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The Properties, Uses, and Safety Hazards of Nitrogen

The six fatalities that occurred at the Foundation Food Group facility during January 2021, coupled with my visit to the ice cream shop in Florida in early 2024, with the liquid nitrogen tank located inside the shop, made me realize how little the population understands the hazards of nitrogen and other inert gases. Nitrogen is perfectly safe when stored and used so that release or loss of containment is prevented in an enclosed space or other areas where personnel are present and ventilation is limited. These gases are inert. However, exposure to concentrated mixtures with air can be and has been deadly. This book will provide more details on what has happened and what can happen when inert gases like nitrogen are released. We will discuss the hazards of these gases, how they can affect the human body and how this contact can be avoided. We will also review several case studies where this has occurred and, unfortunately, how people have died when this occurs.

The US Environmental Protection Agency (EPA) Cameo Database tells us that nitrogen is a colourless and odourless gas. It is non-combustible and non-toxic. Nitrogen makes up the major portion of the atmosphere (78%), but it does not support life by itself. We also know that nitrogen is frequently used in food processing, purging air conditioning and refrigeration systems. Nitrogen can result in asphyxiation by displacement of oxygen in the air. Also, pressurized nitrogen cylinders under prolonged exposure to fire or heat may rupture violently and become projectiles.

Nitrogen is readily available in the environment and makes up 78% (by volume) of the air we breathe. The remainder is 21% oxygen and a minimal amount of argon. Nitrogen is a non-poisonous gas; however, people and animals can die due to nitrogen concentration. They die not from nitrogen but due to oxygen deprivation. Nitrogen displaces oxygen from the air we breathe. In other words, when the nitrogen concentration increases, the oxygen concentration decreases.

Nitrogen is readily available by cryogenic fractionation of air to extract it for industry and other uses. It is slightly lighter than air and is slightly soluble in water. Liquid nitrogen boils at −320 °F (−196 °C) and contact with it can cause significant cold burns if it touches the skin or flesh.

One volume of liquid nitrogen expands to approximately 700 volumes of gas. An unplanned release of liquid nitrogen, for example, from a liquid nitrogen tank, will fill a standard-size room with concentrated nitrogen in seconds. People in the room can be quickly overcome by oxygen deprivation, and they can die, and this can happen in minutes. Cold nitrogen is heavier than air, and it will accumulate at ground level during a release. When liquid N_2 is exposed to air, the cloudy vapour you see is only the condensed moisture from the air, not the N_2 gas. Remember, nitrogen gas is invisible and odourless, and this is the danger!

Nitrogen condenses at its boiling point, −320.4 °F (−195.8 °C), to a colourless liquid lighter than water (liquid nitrogen). Liquid nitrogen is stored in specially designed pressure vessels designed to protect the super low temperature of the stored cryogenic liquid. When withdrawn, the temperature

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is −320 °F (−195 °C), making it very useful as a coolant or refrigerant. This characteristic makes liquid nitrogen useful as a refrigerant for food processing, pharmaceutical manufacturing and other commercial uses.

Nitrogen is non-flammable and does not support combustion. Therefore, it is often considered an inert gas (although it is not truly inert).

Safety hazards of nitrogen:
There are three primary hazards associated with nitrogen. In either form, as a liquid or gas, the deadly characteristic is that nitrogen quickly displaces oxygen from the environment. This has resulted in many incidents of accidental asphyxiation of workers. As stated earlier, it is not the nitrogen that kills; people die due to oxygen deprivation when nitrogen displaces oxygen. See the case studies in this book and the appendix for a discussion of nitrogen-related incidents.

Nitrogen (A frequent cause of fatalities and the primary subject of this book – this is a summary; refer to the Safety Data Sheet (SDS), or sometimes referred to as the Material Safety Data Sheet (MSDS) for additional information):
A general description of nitrogen from the US Environmental Protection Agency (EPA) Cameo Chemicals Database:

Nitrogen is a colourless and odourless gas. It is non-combustible and non-toxic and makes up the major portion of the atmosphere, but it does not support life by itself. Nitrogen may cause asphyxiation by displacement of air containing oxygen, which is needed to sustain life. Under prolonged exposure to fire or heat, containers may rupture violently and rocket.

