Cryogenic Safety
Ch. 11 Flynn

Cryogens are not high on the danger list,
but a few rules must be obeyed

1. Be careful
2. It's cold
3. Don't breath
4. Work together
5. Know your materials
6. Let the gas go

OUTLINE

1. **Properties of Cryogens**
2. **Pressurization of Warming Vessels**
3. **Dewar Safety Issues**
4. **Asphyxiation Risks**
5. **Hydrogen Combustion**
6. **Tank Fire Dangers**
7. **Safe Working Distances**
8. **Hydrogen Gas Evolution Control**
9. **Thermal Contraction of Materials**
10. **Material Properties at Low T**
11. **Metals Effected by Embrittlement**
12. **Hydrogen Embrittlement Sources**

GOALS

- Recognize cryogenic safety issues in:
  - Materials
  - Design
  - Operation
- Develop safe practices

http://www.metacafe.com/watch/126294/kid_gets_his_tongue_stuck_on_a_pole/

Properties of Cryogens

Gas	Boiling Point Centigrade	Boiling Point Kelvin	Volume Expansion to Gas	Flammable	Toxic	Odor
Helium-3	-269.9	3.2	757 to 1	No	No(a)	No
Helium-4	-268.9	4.2	757 to 1	No	No(a)	No
Hydrogen	-252.7	20.4	851 to 1	Yes	No(a)	No
Deuterium	-249.5	23.6	...	Yes	Radioactive	No
Tritium	-248	25.1	...	Yes	Radioactive	No
Neon	-245.9	27.2	1438 to 1	No	No(a)	No
Nitrogen	-195.8	77.3	696 to 1	No	No(a)	No
Carbon monoxide	-192	81.1	...	Yes	Yes	No
Fluorine	-187	86	888 to 1	No	Yes	Sharp
Argon	-185.7	87.4	847 to 1	No	No(a)	No
Oxygen	-183.0	90.1	860 to 1	No	No(a)	No
Methane	-161.4	111.7	578 to 1	Yes	No(a)	No
Krypton	-151.8	121.3	700 to 1	No	No(a)	No

Maximum Pressures of Filled Vessel Warming to 300K without Venting

Explosion caused by improper venting or accidental rapid warming of evaporating cryogen is the single biggest safety hazard. This is because the cryogenic liquids have a much higher density than their gases at room temperature.

Cryogen	Maximum Pressure	
	Mpa	(psi)
Helium	103	(15,000)
Hydrogen	172	(25,000)
Nitrogen	296	(43,000)

Dewar Design to Prevent Over Pressures

Care must be taken to allow venting of any volume which might contain liquid cryogen. Support tubes must be vented with either one end open or small holes placed in wall near top. Joins must be designed so that liquid can not be trapped behind, causing rupture on warming.

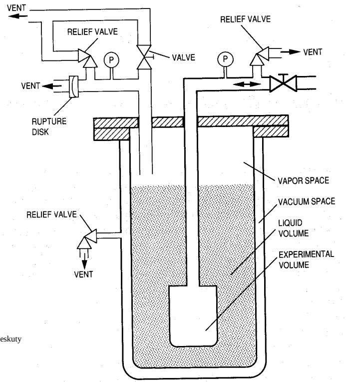


Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W. F. Stewart, Plenum, NY (1996) , p. 54

Dewar Pressurization, Venting, and Liquid Extraction

(Not Liquid Helium)

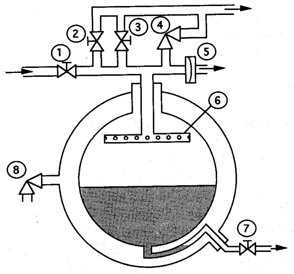


Fig. 5.6. Schematic of typical vent system for a large liquid-hydrogen storage Dewar[1]: (1) Dewar pressurization valve; (2) fast vent valve; (3) normal boil-off control valve; (4) safety relief valve; (5) rupture disk; (6) gas pressurization/vent ring (holes on top side only help preserve thermal stratification and reduce liquid entrainment in vent gas); (7) liquid discharge valve; (8) pressure relief valve for annulus.

