Cryogenic Liquids

1. Purpose / Background

Cryogenic liquids pose a number of hazards with the three primary hazards being listed first. These hazards are asphyxiation due to displacement of oxygen in the air, extreme cold that can freeze human tissue on contact and cause materials to become brittle, and fire or explosion due to pressure buildup. Other hazards are condensation of oxygen from air, or generation of flammable gases. The purpose of this Standard Operating Procedure (SOP) is to describe how cryogenic liquids will be handled safely at MIT.

2. Scope

This SOP describes procedures that have been developed, in accordance with MIT's Environmental, Health and Safety (EHS) Policy, for the safe storage and use of cryogenic liquids. Information on compressed gases is available in MIT's SOP on Compressed Gases (EHS-0001).

NOTE: The safe use of Liquid Nitrogen to make ice cream is described on the EHS website through a provided safety plan template, so it is not included in this SOP.

3. Procedures

3.1 General Procedures for Storage and Use of Cryogenic Liquids

- **Information and Training:** Safety Data Sheets (SDS's) or comparable information for cryogenic liquids shall be made available to workers in areas where these materials are present (29 CFR 1910.1200 OSHA Hazard Communication standard and MIT Chemical Hygiene Plan). Anyone using cryogenic liquids should have adequate training and knowledge of their hazards and of practices and procedures for working with them safely. This includes the online Cryogen Safety course in the Learning Center.

- **Security:** Because of the potential hazards associated with cryogenic liquids, storage in hallways, exit corridors and other public areas should be avoided.

- **Ventilation:** The spaces in which cryogenic liquids are used or cryogenic systems are located shall be ventilated commensurate with the properties of the specific cryogenic liquid being used (NFPA 45). No one should ever work directly over an open vat of cryogenic liquids. Cryogenic liquids shall not be used or stored in cold or warm rooms that have a recirculated atmosphere, or in

other unventilated spaces. If there is any doubt about the adequacy of the ventilation system to provide sufficient oxygen, an oxygen-monitoring system should be installed (see section 4.5 for more information on oxygen-monitoring systems).

- **Selection and Design of System Components:** Cryogenic liquids shall be used and stored only in containers and systems designed for these materials. Design pressure for vessels and piping shall be not less than 150 percent of maximum pressure relief (NFPA 45). Properties of materials should be considered when designing systems to contain cryogenic liquids, because the extreme cold of cryogenic liquids can make some materials brittle, including carbon steel, plastic, and rubber. Also, the materials should be compatible with the cryogenic liquid.

- **Disposal of small quantities:** Small quantities of cryogenic liquids should be evaporated in the hood, never disposed of down the drain. This may cause damage and down time to plumbing systems.

- **Pressure Relief:** Because of the hazards of pressure buildup due to off-gassing vapors, cryogenic liquids shall never be contained in a closed system; each and every portion of a piping system shall have uninterruptible pressure relief. Appropriate pressure relief valves shall be designed into any system that contains cryogenic liquids in order to allow relief of pressure buildup during the most adverse conditions. Relief systems shall not be necessary when piping is designed for a pressure greater than the maximum system pressure that can be developed under abnormal conditions. Pressure relief systems shall be designed to provide a discharge rate sufficient to avoid further pressure increase and shall vent to a safe location (NFPA 45). A qualified engineer should design all components of the system so that it is compatible with the gas and can withstand the temperature range. Pressure relief may be provided in several ways. Frangible disks are recommended as additional relief devices when the capacity of the operational relief device is not adequate to take care of unusual or accidental conditions. This is especially true when insulation of the system is dependent upon maintaining a vacuum in any part of the system, including permanently sealed dewars. Users should not modify or tamper with pressure relief devices.

    - Test if the pressure relief valve for a manifold is leaking during the routine pressure and vacuum checks. If the valve leaks, then the valve may have failed. Do not use the system until repair or replacement has been completed.

    - For outdoor bulk tanks with permanently installed systems, the tank owner has a program for testing of pressure relief devices that is in accordance with manufacturer's or installer's recommendations.

- Dewars should be located so the pressure relief valve is pointed away from where people could be standing or walking, which may be towards the wall. This is to prevent injuries when the dewar vents. This applies to temporary storage in corridors and labs. It also applies when transporting dewars in elevators.

- A pressure relief valve on a liquid nitrogen dewar would only ice over if it has been venting for a long time. The ice would create an obstruction and the valve could become stuck in the open position. Pressure relief vents must be checked periodically for icing and plugging. To remove ice or frost buildup, put on cryogen gloves and tap the relief valve gently. The risk of an explosion would be diminished because very little liquid nitrogen would be left in the dewar.

