NITROGEN

1. Introduction

Nitrogen [7727-37-9], atomic number 7, is a nonmetallic element situated between carbon and oxygen in the Periodic Table. It is the most abundant element accessible to human beings which exists uncombined with any other elements (1). Most of the nitrogen in the atmosphere occurs as a diatomic gas N_2, sometimes referred to as dinitrogen, and comprises 78.03% by volume and 75.45% by weight of the earth's atmosphere. Industry annually isolates millions of tons of nitrogen from air. Nitrogen-containing compounds are essential to all life.

Nitrogen was discovered in 1772 by Rutherford (2), and about that same time, Scheele, Priestly, and Cavendish were also working with this "burnt" or "dephlogisticated" air. The name nitrogen from the Latin *nitrum*, or the Greek combination, *nitron* "native soda" and *gene* "forming" was suggested by Chaptal in 1790 when it was learned that niter and nitric acid were formed from this constituent (3). In the 1780s nitrogen oxides were produced by combining nitrogen and oxygen using an electrical discharge. Nitrogen was first liquified by Cailletet in 1877. In the early 1900s atmospheric nitrogen was first used for large-scale industrial purposes. Calcium cyanamide was first produced in 1895 by the Frank-Caro process. In 1900, Birkeland-Eyde developed the first industrial oxidation of nitrogen. Ostwald was awarded the 1909 Nobel Prize for work that led to the industrial-scale catalytic oxidation of NH_3 to HNO_3. Two more Nobel Prizes were granted for the Haber-Bosch process for the catalytic synthesis of Ammonia (qv) from N_2 and H_2. This process reached industrial scale by 1913. In the 1990s, five of the 15 largest volume industrial chemicals produced in the United States contain nitrogen: ammonia, nitrogen (gaseous and liquified), ammonium nitrate, nitric acid (qv), and Urea (qv) (1,4).

2. Physical Properties

Nitrogen is the lightest of the Group 15 elements and has an atomic weight of 14.008. There are two naturally occurring stable isotopes: ^{14}N (relative atomic mass 14.003, natural abundance 99.634%) and ^{15}N (relative atomic mass 15.000, natural abundance 0.366%). Both of these isotopes have a nuclear spin and are used in nmr experiments (5). The ground state electronic configuration of the nitrogen atom is $1s^2 2s^2 2p_x{}^1 2p_y{}^1 2p_z{}^1$ with three unpaired electrons (^4S). Nitrogen can have oxidation states ranging from +5 to −3. The most common oxidation states are +5 (eg, nitric acid), +3 (eg, nitrous acid), 0 (eg, molecular nitrogen), and −3 (eg, ammonia). The electronegativity of N ($\sim$3 on the Pauling scale) is only exceeded by oxygen and fluorine. It has a single-bond covalent radius of $\sim$70 pm. Unlike the heavier elements of Group 15, nitrogen readily forms multiple bonds with itself and other atoms (6,7). The nitrogen atom typically has a maximum coordination number of four, and can be found in the tetrahedral, pyramidal, planar, angular, and linear geometries. Pentacoordinate nitrogen bonding has been demonstrated in gold(I) complexes with trigonal bipyramid geometry (8). Theoretical calculations indicate that sixfold nitrogen coordination may be possible (9).

Molecular nitrogen, N_2, is a colorless, odorless, diamagnetic, noncombustible gas at standard pressure (101.3 kPa) and temperature (0°C). The gas condenses to a colorless liquid at $-195.8°C$ at atmospheric pressure. Depending on the temperature, solid molecular nitrogen exists in one of two forms at atmospheric pressure, α and β, both of which are white. At extreme pressures and at room temperature, nitrogen solidifies into two additional phases, δ and ϵ. A stable stoichiometric solid compound of nitrogen and helium of composition $He(N_2)_{11}$ at a pressure of 9 GPa (1,300,000 psig) has been reported (10). Other properties of molecular nitrogen are shown in Tables 1 and 2 (6,7,11). Density is represented by Q.

The deviation from the perfect gas law is not great at ordinary pressures and temperatures. At the highest pressure normally encountered commercially, 41 MPa (6000 psig), the compressibility factor of nitrogen is 1.3629 at 25°C (12).

