ETHzürich

Guideline For Cryogenic Liquids and Dry Ice

For pressurized gas cylinders, please see separate document

Cryogenic liquids (e.g. liquid nitrogen or liquid helium) and dry ice are frequently used as cooling agents in the laboratories of ETH Zurich. This guideline contains the most important regulatory, operational and internal provisions, in order to ensure safe working conditions with cryogenic liquids and dry ice at the ETH Zurich.



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1) Introduction

Cryogenic liquids (e.g. liquid nitrogen or liquid helium) and dry ice are frequently used as cooling agents in the laboratories of ETH Zurich. Most of these gases are colorless, odorless and tasteless when evaporated. Although most cryogenic liquefied gases are chemically inert, they also harbor risks:

- Cold-burns / frost-bite: The extreme cold damages human tissue very quickly.
- **Material damage:** Material properties are altered by low temperatures. Metals generally become much harder; other materials such as rubber, plastic, steel become brittle and can break.
- **Condensation:** Formation of ice from the air humidity might cause malfunctioning of safety devices, manometers etc.. when handling gases which have a lower boiling point than oxygen (183°C), oxygen from the air might be condensed inside the installation. This oxygen enrichment causes a higher risk for fire.
- **Bursting:** When evaporating, the gas expands enormously. One liter of liquid nitrogen becomes nearly 700 liters of gas! If the expansion takes place in closed containers, the pressure increases greatly and can under certain circumstances cause the container to burst..
- **Risk of asphyxiation:** Evaporating large amounts of a cryogenic liquid (with the exception of oxygen) in a closed room displaces oxygen from the air, which can lead to.
- **Fire and Explosion:** Oxygen is an oxidizing gas; hydrogen can form explosive mixtures with air upon evaporation..

This guideline contains the most important regulatory, operational and internal provisions, in order to ensure safe working conditions with cryogenic liquids and dry ice at the ETH Zurich.

2) Legal basis

The following documents form the legal basis for handling cryogenic liquids:

- Ordinance on Accident Prevention and Occupational Diseases (VUV)
- Federal Accident Insurance Act (UVG) under article 82
- Federal Law on the Safety of Technical Installations and Equipment (STEG) under articles 1 and 3
- Ordinance on use of pressurized devices (832.312.12)
- EKAS directive «Pressure Equipment» (No. 6516)
- SUVA publication «Gas Cylinders Storage, Gas Networks, Gas Distribution Systems» (No. 66122)
- SUVA publication «Exposure Limits at the Workplace» (No:1903.d)
- SUVA publication «Explosion Prevention» (No. 2153)
- Fire prevention directives (VKF)
- Guideline to Ordinance 3 and 4 to the Employment Act

Pressurized Dewar vessels must comply with the regulation on the transport of dangerous goods on the road (SDR) and the regulation on the transport of dangerous goods by rail (RSD). Open, non-pressurized Dewar vessels have to be safe to operate, i.e. they must not have any bumps or other damages.

The regulatory basis form the minimum requirements. According to specific situations, more strict operational provisions and additional safety measures may apply

3) Scope of Application

This guideline shall apply for all members of the ETH Zurich (employees, students, apprentices, scholars/fellows, academic guests), as well as for spin-offs and third-party companies working in the premises of the ETH Zurich. For any deviation from this guideline, a specific risk assessment has to be done, and they need <u>written approval</u> by SSHE.[1]

Important: for pressurized gas cylinders, please see separate document.

4) Glossary

Cryogenic liquid

A Gas that has been cooled down below its boiling point.

Dewar vessel

Mobile, vacuum-insulated vessel for cryogenic liquids, with a maximum volume of 1000 L. (under pressure or not), including storage vessels for biological samples..

Connected Dewar vessel

Dewar vessel which is directly connected to a device or to a gas network.

spare vessel

non-connected Dewar vessel, which is necessary for an undisturbed functioning of a device or of a local gas network.

storage area

area (place, room) in which non-connected Dewar vessels are stored.