- The pressure relief valve on a liquid nitrogen dewar should not be obstructed by gloves, aprons, etc. being piled on top of the dewar.

- **Implosions and Explosions:** Additional eye and face protection such as a full-face shield should be worn over safety glasses when vacuum systems pose a risk of implosion, or when handling, thawing or opening tubes or vials (referred to as vials from now on) that have been stored in cryogenic liquids, as these vials may explode without warning. These explosions may occur if liquid nitrogen has seeped into the vial in storage through minute cracks in the vial. As the vial warms after removal from storage, the cryogenic liquid evaporates rapidly, resulting in a pressure build up which may cause the vial to explode.

  NOTE: Cryogenic storage vials are designed to be stored in the vapor phase in a liquid nitrogen freezer, not immersed in the liquid itself. Vials that have been immersed in liquid nitrogen are best thawed behind a safety shield or in a heavy-wall container.

- **Personal Protective Equipment:**
  - **Hand Protection:** When the main hazard is skin contact with cold parts, users may wear insulated, loose fitting, water resistant or waterproof protective gloves. Gloves should be easily removable in case of an accident; care must be taken that cold liquid cannot enter the top of the glove and be held against the skin. Tongs should be used when it is necessary to grasp materials immersed in cryogenics.

  - **Protective clothing:** Long pants and long sleeve shirts without cuffs, cargo pockets, or other catch points/openings in clothing or footwear that could trap liquid cryogen against your skin. An impervious apron or coat may be required in some situations. Closed toed shoes shall always be worn in the laboratory; care should be taken to avoid situations where the cryogenic liquid can spill into the inside of shoes. Avoid skin contact with

cryogenic vessels and/or parts of equipment that are not insulated. The skin will become firmly bonded to these very cold materials.

- **Remove jewelry, watchbands, etc.**: It is common for a cryogenic liquid to become trapped under jewelry, watchbands, etc. so it remains in contact with the skin longer and results in serious burns. See MIT Chemical Research Safety Note #12: https://chemistry.mit.edu/about/safety/

- **Eye and face protection:** Eye protection (safety glasses or goggles, face shield) shall be worn at all times when working with cryogenics.

- **Foot protection:** Steel-toed footwear should be worn when moving heavy containers containing cryogenic liquids.

- **Transfer operations:** Transfer operations should be conducted slowly to minimize boiling and splashing. When transferring liquid from a large liquid nitrogen dewar or helium container, a fitted transfer tube designed for this purpose shall be used. When transferring to a secondary container, the secondary container should not be filled to more than 80% of capacity. Refer to the detailed instructions for low and high pressure dispensing on the EHS Chemicals web page.

- **Refill Operations:** Refill of liquid cylinders shall be performed only by trained personnel and only at special refilling stations.

- **Glass Hazard:** Any exposed glass parts of dewars or other vacuum components used with cryogenic liquids should be taped with plastic or rubberized tape, or otherwise protected, to minimize the hazard of flying glass shards in the event of an implosion.

- **Concerns with Condensed Air, Oxygen and Argon:** Systems or apparatus handling a cryogenic fluid that can cause freezing or liquefying of the surrounding atmosphere, shall be designed to prevent contact of the condensed air with organic materials (NFPA 45). Liquid nitrogen, liquid hydrogen and liquid helium shall not be used to cool a flammable mixture in the presence of air, because oxygen will condense out of the atmosphere and will collect. Liquid oxygen forms highly explosive mixtures with many organic materials. Refer to Section 3.3 for more details. Cold traps cooled with Liquid Nitrogen also have this hazard. Also, never cool an apparatus that is under an argon atmosphere using liquid nitrogen. For details, refer to MIT Chemical Research Safety Note #12: https://chemistry.mit.edu/about/safety/ - Section on Cold Traps Cooled with Liquid Nitrogen.

3.2 Special Procedures for Cryogenics that Emit Flammable Gasses

Note that the procurement partner has not supplied this type of cryogenics to any labs on campus. Flammable gases evolved from cryogenic liquids such as hydrogen, methane, or carbon monoxide can burn or explode. Hydrogen in particular forms flammable mixtures over a wide concentration range (4 to 75 percent by volume) and is very easily ignited. The following special precautions are required:

- When working with these cryogenic liquids, keep area free of flames, electrical equipment, sparks, extremely hot objects, and other sources of ignition. The fume hood and general lab ventilation need to keep the flammable vapors below 4%. It is suggested that you contact EHS for a review of the area to assure the ventilation is adequate, there are no ignition hazards, and to determine if the use of explosion-proof electrical equipment is needed.

- Post NO SMOKING – NO OPEN FLAMES signs.

- Store and transfer these materials under positive pressure to prevent infiltration of air and other gases.