3. Chemical Properties

The chemistry of molecular nitrogen is marked by its relative inertness (13). The electronic configuration of the N_2 molecule in terms of molecular orbital theory is $1\sigma^2{}_g 1\sigma^2{}_u 2\sigma^2{}_g 2\sigma^2{}_u 1\pi^4{}_u 3\sigma^2{}_g 1\pi^0{}_g$. There is a large (8.3 eV) energy gap between the highest occupied molecular orbital (HOMO), $3\sigma_g$, and the lowest unoccupied molecular orbital (LUMO), $1\pi_g$. The LUMO is high enough that molecular nitrogen only takes electrons from alkali metals or other strongly electron yielding metals. The HOMO of dinitrogen is so low that the ionization energy (15.6 eV) approaches that of argon (15.75 eV). N_2 has a short (109.76 pm) interatomic distance and high (945 kJ/mol (226 kcal/mol)) dissociation energy. At ordinary pressures, even at temperatures approaching 3000°C, there is no appreciable dissociation (6). The triple bond of dinitrogen is nonpolar and has a significantly lower reactivity than other comparable triple bond systems, such as the isoelectronic compound carbon monoxide. Because of the stability of the nitrogen–nitrogen bond, and highly symmetrical electron distribution of the molecule, the intermolecular forces are generally very small.

Despite the stability of molecular nitrogen, the chemistry of nitrogen is extremely important. There is essentially a limitless supply of nitrogen in the atmosphere. However, most biological species can use only nitrogen which has been chemically combined with some other element or compound, so-called fixed nitrogen, and the abundance of this type of nitrogen is relatively limited. Agriculture and industry depend on an abundance of nitrogen in forms other than gaseous N_2. There is much research interest in elucidating inexpensive methods of converting molecular nitrogen to some form of fixed nitrogen (see NITROGEN FIXATION).

In most solvents, N_2 has a relatively low solubility. The solubility in water at 0°C and 101.3 kPa (1 atm) of N_2 is only 23.5 ppt (by volume) (14). Nitrogen is slightly soluble in iron and steel through the reaction $N_2(gas) \rightleftharpoons 2\ N$ (dissolved), where N (dissolved) represents atomic nitrogen dissolved in iron. The solubility of nitrogen at one atmosphere pressure in pure liquid iron at 1600°C is about 0.045% by weight, and in α-phase iron at 900°C is about 0.0045% by weight (15). Nitrogen has a significant alloying effect in steels. The presence of nitrogen can strengthen low carbon steels at the expense of increased strain aging properties. Nitrogen in amounts up to 0.02% has been used to strengthen high strength low alloy steels (16). Dissolved nitrogen strengthens and increases the pitting resistance of austenitic stainless steels but lowers the mechanical properties of ferritic stainless steels. The quantity of dissolved nitrogen in carbon steels can be controlled by deoxidizing the melt with aluminum, which combines with the nitrogen to form nitrides, producing aluminum-killed steel; by inerting the ladle with argon; by vacuum arc melting; by vacuum degassing; or by electroslag remelting processes. Through these methods, dissolved nitrogen levels can be maintained as low as 40–50 ppm.

Because of the inherent stability of the N_2 molecule, high temperatures are often used to coax its reactivity. Temperature elevation promotes N_2 reactions with chromium, silicon, titanium, aluminum, boron, calcium, strontium, beryllium, magnesium, and lithium to form nitrides; at 400°C, nitrogen reacts with oxygen and chlorine to form nitrosyl chloride; at 900°C, graphite and sodium carbonate react with nitrogen to form carbon monoxide and sodium cyanide; at 1500°C, nitrogen reacts with acetylene to form hydrogen cyanide. Also at high temperatures, N_2 and O_2 react to give NO. Arguably, the most important industrial process which utilizes N_2 as a constituent is ammonia formation at high pressures from nitrogen and hydrogen in the presence of heat and a catalyst, known as the Haber-Bosch process (1,11).

When molecular nitrogen is subjected to the actions of a condensed electrode discharge or to a high frequency, it is changed to an activated, unstable condition, which returns to its ground state with the emission of a greenish yellow glow. In its excited state, the gas is chemically active; it combines in the cold with mercury, sulfur, and phosphorus. This activity is the result of the presence of excited N_2 molecules at various energy levels, as well as the presence of atomic nitrogen. An example of this excited state chemistry is when activated nitrogen causes the dissociation of carbon dioxide that is normally impervious to the actions of ground state N_2 (17).

Dinitrogen complexes are molecules that contain dinitrogen bound to a metal. The first dinitrogen complex, $[Ru(N_2)\ (NH_3)_5]^{2+}$, was reported in 1965 as a product of the interaction of hydrazine and $RuCl_3$ (aq) (18). There are hundreds of complexes with dinitrogen as a ligand (19,20). The bonding of a neutral, dipole-free and not easily polarized N_2 molecule to a metal is generally quite labile. N_2-metal binding can exhibit a variety of geometries, eg, end-on (η^1) and side-on (η^2) or bridging between two metals. End-on η^1 binding is the most common and is a combination of a coordinate bond between the electron pair on one of the nitrogen atoms and an acceptor orbital of the metal, and back-bonding of loosely held metal electrons into the π^* orbital of the N_2 ligand (21).