Ramp

fixed installed device for the connection of two or more Dewar vessels.

gas network

connecting lines (incl. fittings and valves) between Dear vessel(s) or ramp(s) and a piece of equipment or extraction point(s).

centralized gas distribution

gas network for a whole building or large parts of a building.

filling station

extraction point for cryogenic liquids.

5) Risk Assessment – the S T O P Principle

Installation and handling of Dewar vessels, filling stations, installations, ramps and gas networks for cryogenic liquids must be in a way that ensures the protection of people, values and the environment. The safety measures have to be implemented according to the risk posed by the connected or stored gas cylinders. The location, as well as the specific properties of the gases have to be taken into account..

^{[1] &}lt;u>https://www.ethz.ch/content/dam/ethz/associates/services/Service/sicherheit-gesundheit-umwelt/files/gefahrstoffe chemikalien gase/de/Antrag Spezialbewilligung Gasflaschen form public.pdf</u>

To evaluate risks in the use and storage of cryogenic liquids, the following worst-case scenario is assumed:

- The content of the largest container of each gas is released.
- All gas is released immediately
- The gas spreads throughout the room.
- Artificial ventilation is not taken into account.

To eliminate dangers effectively, i.e. to minimize residual risk, the S T O P principle is applied. The effectiveness of the measures decreases from top to bottom:

| S | Substitution | 1st priority |
|---|-------------------------|----------------|
| Т | Technical measures | 2nd priority |
| 0 | Organizational measures | 3rd priority t |
| Ρ | Personal measures | 4th priority |

Accordingly, the most effective method is always to substitute a hazardous gas with a nonhazardous gas or use a different, less dangerous process. If this is not possible, the gas volume is reduced.

Events (e.g. fire) in the lab cannot be completely ruled out without unreasonable effort, which is why the consequences must be minimized and limited to a lab (fire zone). The following applies:

- The risk of explosion must be virtually zero. Possible concentration under LEL (Lower Explosion Limit) or there may be no ignition source in the room.
- **Poisoning of persons is not tolerated.** As a measure of toxicity, the MAC value (maximum allowed workplace concentration) is taken.
- Suffocation of persons is not tolerated. Nonflammable inert gases are generally not dangerous. Exceptions are liquefied inert gases under pressure. For these gases, oxygen displacement must be taken into consideration. 18%Vol oxygen are defined as threshold value.

6) Technical and Constructional Requirements (T)

- Dewar vessels with cryogenic liquids, filling stations, ramps and gas networks should not be installed in the basement floors of a building. If they have to be installed below ground level, special protective measures have to be implemented in order to ensure safety.
- Dewar vessels, filling stations, ramps and gas networks must not be installed at a place where leaking gas could spread in an uncontrolled way and could pose hazard due to accumulation (for gases heavier than air, basement rooms, cavities, pits, rooms on a lower level etc. could be problematic).
- Storage areas, filling stations, ramps and gas networks, incl. valves and fittings have to be placed in a way that allows easy access for handling, control and revision work, as well as for cooling in case of a fire.

6.1 General Requirements for Rooms with Cryogenic Liquids

- Rooms, in which cryogenic liquids are handled or stored, have to be sufficiently ventilated.
 - natural ventilation: Either volume of the room > 4000 m³, or rooms above ground level equipped with two separate, non-closable openings against the outside of the building, of min 20cm² per m² room surface. These openings have to be placed in a suitable way with respect of the density of the gases.

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- **artificial ventilation:** at least 3-5fold air exchange per hour, connection to the chemical exhaust system of the building, exhaust ducts placed below the ceiling or bottom exhaust ducts, according to the density of the gases.
- For rooms below ground level, an artificial ventilation is mandatory.
- Dewar vessels and installations with cryogenic liquids have to be protected against heat, mechanical damage and falling.
 - Dewar vessels must not be placed in any escape route.