3.3 Special Procedures for Liquid Oxygen or other Cryogenic Oxidizers

Cryogenics that give off oxidizing gases include liquid oxygen and nitrous oxide. These oxidizing gases can increase rates of combustion and combine with organic materials with explosive violence. Special precautions are required:

- Systems or apparatus handling liquid oxygen shall be designed to prevent contact of the oxygen with organic materials (NFPA 45). When working with materials that give off oxidizing gases, store materials in a cool, dry, well-ventilated area; keep apparatus and area free of oil and grease; and keep area clear of organic, flammable or combustible materials or fuels. It is suggested that EHS be contacted for a review of areas where oxygen or other oxidizing cryogenics are to be used.

- Liquid oxygen is an extremely strong oxidizer and may initiate combustion or explosion in flammable, organic, and combustible materials. Clothing saturated (even splashed) with oxygen is readily ignitable and will burn vigorously so it must be removed immediately and aired for several hours. It is also extremely important that equipment and systems that will contact liquid oxygen be cleaned of hydrocarbons—such as oil and other organic solvents—before use and kept from becoming contaminated.

- Releases of liquid oxygen can also result in the oxygen enrichment of the surrounding atmosphere. An oxygen enriched atmosphere is considered to be

one containing more than 23.5% oxygen. Inhaling oxygen enriched atmospheres can result in adverse health impacts. These atmospheres can also make some materials more susceptible to ignition and burn with greater intensity. Even some materials that are usually considered non-combustible, such as carbon and stainless steels, cast iron, aluminum, zinc and Teflon, may burn in the presence of liquid oxygen.

- Post NO SMOKING – NO OPEN FLAMES signs.

- If liquid oxygen is spilled on the ground, avoid walking or rolling equipment through the area until at least 30 minutes after all evidence of the spill has disappeared. If this occurs inside, increase the ventilation if possible.

3.4 Special Procedures for Liquid Helium

NOTE: Written procedures should be developed and followed for the transfer of liquid helium.

Liquid helium should be handled in super-insulated, wide-mouthed dewars or in the narrow-neck dewars, which have automatic pressure relief valves to minimize the following explosion risk.

Liquid helium is so cold that metal surfaces in contact with it, such as transfer hoses, will condense air. This condensate, a mixture of liquid nitrogen and oxygen, will drip and form pools. Nitrogen evaporates from the condensed air more rapidly than oxygen. This leaves behind a mixture which increasingly becomes more oxygen-enriched. This oxygen-enriched fluid now presents all of the same hazards as liquid oxygen. An explosive situation may result if oxygen-rich liquid condensate comes into contact with materials which are not compatible with oxygen – such as oil and other organic solvents. Surfaces where liquid oxygen condensate may form must be thoroughly cleaned and degreased with a non-flammable or hydrocarbon cleaner.

Following incidents, The MIT Cryogenic Lab has disposed of all of the older-style narrow-necked dewars that did not have pressure relief valves. Users would have to frequently break up the ice before it plugged up the long narrow neck. MIT Cryogenic Lab currently uses narrow-neck dewars, which have automatic pressure relief valves to minimize the explosion risk.

3.5 Liquid Nitrogen Transfer/ Fill Stations

EHS should be notified of the planned installation and can provide additional information on these recommendations and other design issues as well as design of emergency plans and assistance in training.

An official hardcopy of this document exists in the EHS Office or on the EHS website.
External links are subject to change, please contact environment@mit.edu if you encounter a broken link.
See Legal Disclaimer at: http://ehs.mit.edu/legal-disclaimer

3.6 Bulk Outdoor Storage of Cryogenic Liquids

Contact EHS regarding recommendations for the planning, installation and use of stationary bulk outdoor cryogenic storage tanks.

3.7 Emergency First Aid

If cryogenic liquid contacts skin or eyes, tepid water should be used to flood or soak tissues. All injuries involving cryogenic liquids should be reported to the supervisor as soon as possible, and medical attention should be sought. Refer to the Injury/Illness Reporting webpage for detailed instructions.

3.8 Inventory

MIT EHS, IS&T, and the Procurement Partner have collaborated to develop an on-line inventory which is in progress. Contact the EHS Office at environment@mit.edu for a report. This report can be used as a starting point because a physical inventory still needs to be completed to confirm or correct the report. Refer also to the EHS Chemical Inventory webpage.

4. Roles & Responsibilities

4.1 Supervisor or Principal Investigator (PI) will:

- Ensure that those who work with cryogenic liquids receive adequate training including the Cryogen Safety web-based course (see Section 5: Training).
- Ensure that any necessary PPE and safety equipment is available and in good working order, and that workers know how to use it properly.
- Ensure that cryogenic liquids are handled in accordance with good work practices including those described in this SOP and are used only in well ventilated areas.