Health hazards of nitrogen from the EPA Cameo Chemicals Database and the Safety Data Sheet:
Vapours from liquefied gas may cause dizziness or asphyxiation without warning. The victim may not be aware that they are being overcome. Vapours from liquefied gas are initially heavier than air and spread along the ground.

High concentrations of nitrogen may cause asphyxiation. Symptoms may include loss of mobility and loss of consciousness. The victim may not be aware of asphyxiation. To protect yourself, wear a self-contained breathing apparatus (SCBA) when responding to someone who has been overcome. Remove the victim to an uncontaminated area and keep the victim warm and rested. Call a doctor. If breathing ceases, apply artificial respiration. Additional hazards associated with exposure to oxygen deprivation are highlighted in Chapter 3 including a chart highlighting the effects of low oxygen concentrations on the body.

If you are working near a vessel that is being purged with nitrogen, appropriate warnings and barricades must be in place to prevent personnel from entering areas that may have an oxygen deficiency. Barricades must be designed to keep personnel from entering these areas, including all areas where nitrogen is vented into the atmosphere.

Personnel should be prevented from entering platforms near open access plates or on process vessels with nitrogen venting. Personnel working near nitrogen venting must be properly outfitted with either hose line-supplied breathing air or protected by a self-contained breathing apparatus. Additionally, personnel while wearing self-contained breathing air should continuously monitor other workers who are working in or near an area where nitrogen purge is in progress. No one should be allowed on the platform or near the vessel opening where nitrogen is venting without breathing air.

Warning: As a reminder, a cartridge or chemical respirator is not sufficient for breathing protection when exposed to an oxygen-deficient atmosphere. The respirator must have a supply of hose-line-supplied or self-contained breathing air.

Do I have to be inside a confined space to be overcome by nitrogen?

> NO, you do not! There have been several cases where workers have been outside a vessel being purged with nitrogen and collapsed due to oxygen deprivation and fell into the vessel and died, or they were overcome, fell and died from the fall.

The second hazard is associated with liquid nitrogen. Liquid nitrogen is a cryogenic liquid and is stored in a pressure vessel specially designed to maintain liquids at extremely low temperatures. It is stored at a temperature of −320 °F (−196 °C) and is an extreme risk of causing cold burns. A cold burn is no different from a hot liquid or a thermal burn. It can result in damage to the skin and to the underlying tissue and can require skin grafts and treatment, not unlike a thermal burn.

When liquid nitrogen is released into the atmosphere, it quickly forms a white fog by freezing the moisture in the air. It may also freeze anything nearby and can create an oxygen-deficient atmosphere.

The third significant hazard with liquid nitrogen is the potential ingestion of even a small amount of the liquid, for example, in ice cream or a cold treat. I'll discuss this in more detail in future chapters.

Humans must breathe oxygen to survive and suffer adverse health effects when the oxygen concentration drops below 19.5%. This can happen when the oxygen in the work environment is displaced by an inert gas such as nitrogen, argon, carbon dioxide or another inert gas. Some light hydrocarbons, although not inert, may have similar effects.

The US Occupational Safety and Health Administration (OSHA) has developed a nice chart that clearly details the effects of an oxygen-deficient atmosphere on personnel who may be unaware that this exists around them. This chart is included in Chapter 3 and details that workers who are undergoing any form of exertion rapidly become symptomatic when the oxygen level drops below about 19.5%. At 12–16%, they have increased breathing rates, accelerated heartbeat, and impaired attention, thinking, and coordination, even when at rest. As the oxygen concentration continues to drop, workers may experience poor judgement and exhaustion, even with minimal exertion, and they ultimately have heart failure (cardiac arrest) and die.

The following is extracted from the Chemical Safety and Hazard Investigation Board report on the nitrogen fatalities at the Valero Delaware City Refinery.

> 'Workers may be unaware of another dangerous complication: inhaling nitrogen or other inert gas suppresses the brain's breathing reflex response. The breathing reflex is controlled by the amount of carbon dioxide in the blood rather than the shortage of oxygen. Normally, the ability to voluntarily hold one's breath is eventually overwhelmed by the brain's respiratory control centre, which is triggered by the increased carbon dioxide concentration in the blood, combined with a drop in the blood's pH. If high purity nitrogen or other inert gas is inhaled, the body may simply stop breathing, as carbon dioxide accumulation in the blood is insufficient to stimulate the breathing reflex (Lumb, 2005)'.