6.2 Requirements for Filling Stations and Gas Networks for Cryogenic Liquids

Filling stations or gas networks have to be installed by qualified personnel. Do-it-yourself gas networks with plastic tubes are prohibited. For the installation of a gas network, a work order has to be placed (<u>https://gmis.ethz.ch/</u>).

6.2.1 General Requirements for Filling Stations and Gas Networks for Cryogenic Liquids

- Filling stations have to be protected against unauthorized access.
- Gas networks and gas installations must be laid out so that they correspond to the properties of the gas used. Suitable materials must be used. (All gas installation components require a material compatibility certificate from the manufacturer.)
- Gas networks have to be planned and installed according to the maximum working pressure and the minimum working temperature.
- For gas networks and gas installations, pressure release systems have to be installed, which have a large enough diameter (e.g. quench lines). Leaking fluids (gas, cryogenic liquid) have to be released without posing a risk (in general: out of the building).
- Tubes and lines from gas networks have to be labeled with the name of the gas as well as with the direction of flow. This takes in particular for passages, junctions, branches or valves.
- Coupled fixtures must always be easily accessible and protected against damage

6.2.2 Additional Requirements for Gas Networks for Liquid Helium

If possible, gas networks and gas installations for liquid helium should be connected to the helium recycling system.

6.3 Gas Monitoring

All rooms at ETH in which cryogenic liquids or dry ice are stored or handled, have to be equipped with a gas monitoring system, if – in case of a leak – a risk for people or animals may occur. This might be the case in labs, workshops, rooms with filling lines for liquid nitrogen, storage rooms for cryogenic liquids, animal facilities, refrigeration plants.

To evaluate risks in the use and storage of gases, the following worst-case scenario is assumed:

- The content of the largest container of each gas is released.
- All gas is released immediately
- The gas spreads throughout the room.
- Artificial ventilation is not taken into account (exception: redundant exhaust system also available during an electric power-cut).

For each gas used in the room, the following considerations have tob e made:

- Might there be an explosive mixture with the air? benchmark: Lower Explosion Limit (LEL)
- Is there any health risk for people or animals? benchmark: MAC value

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• Might the oxygen content in the room fall below 18% Vol or raise above 23% Vol?

If at least for one of these three questions, the answer is "Yes", a gas monitoring system is necessary for this gas. At ETH, usually fixed mounted gas monitoring systems are installed (<u>https://gmis.ethz.ch/</u>). Any exemption of this rule has to be permitted by SSHE beforehand.

An overview on the construction requirements for gas monitoring systems, alarm transmission and threshold values are compiled the factsheet <u>Merkblatt «Gasüberwachung»</u>[2] (only available in German). This factsheet also contents information regarding responsibilities, necessary instruction of the users, as well as maintenance of these systems.

7) Organizational Measures (O)

7.1 Labeling

Rooms in which cryogenic liquids are stored or handled must be indicated accordingly (yellow triangular symbol "cold"). If there is danger of suffocation in a room with cryogenic liquids, this must also be indicated. Additionally, Dewar vessels have to be labeled with the warning signs of the gases (e.g. flammable, oxidizing). Labels can be obtained from SSHE (email: <u>stickers@ethz.ch</u>).

7.2 Instruction

Before the start of their activity, all people handling cryogenic liquids have to be instructed about the hazards related to this work and about the necessary precautionary measures. This instruction has to be refreshed regularly. The supervisors are responsible for the instruction (for students in practical courses: the head of the practical course). The instruction has to be documented.

Rules for the instruction regarding gas monitoring systems are available in the <u>factsheet</u>.[Fehler! Textmarke nicht definiert.]

7.3 User Manuals / SOPs

All organizational units in which cryogenic liquids are stored or handled, or which use gas networks or centralized gas distributions, have to ensure that the necessary safety measures are respected. The user manuals, SPOs and checklists have to be available locally.

7.4 Commissioning, Maintenance and Repair

Fixed installations for cryogenic liquids have to be done by specialized personnel. Prior to the first use, after a modification or a repair work, all gas installation have to undergo a leak-testing (above the maximum working pressure) according to the rules of technology. The test have to be documented.

