas}
(OEM manuals and instructional videos are available)



Ice will eventually melt, and may create a hazard for slips / falls, electrical hazard, etc.

Back Strain / Sprain is Frequently Associated with Cryogen Handling - Some Solutions

1) Automatic fill stations

- moving of cryogens not required

- OEM equipment for pressurized transfer

2) Dewars appropriately sized

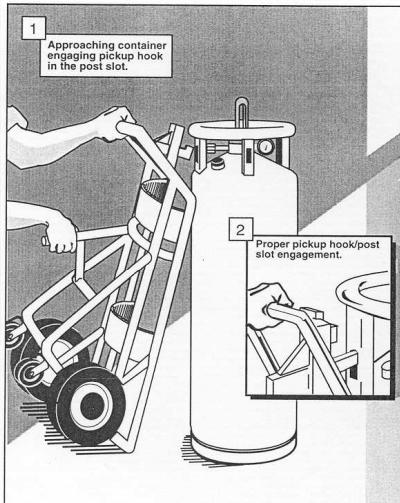
- cryogens easier to move

- follow OEM operating instructions

3) Proper handling equipment

- wheeled-base

- engage hand cart properly



Pressure Hazard - Trapped Liquid = Pressure Build-up



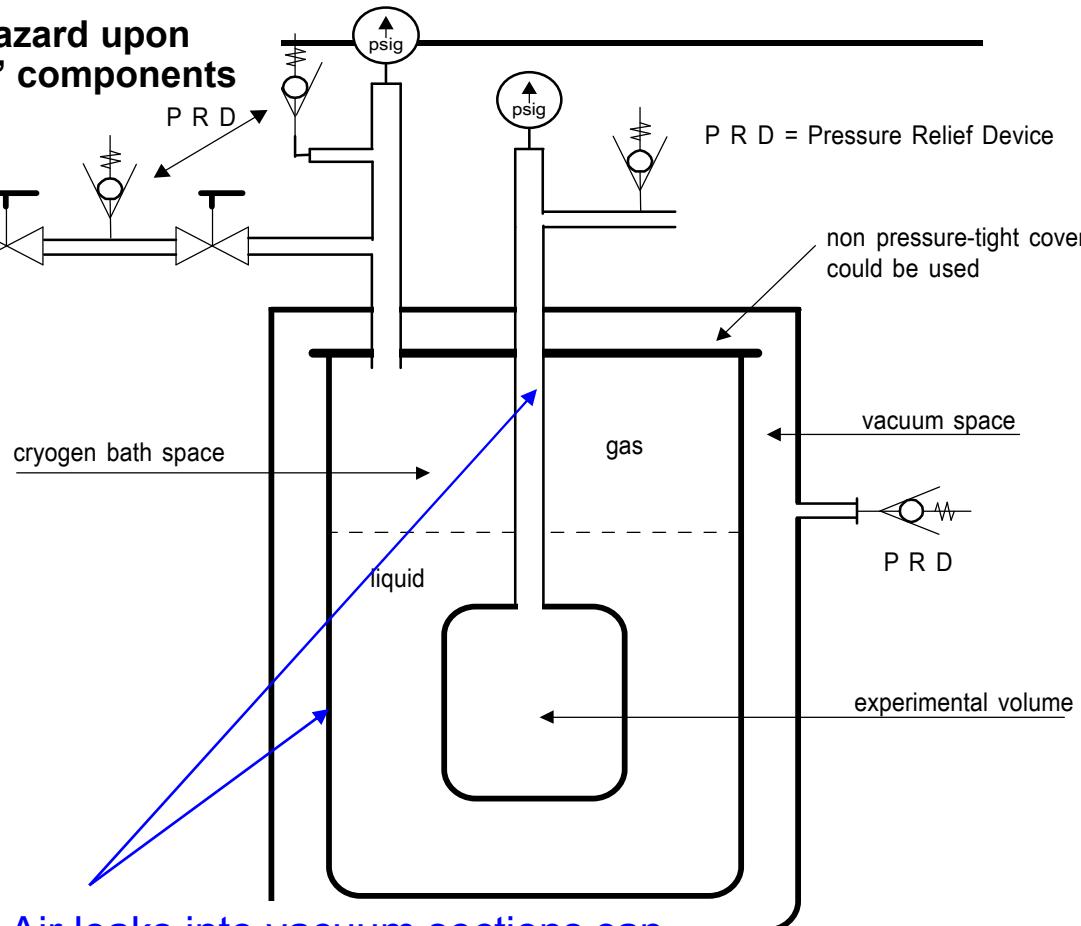
Pressure build-up hazard upon warming of "chilled" components