4. Manufacture and Processing

Atmospheric air is the feedstock for all commercial nitrogen production processes. Nitrogen is separated from air commercially by cryogenic distillation, pressure swing adsorption, membrane permeation, or hydrocarbon combustion processes. Cryogenic distillation is the most cost-effective technology for production of large quantities of relatively pure nitrogen and is the most commonly used. Pressure swing adsorption and membrane permeation are the most economical processes for production of lower purity nitrogen in low to moderate volume ranges (25–500 m^3/h (1000–20,000 SCFH)). All statements of volume (m^3) are at normal conditions ($t = 25°C$, $pressure = 101.3$ kPa). Both are rapidly growing technologies. Industry estimates indicate that noncryogenic separation will eventually account for greater than 30% of all commercial nitrogen production (22). Combustion-based processes are in decline in most applications due to displacement by noncryogenic processes but are still widely used in heat treatment where residual contaminants play an active process role. The choice of the most economic technology is principally driven by required nitrogen purity and flow rate as shown in Figure 1. Liquid nitrogen is produced exclusively from cryogenic processes.

4.1. Cryogenic Air Separation. This method has been in commercial use for the production of nitrogen since the beginning of this century. Most nitrogen is produced in large tonnage cryogenic distillation plants with oxygen and argon as coproducts. The nitrogen and oxygen are either utilized directly in gaseous form at adjacent industrial facilities with distribution by pipeline, or some or all is liquified to enable distribution and storage in vacuum-insulated vessels. The delivered liquid nitrogen is then used directly or vaporized as needed or is vaporized and stored under pressure in cylinders.

If the required gaseous nitrogen flow rate is relatively constant and is greater than about 400 m^3/h (15,000 SCFH), an on-site cryogenic production plant may be the most economical mode of supply. Figure 2 shows a typical cryogenic nitrogen separation process. Air is compressed, cooled to remove excess water vapor, and purified to remove residual carbon dioxide, water vapor, and other contaminants which could freeze in the process by either reversing heat exchangers or molecular sieve pressure swing adsorption (Fig. 3). In the reversing heat-exchanger process, the incoming compressed air is cooled by countercurrent heat exchange with cold oxygen-rich waste gas and nitrogen product exiting the process. Residual contaminants in the air are frozen out onto the heat-exchanger surfaces. At periodic intervals, the flow through the heat exchangers is reversed to remove the contaminants. In the molecular sieve process, two beds of activated alumina and activated carbon are used to remove the contaminants by reversible adsorption, with the incoming air flow alternating between beds to allow regeneration of the depleted bed. The molecular sieve process is advantageous in nitrogen plants that may have insufficient waste gas available to clean out the reversing heat exchangers or that must be started up and shut down frequently. Most nitrogen plants use the molecular sieve process due to increased reliability and lower cost (see MOLECULAR SIEVES).

The clean compressed air is then further cooled to near the dew point of air (ca −176°C at 450 kPa) through countercurrent heat exchange with outflowing streams of waste gas and cold nitrogen product and is separated into its constituents in a single distillation column. Nitrogen product emerges from the top of the column and is available at ca 140–450 kPa (20–65 psig). Additional refrigeration is required to accommodate heat losses in the system from process efficiencies and imperfect thermal insulation. This is provided by either expanding a portion of the incoming compressed air through an expansion turbine coupled to an external brake to provide isoenthalpic cooling, or through the vaporization of a small quantity of delivered liquid nitrogen. In larger plants with an expansion turbine, liquid nitrogen in volumes between 1 to 5% of the capacity of the plant can be produced for use as backup. If more liquid nitrogen production ($\leq$10%) or higher nitrogen product pressures (ca 450−1000 kPa (65−145 psig)) are required, an alternative cycle can be used which expands a portion of the oxygen-rich waste gas rather than the incoming air through the expansion turbine.

Capacities of on-site cryogenic nitrogen plants range from 250 to over 50,000 m^3/h (10,000 to over 2,000,000 SCFH). A level of 1 ppm residual O_2 is readily achievable with present technology. Through the addition of more separation trays and at the expense of reduced nitrogen recovery, levels of less than 1 ppb O_2 are possible for demanding semiconductor manufacturing applications (see SEMICONDUCTORS, SILICON-BASED SEMICONDUCTORS).