How long does it take for the oxygen level to drop to a dangerously low level when liquid nitrogen is released into a confined space?

The answer is that when nitrogen is released into the environment, the oxygen level only takes a few minutes to reach deadly concentrations. Also, it is just as important to understand that the victim or victims will not perceive or understand what is happening to them. There is no odour or other indication that they are in danger of being killed.

Case Study Documented by the National Library of Medicine and National Center for Biotechnology Information:

These US National institutions documented the following tragic case study: This case study confirms that the oxygen level will quickly drop to very low levels when nitrogen is released into the environment, especially in confined spaces or areas where there is little air circulation.

> 'A 27-yr-old postgraduate student was found lying on the floor of an unsealed underground dry area, where a valve-opened empty cylinder of liquid nitrogen (150 L) (5.3 Cu Ft) was connected to a cap-removed empty Dewar-flask (10 L) (.3 Cu Ft) via a copper infusion tube.
>
> It is obvious that the student was draining liquid nitrogen from the cylinder into the flask when he was overcome by the lack of oxygen, collapsed and subsequently died. The liquid nitrogen was to be used in a subsequent class study.
>
> No injury was found externally or internally. There were petechiae in the bilateral conjunctive and periorbital skin (pinpoint, round spots forming around the skin around the eyes, sort of like a rash).
>
> The dry area (where the student was collecting the liquid nitrogen), measured 300 × 130 × 260 cm (9.8 Ft. × 4.3 Ft. × 8.5 Ft.)., had a communication to the basement of the research building by a window measuring 90 × 60 cm (3 Ft. × 2 Ft.) in size at 130 cm (4.3 Ft. above the floor).
>
> The scene reconstruction and atmosphere gas analysis revealed that the O_2 concentration at 60 cm (2 Ft.) above the base dropped to 12.0% in 3 min and 10 sec, 10.0% in 8 min and 53 sec, 6.0% in 18 min and 40 sec, and 4.2% in 20 min and 28 sec. The primary cause of death was asphyxia by evaporated liquid nitrogen'.

These extremely low oxygen levels will not sustain life, and this case study confirms that they will occur within minutes of a release of liquid nitrogen into a confined space. Please refer to Figure 1.1 for a visual of the rapid drop in available oxygen resulting in this fatality.

This chart, reconstructed using data from the National Library of Medicine, illustrates the rapid decline in available oxygen that resulted in a fatality. Thanks to the National Library of Medicine for making this data available.

The minimum safe oxygen concentration is 19.5%, as defined by the US Occupational Safety and Health Administration (OSHA). OSHA says health effects start when oxygen concentrations are below 19.5%.

In this incident, the oxygen level dropped below 19.5% in less than a minute and to 12% in 3 minutes. This is well below the level required to sustain life. Within 20 minutes, the oxygen level was at around 4%. This means certain death for everyone who was exposed.

The 27-year-old postgraduate student was found non-responsive in an underground dry area adjacent to a research building lying on plastic pallets. He was lying beside an empty Dewar flask connected to an empty liquid nitrogen cylinder. The valve on the cylinder was in the open position, indicating that the student was filling the flask when he was overcome by the lack of oxygen (due to a release of nitrogen vapours). The larger nitrogen cylinder had been filled the day before this incident. Please refer to Figure 1.2, which illustrates the empty liquid nitrogen cylinder connected to a smaller nitrogen Dewar flask. The student's body was found lying adjacent to the empty cylinder.

Please note the liquid nitrogen cylinder is set up to drain into the Dewar flask, potentially releasing nitrogen vapours into the surrounding environment.

After seeing this, please give more thought to my 'nitrogenated ice cream' story in the Foreword section of this book. Please note from the graph (Figure 1.1) that the available oxygen dropped