* Be sure to have a pressure relief valve between supply dewars and temperature chambers



Each Space in Contact with the Cold Must Have Pressure Relief

Some designs call for dual relief devices - a burst disk in parallel with a pressure relief valve



Air leaks into vacuum sections can condense into liquids or solids - and plug vent tubes or produce pressure build-up hazards upon warming



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Pressure Build-up - Engineering Controls

Each space must have pressure relief

Pressure relief is provided by:

1) pressure relief valves

and evacuation / relief ports

- do not “cold shock”

- rated for the application (LN₂ vs CO₂)

- applies to other types of valves too

2) burst disks

3) loose fitting covers / caps

4) vent lines

5) relief {vacuum} disk

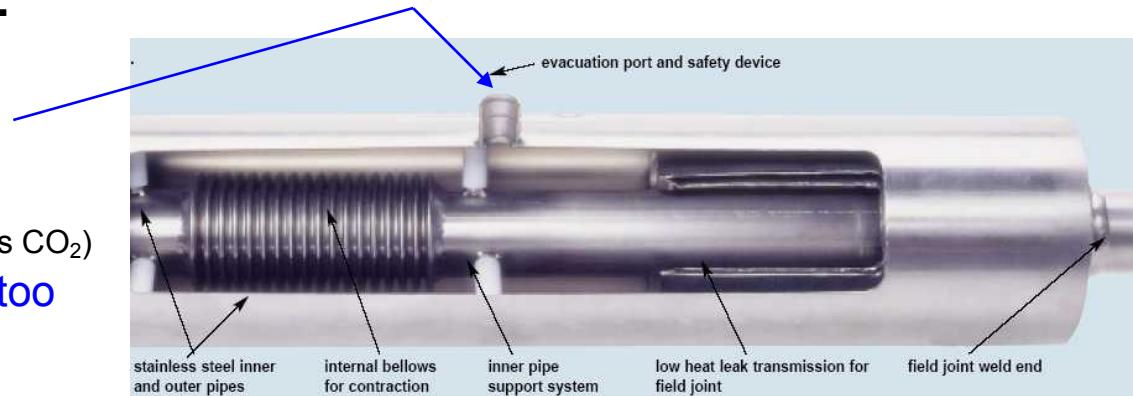
held in place by vacuum

6) apply vacuum pump during warming

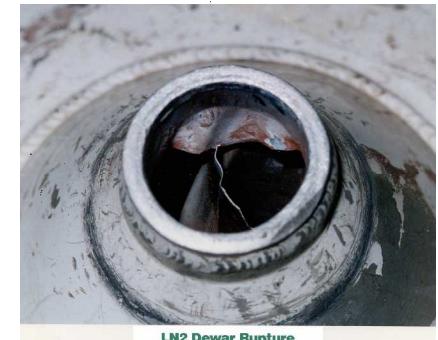
(compatibility with condensed oxygen)

*** Do not allow relief device to
ice over (or ice plugs in vent lines)**

*** Do not modify commercial
pressure relief designs**



1960's vintage Linde dewar
without pressure relief
on vacuum space



Laboratory Storage Dewars



1) Non-pressurized storage dewars

- hand pour or use OEM transfer equipment (at a few psig)
- loose fitting cap
- pressure relief on vacuum space