All installations have to be maintained according to the supplier' specifications. The maintenance has to be done by specialized personnel. The instructions for the maintenance have to be available locally. All maintenance work has to be documented.

Inoperable installations have to be secured against unintended use, and have to be labeled as such.

^{[2] &}lt;u>https://www.ethz.ch/content/dam/ethz/associates/services/Service/sicherheit-gesundheit-umwelt/files/gefahrstoffe_chemikalien_gase/de/MB_Gas%C3%BCberwachung_DE_20160922.pdf</u>

8) Personal Protective Equipment - PPE (P)

All people handling cryogenic liquids or dry ice have to be equipped with the appropriate Personal Protective Equipment (PPE) by the employer (professor, institute, etc.), e.g. protective clothes, safety shoes, respiration protection, safety glasses / face shield or protective gloves. Clothes must be loose-fit, completely covering arms and legs. Open pockets, rolled-up sleeves or pant legs have to be avoid-ed. Rings, bracelets, wristwatches, etc. have to be removed before working. The use of the PPE has to be stipulated and controlled by the supervisor (for students in practical courses: by the head of the practical course)

9) Handling of Dewar Vessels / Working with Cryogenic Liquids and Dry Ice

9.1 General Rules

- At the point of use (e.g. in laboratories or workshops) only the amount of cryogenic liquids or dry ice that are required for operation may be present (no storage)..
- The Dewar vessels should be positioned so that the mounted fittings are always easily accessible and protected against damage.
- Dear vessels must always be secured to prevent them from falling over or rolling away.
- Pressurized gas cylinders may never be placed near a heat source (radiator, heating bath, oven,...).
- The user manual for the Dewar vessel has to be available and the instructions therein have to be observed.
- Only the regulating valve approved for the respective gas may be used, the use of adaptors is prohibited. For cryogenic oxygen use only fittings which are absolutely free of oil and grease and which are equipped with non-flammable seals (approved by Swiss Association for Welding Technology).
- Extreme caution is required when working with cryogenic liquids (particularly when transferring into containers). WARNING: Cryogenic liquids are at boiling point under normal pressure. When filling into vessels which are at room temperature, boiling increases intensely!
- To prevent ice formation, oxygen condensation and overpressure build-up, cryogenic liquids may only be kept in vessels designed especially for this purpose. Household thermos bottles may not be used for cryogenic liquids.
- Non-insulated pipes or containers which contain cryogenic liquefied gases may never be touched with bare hands
- Storage of cryogenic oxygen in open vessels is prohibited.
- Damaged, brittled or fissured gas tubes have to be replaced.
- Connecting Dewar vessels to a gas network or a ramp may only be done according to the respective checklists in order to avoid incorrect handling by the user. The checklists must be posted clearly visible by the gas cylinder cabinets. Before filling the gas network or ramp, the main valves have to be closed. All valves then have to be opened slowly and carefully.
- When working with cryogenic liquids or dry ice, personal protective equipment must always be worn.
- The material safety data sheets (MSDS) of all the gases used must be stored safely and the guidelines contained therein observed carefully.

9.2 Additional Requirements for Filling Stations, Gas Networks and Ramps

• Dewar vessels must not be left unattended when filling. The local regulations of the filling stations have to be observed.

- When a gas network or ramp is not in use for a longer period of time, the pressure has to be released. When releasing the pressure, the gas has to be sucked away without posing a risk (i.e. via the lab exhaust system).
- Non-used connections of a gas network have to be removed (work order <u>https://gmis.ethz.ch/</u>) or have to be sealed tightly against unwanted gas release (e.g. screw cap).Only closing the valve does not count as tight sealing.

9.3 Defective Dewar Vessels / Defective Gas Installations

Do not use defective Dewar vessels or gas installations. They must be marked as "defective" and have to be blocked against further use. Defective Dewar vessels must be stored in a safe, well-ventilated place until picked up by the supplier.