7. Liquid extraction valve has gas trap which prevents constant heat leak from liquid exposed to room temperature.

Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 64

Example Mishap:
Misuse of salvaged Oxygen Dewar

- ■Improper methods for using scrap dewar (cylinder)
- ■Unsafe modifications to cylinder design

Personnel Involved:

- ■Two individuals (ages 42 and 60) found a liquid oxygen cylinder that had been removed from service and left at a scrap metal dealer
- ■The individuals were self-employed in scrap metal cutting operations and intended to use the cylinder in their work
- ■The individuals had access to a liquid oxygen supplier where cylinder ownership would not be questioned

The incident described in the following presentation did not involve an Airgas company. Airgas supplied the following 19 slides.

Accident Profile

- Jury-rigging fill connections, the first attempt to fill the cylinder resulted in rapid venting through the Pressure Relief Device (PRD)
- The PRDs were removed and plugged
- The cylinder was filled while onboard a pickup truck
- The cylinder, which had no vacuum, was now unable to vent excess pressure
- While being transported down a busy highway, the pickup truck experienced a flat tire
- Shortly thereafter, the cylinder exploded with the results shown in the following slides

Pickup truck on which the cylinder was being transported

More Pickup truck …

Pickup and cylinder remains

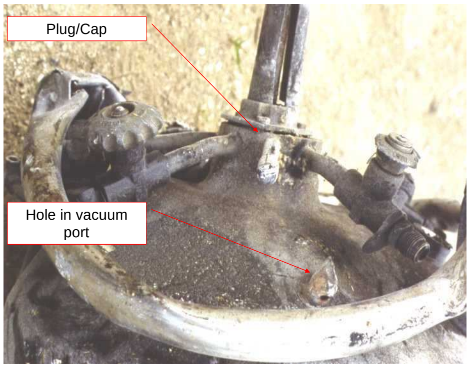
Cylinder top

Cylinder outer shell, bottom

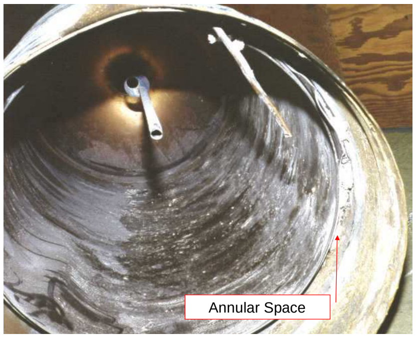
Cylinder bottom shell

PRD location was plugged using a threaded cap

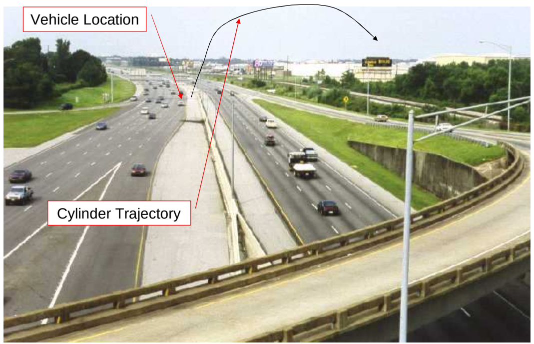
Top of Dewar



Both inner and outer shells separated at bottom welds

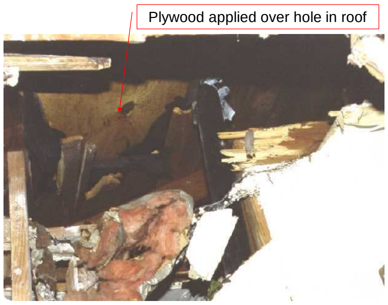


Cylinder exploded at 12:40 PM while transport vehicle was parked on busy Interstate highway



The blast blew one individual across 5 lanes of traffic. The other was blown approximately 40 feet. Both survived