2) Liquid dewars (pressurized) various sizes

- liquid withdrawal LN_2 = 22 psig max LHe < 5 psig
- vent / gas phase
- gas use = 230 psig (or higher?)
- pressure building circuit (adjusted by TriGas or external pressure source for transfer – use a PRV)
- redundant pressure relief



* Pressure Relief Concern

Often overlooked – a PRV is needed to connect dewars to temperature chambers (the possibility of 2 closed valves may exist)



*** Do not use consumer containers {thermos bottle, etc.} for cryogenic fluids**

Dewar Filling Procedures & Concerns

Dewars should be filled outside (or in well ventilated areas)

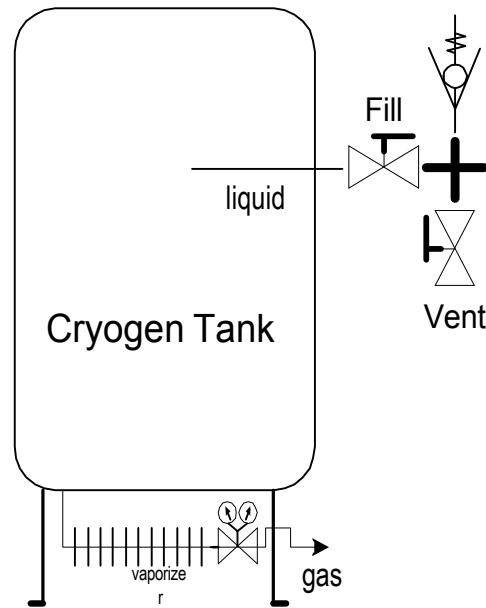
* Don the applicable PPE prior to filling

Open dewar fill procedure

- 1) confirm dewar is at low pressure (22 psig)
- 2) insert transfer line into the receiving dewar (use a phase separator to reduce splashing)
- 3) slowly open liquid valve
- 4) close the liquid valve when the receiving dewar is full (exhaust gas contains liquid)

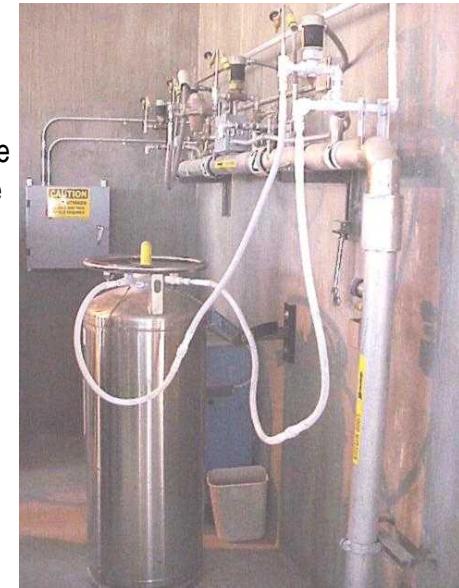
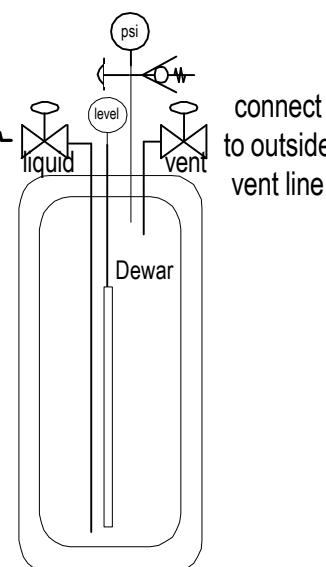
Notes:

There is no (easy) way to capture the boil-off gas – very important to stay in the near-by area while filling. Accidental overflows will create immediate hazards.