If large amount of a cryogenic liquid leaks from a Dewar vessel or from a gas installation, immediately contact the ETH Emergency Desk (phone 888).

10) Purchasing and Acquiring of Cryogenic Liquids and Dry Ice

10.1 General Rules

Dewar vessels for labs or workshops may only be procured in the smallest possible size. In buildings with a central filling station for liquid nitrogen or argon, this station has to be used. Users in buildings without central filling stations can obtain liquid nitrogen from the \rightarrow <u>Gas Liquefaction Service of D-PHYS</u>. The Gas Liquefaction Service also provides liquid helium for all ETH users.

10.2 Purchasing and Acquiring of Dry Ice

Dry ice can be purchased from the HCI shop.

11) Storage of Cryogenic Liquids and Dry Ice

11.1 General Requirements

- Storing Dewar vessels together with flammable or self-igniting materials (paper / cardboard boxes, solvents, etc.) is prohibited.
- Dewar vessels are not to be kept in escape routes.
- Dewar vessels have to be stored standing upright.
- In storage areas, the full Dewar vessels have to be stored separately from the empty ones.

11.2 Constructional Requirements for Storage Areas of Cryogenic Liquids

- Storage areas have to be ventilated sufficiently (requirements according to chapter 6.1).
- Storage rooms and rooms with Dewar vessels for centralized gas distributions, have to be built as separate fire zones (EI 90, doors EI30). All doors have to be equipped with a mechanical closing system.
- Escape routes from storage rooms have to be kept clear and labeled as such.
- Outdoor storage areas have to be protected against unauthorized access (e.g. cage construction, fence).
- In storage areas, Dewar vessels have to be protected from extreme heat.

11.3 Additional Requirements for Storage Areas of Flammable Cryogenic Liquids

In storage areas for flammable cryogenic liquids (e.g. hydrogen), the necessary EX protection measures have to be implemented. When planning such storage areas, SSHE has to be involved.

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11.4 Additional Requirements for the Storage of Dry Ice

Dry Ice should be stored outdoors, or in well-ventilated rooms. A storage in cooling rooms, freezer room etc. is prohibited.

12) Transportation of Dewar Vessels

Cryogenic liquids are often transported and stored using mobile cryo-vessels. These can be tightly sealed compressed gas cylinders suitable for internal overpressure (closed systems) as well as open non-pressurized Dewar vessels (open systems). Open vessels must be transported in such a way as to prevent them from tipping or falling down; mobile containers must be tip-proof. The lid on open vessels may only be loose fitting.

For transporting gas cylinders, only the freight elevators (large vessels) or staircases (small vessels) are allowed to be used. Simultaneous transport of people and gas cylinders in an elevator is prohibited.

For external transport (public street), please observe the ADR/SDR guidelines (<u>Request for Transport</u> <u>of Hazardous Goods</u>).[3] Pressurized vessels have to be checked periodically (as indicated on the surface of the vessel; after maximum 10 years, or 5 years for the pressure release system). Vessels which don't fulfill the requirements, must not be used for transportation; except empty vessels for the check or for disposal guidelines (<u>Request for Transport of Hazardous Goods</u>).[4]

For "Dry Shipper" vessels which have been filled according to their user manual, the transportation regulations don't apply. Therefore, such a vessel is recommended for the transport of biological samples. Courier services (e.g. Word Courier) provide such vessels.

13) Audits / Checks

The SSHE can conduct (announced or unannounced) inspections of the individual institutes and work groups to check adherence to the safety guidelines on a random basis..

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^{[3] &}lt;u>https://www.ethz.ch/content/dam/ethz/associates/services/Service/sicherheit-gesundheit-umwelt/files/gefahrgut-transport/de/Transportauftrag_Gefahrgut.pdf</u>

^[4] https://www.ethz.ch/content/dam/ethz/associates/services/Service/sicherheit-gesundheit-umwelt/files/gefahrguttransport/de/Transportauftrag_Gefahrgut.pdf