Cylinder flew approximately ¼ mile before plunging through the roof of an apartment, severing a main natural gas line and coming to rest in the living space



Despite heavy damage, no injuries to apartment tenants were reported

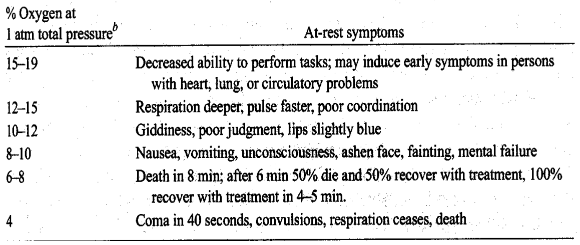
More apartment interior

Note that the media reported the event as a Butane cylinder explosion

Butane explosion on I-10 hurts two, hits apartment

Evolving Cryogens displaces Oxygen in Air

Symptoms of oxygen depravation

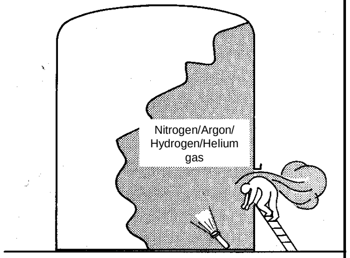


% Oxygen at 1 atm total pressure[b]	At-rest symptoms
15–19	Decreased ability to perform tasks; may induce early symptoms in persons with heart, lung, or circulatory problems
12–15	Respiration deeper, pulse faster, poor coordination
10–12	Giddiness, poor judgment, lips slightly blue
8–10	Nausea, vomiting, unconsciousness, ashen face, fainting, mental failure
6–8	Death in 8 min; after 6 min 50% die and 50% recover with treatment, 100% recover with treatment in 4–5 min.
4	Coma in 40 seconds, convulsions, respiration ceases, death

Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 13

Asphyxiation in a Tank

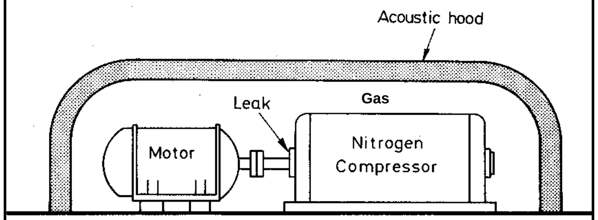
The gas remaining in a tank can cause a worker to become unconscious before s/he is aware of the danger. This includes most gases,such as nitrogen, argon, helium, and hydrogen



Work in teams, with one person always outside the danger zone and able to observe the worker in danger. Link the two with a rope if necessary.

Figure adapted from *Cryogenic Engineering* by B.A. Hands, Academic (1986), p. 74

Asphyxiation or Explosion Risk in Enclosures



Any enclosure may trap gas. Dangerous build-up of gases is common in cases of high pressures such as when using compressors. Use monitors, such as for Hydrogen.

Figure adapted from *Cryogenic Engineering* by B.A. Hands, Academic (1986), p. 75

Hydrogen Combustible Cloud Length

Hydrogen is flammable in air at 1 atmosphere for a concentration of 4% to 74%. Depending on the release rate of the hydrogen, the flammable cloud will extend according to the graphs at right.

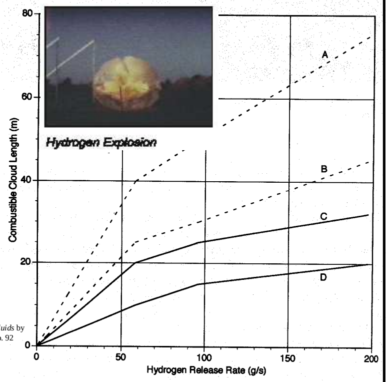
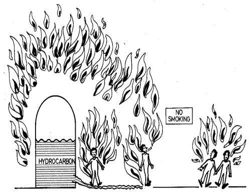
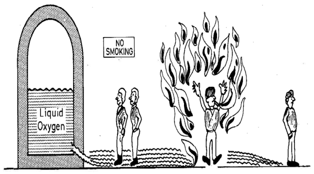


Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 92

Tank Fire Dangers





Spill from a tank of liquid hydrogen or natural gas, when ignited, will burn everything in its path.