Pressurized dewar fill procedure

- 1) connect the supply to the dewar fill valve
- When possible, connect the vent valve to a vent line and direct the boil-off gas to a safe location
- 2) open the vent and liquid valves on the receiving dewar
- 3) slowly open the fill valve on the source
- 4) close the liquid and vent valves on the receiving dewar when full (weight / gauge / venting liquid)
- 5) close the fill valve on the source - and vent pressure in the transfer line



Warning Signs System malfunctions or variations from normal operating conditions - must analyze the safety implications

1) Apollo 13 - warning signs

2) Normal pressure or vacuum readings

confirm dewar pressure

3) Normal operation / procedures

- venting (noise)

- transfer of liquids or gas

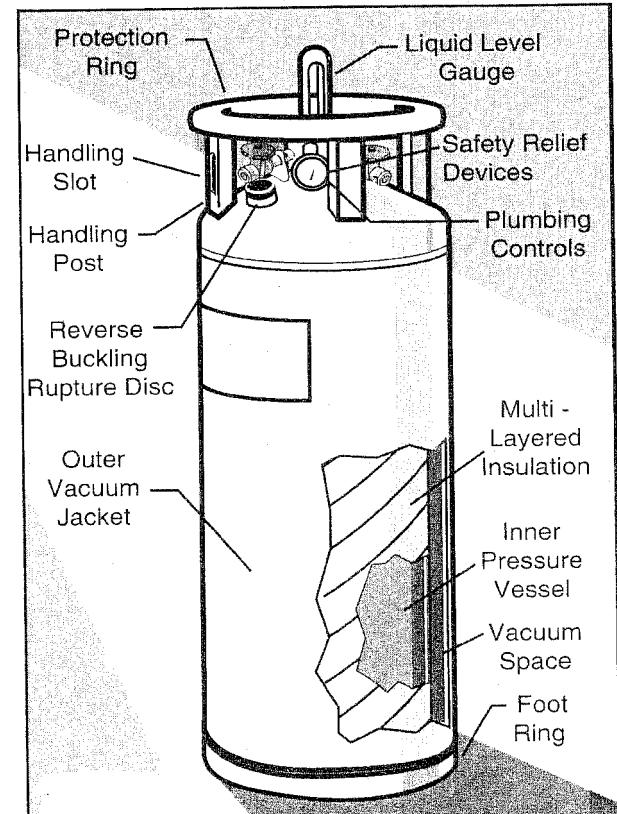
(liquid level / usage rates)

4) Frost - can represent a hazard

- room temp. seals can leak when cooled

- low temperatures can cryo-pump air and result in a

pressure hazard upon warming



Low Temperature Materials Concerns

- Materials may become brittle {bcc structured metals}

Nickel Steel (with < 7% nickel)

Iron, Carbon, & low alloy steels (martensitic steels)