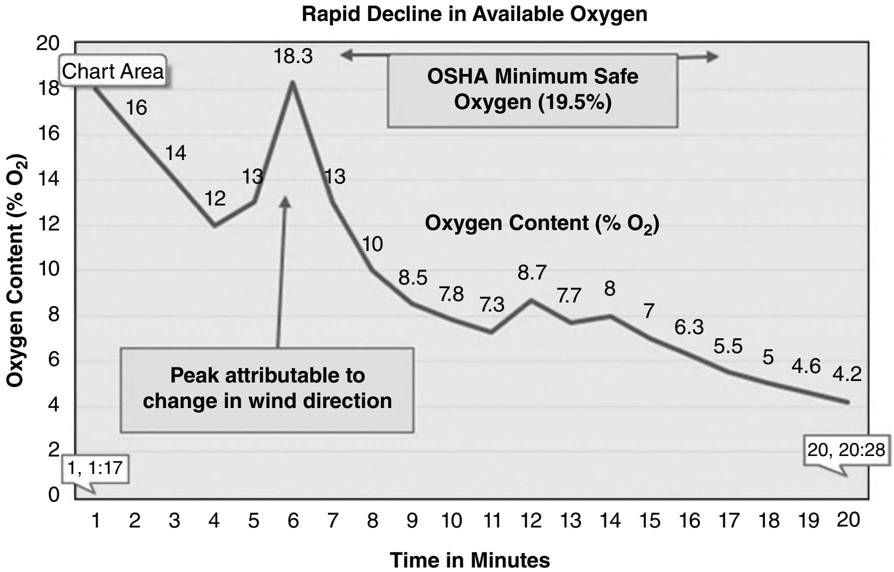

Figure 1.1 National Library of Medicine, National Center for Biotechnology Information data confirm that the oxygen level in a confined space will quickly drop to very low levels in minutes, ensuring certain death for those exposed.

below the OSHA 'Deficient Oxygen' criteria of 19.5% in about 1 minute. In other words, the nitrogen quickly displaced the available oxygen in the room. The available oxygen concentration dropped rapidly and, within the first couple of minutes, was well below that required to sustain human life.

Going back to the ice cream shop, what if the liquid nitrogen release, which occurred overnight the week before, had occurred during the day when the shop was full of teenage attendants and children? Possibly, the alarm would have sounded, and there would be a white fog, but there would have been no odour or other indication that their lives were at risk. The teenage attendant explained that 'they are supposed to go outdoors if the alarm goes off' – she didn't say they will immediately go outdoors if the alarm goes off, and there was no sense of urgency or even an understanding of the potential hazard.

I am very concerned about having liquid nitrogen tanks and fittings inside an enclosure like an ice cream shop – or any enclosure. We also know a liquid nitrogen release occurred at a different ice cream shop in Weston, Florida, sending responders to the hospital for oxygen deprivation injuries. I can't resist thinking if they realized how close they were to death.

The case study, as documented by the National Library of Medicine and National Center for Biotechnology Information, confirms that in the event of a release of liquid nitrogen, the oxygen level would quickly drop to levels well below that required to sustain life.

To expand on this point further, liquid nitrogen has an expansion ratio of 1:696. For example, 10 gallons equals 1.34 cubic feet. If we were to spill only 10 gallons of liquid nitrogen into a small room, for example, an ice cream shop, we would release 933 cubic feet of nitrogen into a confined space.

This would have an effect very similar to the case study shared by the National Library of Medicine, where one person was killed by asphyxiation due to nitrogen, and the Chemical Safety

Figure 1.2 Location of the nitrogen-induced fatality. *Source:* National Library of Medicine (NLN), National Center of Biotechnology Information / Public domain. NLM is part of the National Institutes of Health (NIH), US Department of Health and Human Services, and is located in Bethesda, Maryland.

Board report on the Georgia poultry processing plant, which resulted in six deaths. In this example, the available oxygen level in the room would almost immediately drop to below what is required to support human life.

Transport and storage of liquid nitrogen and other cryogenic gases:
Liquid nitrogen is shipped and stored in specially constructed double-shell tanks. These tanks, sometimes called cylinders, are specially constructed to hold the cryogenic liquids, which are super cold and are designed with a vacuum between the inner and outer shell and several layers of insulation to prevent ambient heat from penetrating the shell to the cold liquid inside. These large cylinders allow the transport of a significant amount of nitrogen; remember, liquid nitrogen expands nearly 700 times when it vapourizes to gaseous nitrogen. Also, liquid nitrogen is a cryogenic liquid meaning that it is supercold and requires very little pressure when compared to nitrogen in a pressurized gaseous state.

Consumers of liquid nitrogen should be aware that ambient heat will penetrate through the cylinder shell and the insulation to the liquid and gradually increase its temperature. This will result in vaporization and a build-up of pressure in the cylinder, referred to as ‘head pressure’. This pressure will periodically vent off through the loosely fitting cap or the relief valve. I do not believe liquid nitrogen storage should be in a confined area due to the potential for a release, but if it is, the relief valves must vent outdoors. We must recognize that if the cylinders are located indoors and even with the relief valves venting outdoors, there is still the possibility of a pipe or fitting failure, such as what happened at the ice cream shop.