Liquid oxygen is more insidious, lowering the ignition temperature and causing fires in isolated areas.

Figure adapted from *Cryogenic Engineering* by B.A. Hands, Academic (1986), p. 74

Safe Distances

This table shows safe distances to maintain for various operations when setting up storage or experimental containers for flammable cryogens.

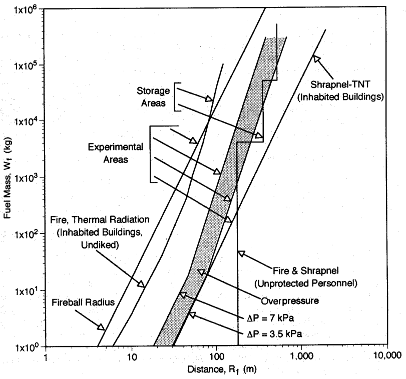


Figure adapted from *Safety in Handling of Cryogeni*
F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996

Hydrogen Flame Stack

Design of flame stack used to burn off hydrogen gas evolving from a large liquid hydrogen storage tank.

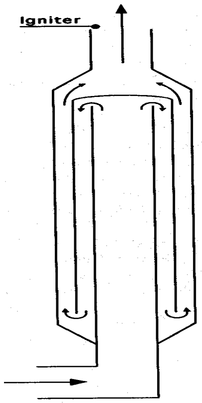


Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 98

Burn Pond at KSC

Burn pond for igniting hydrogen gas evolving from the space shuttle during launch preparation. Pond is empty allowing a good view of the plumbing and burn nozzles.

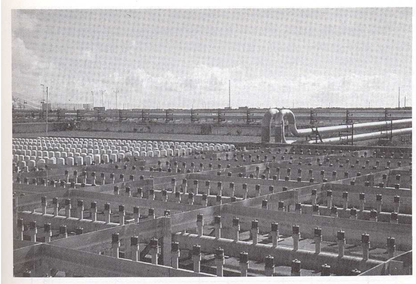
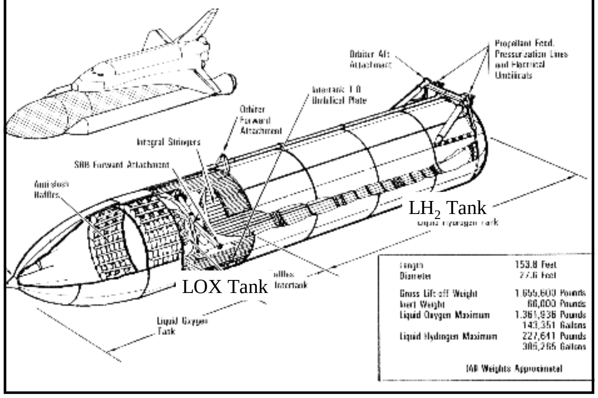


Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 89

Cryogens on Shuttle



LH_2 Tank

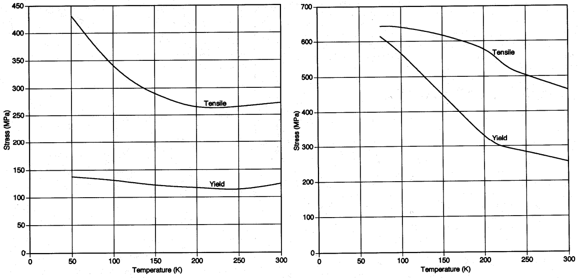
LOX Tank

Length	153.8 Feet
Diameter	27.6 Feet
Gross Lift-off Weight	1,655,600 Pounds
Inert Weight	66,000 Pounds
Liquid Oxygen Maximum	1,361,936 Pounds 143,351 Gallons
Liquid Hydrogen Maximum	227,641 Pounds 385,265 Gallons