soft tubing - tygon

- Acceptable materials {fcc structured metals}

300 Series Stainless Steel (Swagelok & VCR connections)

Copper

Brass

Teflon seals {or indium}

* silicone (surgical) tubing

only for small volume applications - frequent replacements

- Application Notes

thermal contraction / stresses

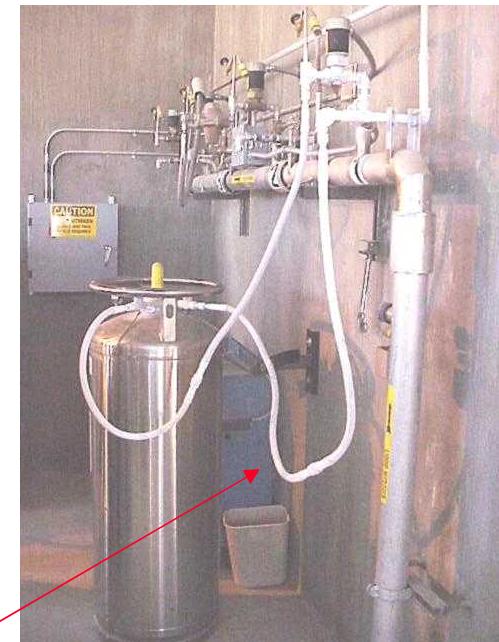
procedures - slow cool-down

joining of dissimilar materials



Don't Neglect the Asphyxiation Hazard

- **Cryogens flash to very large gas quantities**
 - use slow cool-downs to minimize the generation of boil-off gases
 - equipment failures can cause accidental releases or unusually high boil-off rates that can present an asphyxiation hazard.
- **Cold gas from LN₂ boil-off is heavier than air**
 - displaces air / travels to lowest elevation
- **Result is serious oxygen-lean environment**
 - Normal O₂ level is 20.9 %
 - 19.5% = Oxygen Deficient Atmosphere
 - = Do Not Enter / Evacuate the area
- **Asphyxiation hazard is directly related to volume**
 - “House” systems represent a much greater hazard than intermediate sized dewars.



Example – dewar filling from a “house” source.

Connect the vent valve to an outside vent line.

Automated systems are available to prevent overflow.

Asphyxiation Hazard {continued}

Get specific guidance from your Industrial Hygienist

| % Oxygen | “At-rest” Symptoms |
|-------------------------|--|
| 20.9 % | none – standard atmospheric conditions |
| 19.5% | OSHA “oxygen deficient” level – no noticeable symptoms (some minor physiological effects) |
| 16% | Impaired thinking, reduced coordination, ... |
| 14% | abnormal fatigue, emotional upset, impaired coordination / judgment, ... |
| 10 - 12.5% | impaired respiration (potential permanent heart damage), nausea & vomiting, ... |
| < 4% | Unconscious within seconds (death within minutes), ... |

Be aware – an uncontrolled release of house nitrogen (gas or liquid phase) can create a < 4% oxygen environment in the typical R&D laboratory!

Asphyxiation Hazard {continued}

Hazard Mitigation

ES&H Support Team evaluation

Industrial Hygiene & Safety Engineering

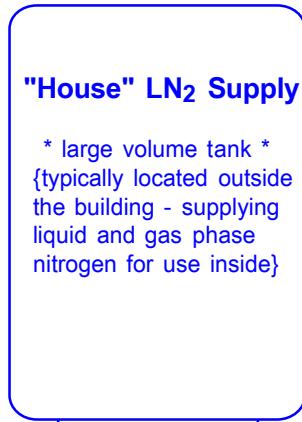
- consider volume of cryogen vs room size & ventilation
- House supply vs stand alone dewars
{SNL buildings have House liquid and gas supplies}
- manual valves = attended when open and in use
- automated / un-attended systems = avoid single-point failures
 - * replacement intervals for critical components
- adequate ventilation (equipment vented)
- slow cool-down procedures
- flow limitation / restriction or auto shut down
- avoid low places, confined places, air intakes
- cryogen monitors as required {O₂, CO₂, ...}

"House" Supplied Gas and Liquid Nitrogen Hazards

possible SNL piping configuration

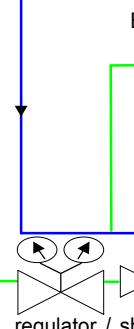
— = liquid phase path

— = gas phase path



liquid phase

The **by-pass valve** may be opened only long enough to cool down the piping - **do not leave unattended.**



By-pass Valve

PRV

Supply Valve

regulator / shut-off valve

To the users equipment (dewar, temperature chamber, fill station, etc...)

Hazards: **DO NOT** leave either the "supply" or the "by-pass" valve(s) un-attended while open.
Laboratory personnel are not authorized to modify Facilities-owned "House" distribution systems

1) Leaving the **supply valve** on and un-attended can overflow LN₂ into the lab air space presenting immediate **thermal** and **asphyxiation hazards**. NOTE: accidental releases from "house" nitrogen (gas phase) systems can also present **asphyxiation hazards**

2) The **by-pass valve** is used to pre-cool the LN₂ supply line. Leaving the by-pass valve on and un-attended will dump liquid phase nitrogen into the exhaust ducts. The ducts are not designed for these temperatures or the weight of the LN₂ and the ice that will accumulate. If the duct breaks, there could be a large release of LN₂ into the chase / building. This would present a **thermal hazard** and would also evolve large quantities of N₂ gas which could present an **asphyxiation hazard** very quickly!