4.2 EHS Representative (Rep) will:

- Work with the supervisor or PI to provide Lab Specific Chemical Hygiene Training and other necessary training related to cryogenic liquids.

4.3 EHS Office will:

- Provide training, advice and other support to Supervisors, PIs, EHS Representatives and other personnel in the safe storage, handling and use of cryogenic liquids.

4.4 Procurement Partner for Cryogenic Liquids has the responsibility for:

- Reporting safety hazards related to cryogenic liquids to the EHS Office. They will work with the EHS Office and EHS Coordinators to correct these hazards.

- Checking that a safety plan has been approved by EHS before confirming any orders that are delivered to dormitories and offices.
- Being a technical resource on cryogenic liquids safety and working with EHS to evaluate the safety of situations.
- Removing unsafe dewars from campus as soon as possible.
- Being a technical resource on bulk cryogenic tanks (of various sizes) whether existing or planning a new installation. Linde and Airgas lease most of the bulk cryogenic tanks to MIT and are responsible for the periodic testing/ maintenance of the bulk cryogenic tanks.

5. Training

All those working with cryogenic liquids should have completed General Chemical Hygiene Training (web-based or classroom training) and the Cryogen Safety course in the Learning Center. A laboratory's PI or EHS Representative shall train those workers who use cryogenic liquids on their hazards and safe use; the location and function of specialized equipment needed for safe storage and use; and procedures to be used in case of an emergency involving cryogenic liquids. This may be done as part of the Lab-Specific Chemical Hygiene Training. Awareness level training shall be given to others who work in areas where cryogenic liquids are present.

EHS provides a web-based training, which is recommended unless a DLC has indicated it as a required training, when user selects 'Work with Cryogenic Liquids."

6. Monitoring Requirements

See Section 3.1 for recommendations regarding programs to inspect relief valves, and Section 3.5 for recommendations regarding oxygen-monitoring systems.

7. Record Management

All records related to use of cryogenic liquids shall be maintained as per the EHS Administrative SOP on Records Retention (EHS-04-0044).

8. References

8.1 Standards

- OSHA – 1910 Regulations, Subparts H, M and Q
- DOT 49 CFR, Parts 171 - 179
- Factory Mutual Global – Data Sheet #7-50 – Compressed Gases in Cylinders (deals only with gases, not cryogenic liquids)
- NFPA Standard 45, Fire Protection for Laboratories Using Chemicals
- NFPA Standard 50, Bulk Oxygen Systems at Consumer Sites
- NFPA Standard 50B, Liquefied Hydrogen Systems at Consumer Sites
- ANSI Standard Z48.1 – Method of Marking Portable Compressed Gas Containers to Identify the Material Contained

- Compressed Gas Association –CGA P-12 – Safe Handling of Cryogenic Liquids
- Prudent Practices in the Laboratory (reference book), National Research Council, National Academy Press, 1995.
- Chemical Research Safety Note #12, written by Professor Rick L. Danheiser, et al September 29, 1995

8.2 Other SOP/SOGs

To view the SOPs/SOGs go to https://ehs.mit.edu/sops/ and search for the SOP/SOG listed. MIT Certificates are required to view SOPs/SOGs.

- EHS-0001: Compressed Gases
- EHS-04-0044: Records Retention, EHS Office
- EHS-0008: Reporting Work-Related Injuries and Illnesses

9. Definitions

9.1 Cryogenic Liquids

Compressed liquefied gases that are kept in their liquid state at very low temperatures in special insulated containers. All cryogenic liquids are gases at normal temperatures and pressures and have boiling points below -150ºC (-238ºF). These liquids are stored at relatively low pressures in specially constructed multi-walled, vacuum insulated containers.

9.2 Frangible (Bursting) Disc

A metal disk that is part of a safety device and is intended to burst and allow gas to escape within predetermined pressure limits to prevent rupture of the device on which it is installed. It is similar in function to a safety relief valve; however, it has no reseat capability.

9.3 Liquid Cylinders

Liquid cylinders are pressurized containers designed to hold cryogenic liquids. Liquid cylinders have valves for filling and dispensing the cryogenic liquid, and a pressure-control valve with a frangible (bursting) disk as backup protection. Liquid cylinders may be designed for dispensing gas only, liquid only, or both gas and liquid.

9.4 Liquid Dewar Flasks

Liquid dewar flasks are non-pressurized, vacuum-jacketed containers. They should have a loose-fitting cap or plug that prevents air and moisture from entering, yet allows pressure to vent. Flasks containing hydrogen, helium and other low-boiling liquids have an outer vessel filled with liquid nitrogen for insulation.

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