(All Weights Approximate)

Material Properties change at Low T

Examples: Aluminum   Stainless Steel

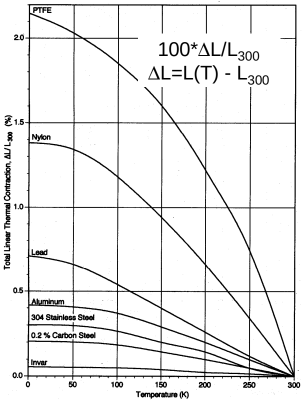


In general strength of materials increases as T goes down

Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 22-23

Thermal Contraction of Materials

Relative percent change in length on cooling from room temperature (T=300K) for selected materials. Strains developed due to differential contraction damaged the liquid hydrogen fuel tank on the X-33 space plane, causing the entire program to be abandoned.



$100*\Delta L/L_{300}$

$\Delta L=L(T) - L_{300}$

Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 36

Materials Effected by Embrittlement

Materials fall into 2 categories:

Remain Ductile at Low Temperature:	Become Brittle at Low Temperature:
•Most FCC lattice structures	•Most BCC lattice structures
•http://www.ider.herts.ac.uk/school/courseware/materials/metals/stucture.html	
Cu, Ag, Au, Ni, Pd, Pt, and their alloys	Molybdenum
Nickel, and their alloys	Niobium
Aluminum and its alloys	Zinc
Stainless steels >7% Nickel	Most plastics
Titanium	
Polytetraflourethylene	

Metals Effected by Embrittlement (I)

Environmental hydrogen embrittlement	Internal hydrogen embrittlement	Hydrogen reaction embrittlement
High-strength steels 18Ni maraging, 401, 440C, 430F, 403, 431, H-11, 4140, 1042 (Q&T), Fe–9Ni–4Co, 17-7 PH	*High-strength steels* 4340, 4140, H-11, AM355, 18Ni maraging, E8740, 17-4PH, 17-7PH	*Hydrides* (MH$_x$) H reacts with matrix Ti, Zr, Hf, V, Nb, Ta, Mn, Ni, Pd, U, Pu, Th, rare earths
Nickel and nickel alloys Electroformed nickel	Experimental Fe–Ni–Cr alloys	Alkalis
Nickel (200, 270, 301)	Experimental Fe–Cu alloys	
Inconel (625, 700, 706, 718, X), Rene41, Hastelloy x, Udi-ment 700, Waspaloy, IN100, MAR M-200DC		
Low-strength steels Armco iron, CK22, CK45, 1020, 1042 Nor., HY-80, HY-100, A-302, A-515, A-517, A-5338, 1146a, HY-130, SA-105	Ti, Zr, V, Nb, Ta, Cr, Mo, W, Co, Ni, Pt, Cu, Au, Al, Mg, and/or some of their alloys	H reacts with elements in MgZr, MgTh alloys High-pressure gas bubbles (H forms H_2) steels

Figure adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 30

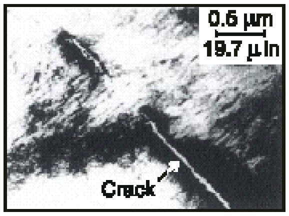
Metals Effected by Embrittlement (II)

Environmental hydrogen embrittlement	Internal hydrogen embrittlement	Hydrogen reaction embrittlement
Titanium alloys Ti-6Al-4V, Ti-5Al-2.5Sn Molybdenum-TZM *Cobalt alloys* HS-188, L-605, S-816	*Metastable stainless steels* 304L, 310	H reacts with foreign elements in matrix to form: CH_4 in low-alloy steels and Ni alloys H_2O in welded steels and Cu, Ni, Ag, NH_3 in molybdenum
Metastable stainless steels 304L, 305, 310, 309S K Monel, Be-Cu alloy 25, pure titanium	*High-strength nickel alloys* Inconel 718, Rene 41, Waspalloy, Hastelloy x *Stable austenitic steels* 316, A-286, U-212, 21-6-9	
Stable stainless steels 316, 321, 347, A-286, Armco 21-6-9, 22-13-5 Copper alloys, OFHC Cu TD-Ni, TD-NiCr		

adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 30

Metals Effected by Embrittlement (III)