In addition, ducting cooled to LN₂ temperatures will condense air - enriched to 50% oxygen - which presents additional hazards in the chase - namely, **fire** and / or **explosion hazards**.

Building Exhaust System

air flow to roof

air flow to roof

basement



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Things you should know about your “**House**” **LN₂** system

1) Where does the **LN₂** supply line vent?

- through your chamber into the room?
- or into a house exhaust system?
- how do you prevent large volume accidental releases?

2) Does a **by-pass** valve exist?

and if so, where does it vent?

- how do you assure it's not left open?

3) Where does the PRV vent?

- replacement interval?

4) Does automated equipment tie into the **House** supply? - **unattended operation?**

- does a single point (single component) failure lead to a large volume accidental release?

This configuration applies to many building designs

890 / 890 / 858 / 893 / etc.



Fill valve



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Things to know about your “House” LN₂ Application

continued

- 5) If House exhaust systems are associated with your cryo piping, has the exhaust duct been inspected?
 - stainless steel vs galvanized construction?
- 6) Has your ES&H Team evaluated the safety of your House installation? - and evaluated the potential for oxygen deficiency?
- 7) Do you know your building point of contact for the House system?

* Note on “House” cryogen tanks

- in case of emergency, the user may close all “red-handle” valves (this message should be posted on the tank)
- users / line organization personnel are not authorized to perform operational adjustments (pressure or other) of the tank

Example - Valve Sequencing Instructions

- Checklist should be site-specific

- Preparation for use

- 1) check O₂ monitor and dewar pressure {if applicable}
- 2) make connections / arrange transfer lines / position dewar
- 3) don applicable PPE

- Use {* must not leave manual valves un-attended! }

- 4) if applicable, pre-cool lines by opening the by-pass valve
- 5) close by-pass valve
- 6) slowly open the fill valve (while standing back from the point of discharge)

- Shutdown

- 7) close the fill valve
- 8) vent residual pressure / disconnect transfer lines
- 9) check that the appropriate valves are fully closed



Oxygen Hazards

- 1) Liquid Oxygen systems require compatible materials and special procedures.**
 - clean for oxygen service
 - high pressure gas applications & cryo applications
- 2) Oxygen enrichment - $O_2 > 23\%$**
 - greatly enhanced combustion hazard
 - permeate porous materials - clothing
- 3) Hydrocarbon contamination**
 - shock / friction sensitive
 - fires or explosions
- 4) Store separate from flammables / other incompatibles**

Oxygen Enrichment Hazards:

Unforeseen oxygen enrichment in LN₂ applications

Air condensed at around 82 K (or lower) is approx. 50% oxygen (N / A with liquid argon)