The uses of nitrogen:
Nitrogen is the most widely used industrial gas, especially by petroleum refineries and petrochemical plants. It is also widely used by pharmaceutical manufacturers, glass and ceramic manufacturers, steel and other metals refining and fabrication companies, and pulp and paper manufacturers. It is commonly known as nitrogen or N_2 but also reported to sometimes be referred to as GAN or GN when in its gaseous form or LIN or LN when in its liquid form (although I have never seen these references). Nitrogen is especially useful to the petroleum refining or petrochemical industry because it is an inert gas that eliminates oxygen, thereby preventing a reaction with hydrocarbons or other chemicals that may result in a fire or explosion.

As a gas, nitrogen may also be used for any or all of the following (Nitrogen has many uses – the following is not intended to be a complete list):

- Nitrogen is used in food processing, purging air conditioning and refrigeration systems, and pressuring aircraft tires. It is also regularly used in petroleum refining and petrochemical processes for tank blanketing, purging oxygen-containing equipment, laboratory use, and instruments and analysers.
- Nitrogen may be supplied by pipeline as compressed gas or delivered in a liquefied state in compressed storage tanks or tank trucks.

In the petroleum refining and petrochemicals industry:

- Preparing equipment by purging hydrocarbons before opening equipment to the atmosphere.
- Remove oxygen from piping and process vessels during start up and before bringing in hydrocarbons.
- Nitrogen is also frequently used as a testing agent when pressure testing the ‘tightness’ of piping circuits or pressure vessels in preparation for a unit start-up after turnaround or maintenance repairs. This is especially true for tightness testing high-pressure circuits.
- Blanketing tanks to prevent the accumulation of flammable mixtures or products that are sensitive to air.
- For inerting equipment prior to maintenance or mechanical work. For example, ensuring that process vessels such as reactors are essentially free of oxygen for catalyst replacement when the catalyst is pyrophoric. This prevents the catalyst from self-ignition by contacting air.
- Purging equipment of oxygen and other reactive gases before placing it into long-term storage or ‘mothballing’. This is done to prevent oxidation or corrosion during storage.
- Pressurized nitrogen may be used to clear plugs in pipelines or to pig lines for cleaning or prior to inspection or maintenance.
- Nitrogen may also be used to pressurize tank cars or railcars to aid in offloading products to storage tanks or other dispositions. Nitrogen is inert and will not react with the hydrocarbons or other chemicals that may be in the railcar.
- For some process and laboratory analyser operations. Process instrumentation or analysers are frequently purged with nitrogen gas.
- For specific welding operations to eliminate air that can interfere with the welding process, contaminating the weld.

In the food processing industry:

- Liquid nitrogen is used as a refrigerant to flash-freeze food products and prepare to ship to the customer.

- Liquid nitrogen is also used as a refrigerant to flash-freeze dairy products to make ice cream or cold treats or fuming drinks such as dragons' breath.

Other uses for nitrogen as a gas:

- Nitrogen is sometimes used to inert aircraft fuel tanks to prevent an explosive mixture in the vapour space. Nitrogen is inert and displaces oxygen, preventing a flammable mixture from occurring in the storage tanks.
- Nitrogen is important to support plant growth and can be added to the soil as an ingredient in fertilizers.
- Nitrogen is frequently used as a filler in light bulbs to eliminate oxygen, thereby preventing combustion of the tungsten filament.
- Nitrogen is widely used in pharmaceuticals and is in every major pharmacological drug class. For example, nitrogen is in most antibiotics.
- Nitrous oxide is sometimes used as an aesthetic.
- Nitrogen forms nitric oxide and nitrogen dioxide with oxygen, ammonia with hydrogen and nitrogen sulphide with sulphur. Some nitrogen compounds can also be formed naturally through biological activity.