Environmental hydrogen embrittlement	Internal hydrogen embrittlement	Hydrogen reaction embrittlement
Magnesium alloy HM21A		
Aluminum alloys 1100, 2219, 6061, 7039, 7075		



Hydrogen Embrittlement

adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 30

Hydrogen Embrittlement Sources (I)

Characteristic	Environmental hydrogen embrittlement	Internal hydrogen embrittlement	Hydrogen reaction embrittlement
Usual source of hydrogen	Gaseous hydrogen	Processing, electrolysis, corrosion	Gaseous or atomic hydrogen from any source
Typical conditions	10^{-6}–10^{8} Pa H_2 pressure. Most severe near room temperature. Observed from –100 °C to 700 °C. Gas purity is important. Strain rate is important.	0.1–10 ppm average H content. Most severe near room temperature. Observed from –100 °C to +100 °C. Strain rate is important.	Heat treatment or service in hydrogen, usually at elevated temperatures
Test methods	Notched tensile, unnotched tensile, creep rupture, fatigue, fracture toughness, disk pressure test	Notched failure, slow strain rate tensile, bend tests	Can be observed visually or metallographically

adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 25

Hydrogen Embrittlement Sources (II)

Characteristic	Environmental hydrogen embrittlement	Internal hydrogen embrittlement	Hydrogen reaction embrittlement
Test methods	Notched tensile, unnotched tensile, creep rupture, fatigue, fracture toughness, disk pressure test	Notched failure, slow strain rate tensile, bend tests	Can be observed visually or metallographically
Crack initiation	Surface or internal initiation	Internal crack initiation, incubation (reversible), slow discontinuous growth, fast fracture	Usually internal initiation from bubbles or flakes
Rate-controlling step	Adsorption is transfer step, absorption or lattice diffusion is embrittling step.	Lattice diffusion to internal stress raisers	Chemical reaction to form hydrides or gas bubbles

adapted from *Safety in Handling of Cryogenic Fluids* by F.J. Edeskuty and W, F. Stewart, Plenum, NY (1996) , p. 25

Cryo-Disasters

1. Drinking LN_2
2. LN_2 Dewar at Texas A&M
3. Challenger Disaster
4. Apollo near-Disaster
5. Columbia Disaster
6. Vostok Disaster
7. X-33 space plane
8. CO_2
9. Nursing Home gas mix-up
10. LPG
11. Hydrogen Bomb

Drinking LN_2

Worcester Polytechnic Institute in Massachusetts. Senior physics student, Michael Mazur, was gathering with members of the school's chapter of the Society of Physics Student for their annual "welcome back to campus" ice cream social.

He demonstrated Leidenfrost. Then swallowed 3-4 cc of LN2

X-rays indicated that a perforation of the stomach had occurred and he was at risk of perforating his esophagus as well. He immediately was taken into surgery, where part of his stomach had to be removed.

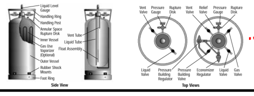
Michael begin to breathe on his own after just a few days, sitting up within a week, and walking and eating in two weeks. Full recovery took about eight weeks.

Rupture Disk "Repair" on LN2 Dewar

Rupture disk leaking, so replace with metal plug.

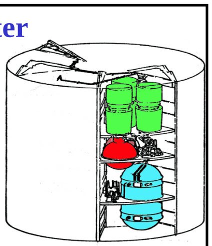
At 3 am tank drove through concrete floor above it and finally settled on the third floor of the Chemistry Building. It struck two 3 inch water pipes as well as the electrical wiring, flooding the first two floors. The loss of water pressure was observed on other parts of the campus. It left a twenty inch diameter hole through both floors.