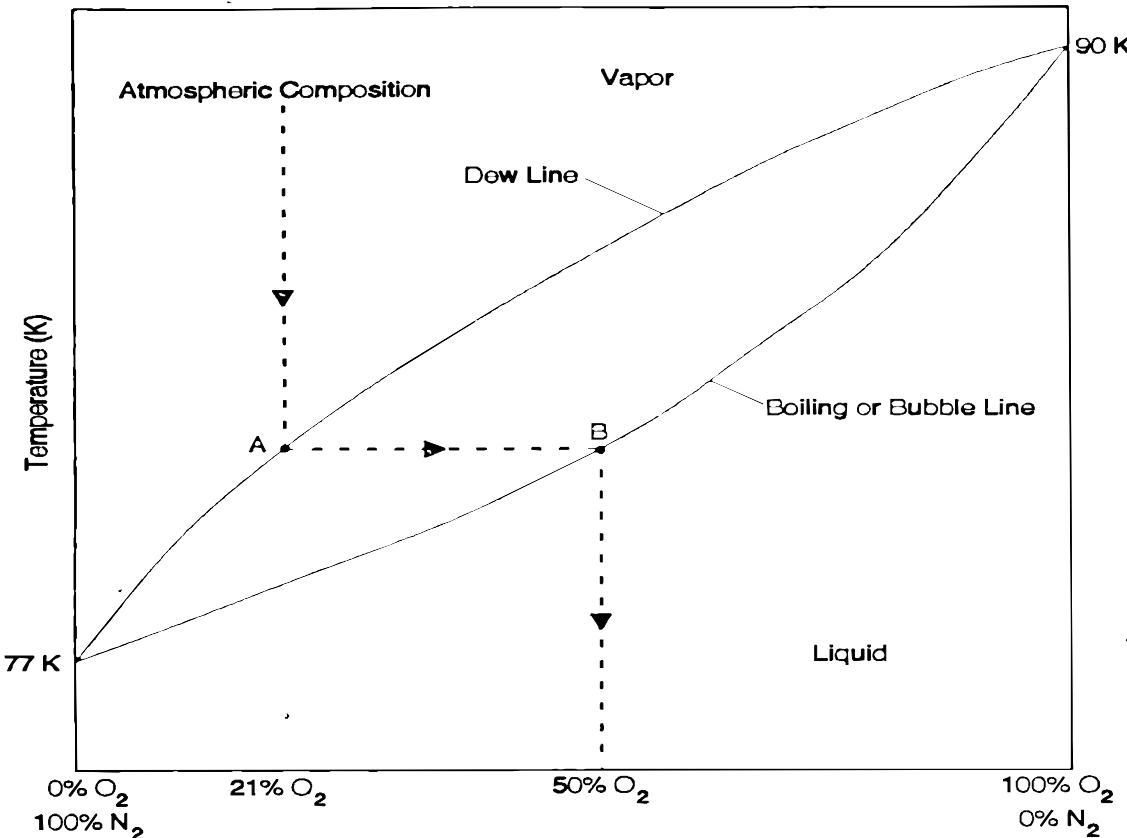
Non-insulated piping or air leaks into vacuum spaces

Oxygen compatibility issues with:

- vacuum pumps
- insulation materials
- spills onto asphalt
- flammable cryogens (LH₂)

O₂ enrichment of open LN₂ dewars

- LN₂ contaminated with O₂ is slightly **blue**



Common Accident Scenarios {Lessons Learned}

1) Accidental releases - manual valves & unattended operation

- automated valves / equipment failures
- into labs or into exhaust systems
- house system vs stand alone dewar

2) Pressure relief devices

- must vent to a “safe” location
- proper selection for the application
- must NOT be allowed to ice over
- replacement intervals (frequently fail open)

3) Cryogen containers

- modified / deficient OEM equipment
- dewar configuration / expected pressure range?
- “consumer” containers {Thermos bottle}
- rapid cool-down = asphyxiation concern

4) Dewar handing - back injuries

- tipping hazard / dewars can weigh 600 lbs or more!

5) PPE as appropriate to the operation

- safety glasses / face shield / gloves / etc...

Misc. Cryo-related Hazards

- 1) Flammable cryogens (condensed air hazards)
- 2) Toxic (air quality issues with CO₂ or other)
- 3) High Ionizing Radiation Fields - possible ozone hazard
 - liquid oxygen
 - liquid nitrogen with condensed air
(oxygen converted to ozone)

★ These hazards must be separately analyzed

- contact ES&H Support Team for assistance

Available Assistance

- **ES&H Support Team**
Safety Engineering Org 10322
Roger Shrouf / Shane Page / Steve Walcott
- **Industrial Hygiene**
- **Pressure Safety Program Personnel**
Appendix F , SNL Pressure Safety Manual
Facilities personnel and contractors
Pressure Advisors
PSC Library
- **Vendors / Consultants**
Tri-Gas, JIT supplier for gases
CRYOCO - courses and consulting



Work smarter, not harder!