As a liquid for storage or transport (liquid nitrogen from pressurized cylinders or tank trucks):

- Liquid nitrogen is a cryogenic liquid, that is, it is stored in a pressure vessel specially designed to maintain liquids at extremely low temperatures. When liquid nitrogen is stored, it is at a temperature of −320 °F (−195 °C), making it very useful as a coolant or refrigerant. Therefore, it has many uses in laboratories, or in the food processing industry, to flash freeze various foods for processing or for shipment. Liquid nitrogen is also used to preserve biological specimens such as sperm, blood or eggs.
- It is also sometimes used in the field to freeze lines when isolation valves are leaking through.
- Liquid nitrogen, when released to near atmospheric pressure, expands 700 times in volume. Therefore, it is also used to store large quantities of nitrogen or transport nitrogen gas in large quantities.

At high temperatures and with the aid of catalysts, nitrogen can combine with some metals to form nitrides. For example, nitrogen and catalysts can combine with lithium, magnesium and titanium at high temperatures to form nitrides. This is a valuable contribution to compounds that can be used as hard coatings or insulators.

Nitrogen is necessary to support some biological processes. For example, it is frequently used as a fertilizer, typically as ammonia or ammonia-based compounds. Some compounds formed with halogens and certain organic compounds can also be explosive.

End of Chapter 1 Review Quiz

1. Why is nitrogen an important compound for use in the petroleum refining and petrochemical process industry?
   Answer(s):

2. Nitrogen is used for petroleum and petrochemical storage tank blanketing to prevent the accumulation of __________ __________ or for products that are sensitive to __________.
   Answer(s):

3 Please explain why liquid nitrogen is frequently used as a refrigerant in food processing and the pharmaceutical industries.
Answer(s):

4 What properties make nitrogen more suitable as a gas to pressurize tank cars or railcars to aid in offloading products to storage tanks or other dispositions?
Answer(s):

5 Why is nitrogen sometimes used to blanket aircraft fuel tanks?
Answer(s):

6 Nitrogen makes up about ______% (by volume) of the air that we breathe.
Answer(s): Please select the correct answer(s).

A 52%

B 85%

C 78%

D 26%

7 Can you name four of the characteristics of nitrogen?
Answer(s):

8 When liquid nitrogen is released into the atmosphere, it quickly forms a white fog by freezing the __________ in the air. It may also freeze anything nearby and can create an oxygen-deficient atmosphere.
Answer(s):

9 One volume of liquid nitrogen expands to approximately _______ volumes of gas.
Answer(s):

10 An unplanned release of liquid nitrogen, for example, from a liquid nitrogen tank, will fill a standard-size room with concentrated nitrogen in __________. People in the room can be quickly overcome by oxygen deprivation, and they can ________.
Answer(s):

11 What mechanism makes nitrogen so dangerous to work with and around?
Answer(s):

12 Cold nitrogen is ________ than air; therefore, it will tend to concentrate along the __________ or when in a building or room, along the _________.
Answer(s):

13 Another significant hazard when working with liquid nitrogen is the possibility of _______ or ___________ from contact with the cold liquid.
Answer(s):

14 Why is nitrogen purge used before unit start-up for process piping and vessels?
Answer(s): Please select the correct answer(s).

A As a verification that there are no leaks in the piping or vessels before introducing hydrocarbons.

B To eliminate oxygen from the piping or vessels before introducing hydrocarbons.

C To ensure that the piping or vessels will not fail during the start-up process, releasing hydrocarbons into the atmosphere.

D As a verification that there will be no product contamination during the start-up process.

15 How is nitrogen added to plants to help support plant growth?
Answer(s): Please select the correct answer(s).

A Liquid nitrogen is injected into the soil directly below the plants.

B Nitrogen is converted into ammonia or ammonia-based compounds and used as fertilizer to support plant growth.

C Nitrogen is fed to plants by creating a nitrogen atmosphere during the plant's early life.

D Nitrogen is converted into ammonia, and the ammonia is provided to the plant in the nursery.

16 Liquid nitrogen is a ____________ liquid; that is, it is stored in a pressure vessel specially designed to maintain liquids at extremely low temperatures.
Answer(s): Please select the most correct answer(s).

A condensed

B cryogenic

C mixed

D pure

17 When liquid nitrogen is stored, it is at a temperature of ___________°F making it very useful as a coolant or refrigerant.
Answer(s): Please select the most correct answer(s).

A 212 °F

B −200 °F

C 32 °F

D −320 °F

18 Nitrogen is used for tank blanketing to prevent the accumulation of ___________ ___________ or for products that are sensitive to ___________.
Answer(s):

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