Pressure from the explosion blew the doors from the hinges and the windows from their frames. The walls were found to have been driven four to eight inches from their original position.



Rupture disk that worked

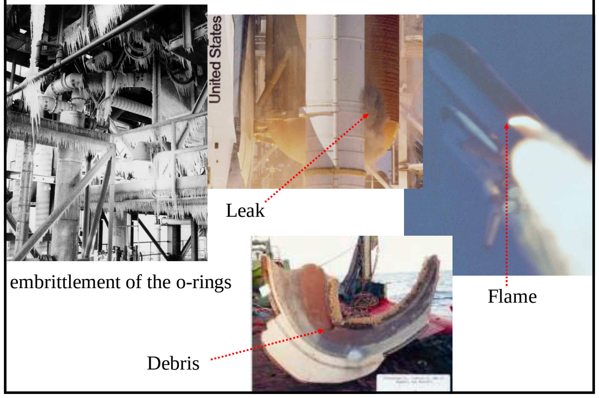
Apollo 13 Disaster



Module Map:: A cutaway diagram of the service module. The fuel cells, in green, provided water and electricity by combining oxygen and hydrogen stored in cryogenic tanks, marked in red and blue respectively. Oxygen tank 2, bright red, exploded during the Apollo 13 mission, almost killing the crew.

Make shift breathing device

Space Shuttle Challenger-January 28, 1986



Leak

embrittlement of the o-rings

Flame

Debris

X-33 Space Plane

Vented gases from cryogens ignited under plane on liftoff

Successful Liftoff

Explosion

Vostok Disaster

In 1980 Vostok-2M rocket was being fueled with LOX and kerosene at the Plesetsk Cosmodrome is Russia; an explosion tore through the launchpad incinerating the rocket and killing 48 people.

Cryogenic tank for liquefied carbon dioxide ruptured upon closing of safety valves

Fukushima, Japan - Small leak “fixed” by blocking vent port. Pressure rise caused small rip in tank. Rapid exhaust of gas caused lowering of temperature and further rupture

The explosion proved disastrous for the steel mill, its workers, and the repair company. There were three deaths and 38 injuries resulting from the incident, as well as a vast amount of structural property damage. The explosion caused the tank to tear into at least 7 large pieces of debris which then flew up to 60 meters (197 feet) away. A factory within 50 meters (164 feet) was completely destroyed, leaving only the pillars that had supported the rest of the building. Tiles from the roof of the steel mill were scattered in a circle around the mill with a radius of up to 100 meters (328 feet) which damaged windows and doors of nearby buildings. Also, all of the houses within an incredible 500 meters (1641 feet. This is over 5 football fields away) had damage to their windows.

Nursing Home gas mix-up

The nursing home received a shipment of four portable cryogenic medical gas containers labeled as medical oxygen, but one was LN2 filled vessel (oxygen label and a nitrogen label). When the current oxygen supply began to decrease an employee was dispatched to attach a new tank to the oxygen system. The employee picked the nitrogen filled container. “The container’s nitrogen-specific-gas-use-outlet connection was incompatible with the connector on the facility’s oxygen supply system.” The employee was initially unable to link the container to the oxygen system. Next, the employee swapped the nitrogen connection for an oxygen-specific gas-use-outlet and hooked it up, killing four residents and injuring six.

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LPN-983-Buffalo

Vessel contained 230 gallons of liquid propane (LP) Fell off forklift. The explosion turned an entire residential city block into what looked like a massive war zone. Buildings were flattened and mass destruction had occurred. The explosion caused six human fatalities while 70 more people were injured. In total, 56 homes were destroyed and 102 more were damaged. Other buildings completely destroyed consisted of a church and the warehouse. Also, five large vehicles were destroyed in the explosion consisting of fire trucks and large cranes.

Hydrogen Bomb-Tested Nov. 1, 1952

“Mike” test with cryogenic equipment attached.

Video of First American test 1952

Cryo Disasters Everywhere!