4.2. Pressure Swing Adsorption. PSA systems operate on the principle of reversible selective adsorption of oxygen on a carbon molecular sieve (CMS). This process was invented in 1965 and commercialized in the 1970s by the German research institute on coal (qv), Bergbau-Forschung GmbH. Modern CMS is manufactured from bituminous coal which is oxidized in air at a temperature below the ignition point and mixed with an organic binder to form pellets which are carbonized and processed. These pellets have pores with diameters similar in size to oxygen and nitrogen molecules. Oxygen is adsorbed by the CMS at a faster rate than nitrogen due to polarity and molecular size effects, the oxygen molecule being smaller than nitrogen.

A typical nitrogen PSA system is shown in Figure 3. Air is compressed, filtered, cooled to remove excess moisture, and passed alternately through two beds of CMS. Oxygen, carbon dioxide, and water vapor are selectively adsorbed in the CMS matrix. When one bed is saturated with oxygen, the air flow is diverted to the second. The first bed is depressurized to atmosphere, releasing the adsorbed oxygen, carbon dioxide, and water vapor and the process is repeated. Product nitrogen is collected in a nitrogen receiver and is available at ca 690 kPa (100 psig). Atmospheric argon is concentrated in the product nitrogen.

Nitrogen PSA systems are economical for producing gaseous nitrogen on-site at flow rates ranging from 25 to 800 m^3/h (1,000 to 30,000 SCFH) at purities up to 99.8% ($\sim$0.2% residual oxygen). More production can be obtained from a given system at lower purities, provided sufficient air is available. For higher purities, the residual oxygen can be combined with hydrogen (qv) in a supplemental deoxo system. The water reaction product is removed in a regenerative dryer. However, residual hydrogen may be present in the product nitrogen and there are significant additional costs of hydrogen supply and the deoxo system.

4.3. Membrane Permeation. The use of hollow-fiber polymeric membranes for air separation is a newer technology, commercially viable since the early 1980s. Membrane systems are displacing PSA systems in the lower purity, lower flow rate range. Membrane nitrogen generation systems operate on the principle of selective gaseous permeation through a membrane. Commercially available systems use hollowfiber membrares (qv) fabricated from polymers such as polysulfones, polyimides, and polycarbonates which permeate oxygen faster than nitrogen through a solution–diffusion mechanism. A typical membrane fiber outer diameter is 100–200 μm with a wall thickness of 30–50 μm. In the membrane process shown in Figure 4, air is compressed and passed through a series of filters to remove any residual oil, which can be detrimental to membrane longevity, from the compressor and excess water vapor. The air is then heated to the optimum process temperature for the given polymer (usually 40–60°C) and is fed axially into the center of thousands of the hollow fibers packed in a tube-and-shell configuration. The nitrogen is concentrated during its passage down the fibers and is collected as the nitrogen product. Atmospheric argon is also concentrated in the product stream (see MEMBRANE TECHNOLOGY).

Nitrogen membrane systems are economical for producing gaseous nitrogen at flow rates ranging from 3 to 3000 m^3/h (100–100,000 SCFH), depending on purity produced. Purities up to 99.5% are economical, depending on flow rate. As with PSA systems, the residual oxygen can be removed by use of a supplemental deoxo system. Membrane technology has proven versatile because of the simplicity of the process and the light weight of the membranes.

4.4. Inert Gas Generators. Inert gas generators remove atmospheric oxygen by combustion with natural gas or propane. These systems find wide application in metal heat treating but have been largely displaced by other more cost-effective and reliable nitrogen generation technologies in other applications. In metal heat treating, inert gas generators are commonly called exothermic generators. Combustion products include controllable amounts of CO, H_2, CO_2, and water vapor, depending on the specific air–fuel gas input mixture. Excess water vapor and CO_2 can be removed through a refrigerant dryer and a molecular sieve adsorber, respectively. Two types of exothermic atmospheres, rich and lean, are commonly specified in heat treating applications. Rich exothermic gas contains 10–21% CO and H_2, and 5% CO_2, produced with a 6.5 to 1 air–fuel gas input ratio. Lean exothermic gas contains 1–4% CO and H_2, and 11% CO_2, produced with a 9.0 to 1 air–fuel gas input ratio (23). The balance of both atmospheres is nitrogen with a dew point of 40°C. These gas mixtures are commonly used for annealing ferrous and nonferrous materials where decarburization and brightness are not factors. Exothermic generators produce surplus heat which can be used to generate steam.

5. Shipment

Nitrogen is shipped and stored in gaseous form in steel cylinders under high pressure and in liquid form in vacuum-insulated containers. Because of the weight of high pressure storage vessels and the volatile nature of liquid nitrogen, most nitrogen is produced and consumed locally within a radius of less than 250 km. An exception is the large-scale distribution of nitrogen at moderate pressures (4000 kPa (600 psig)) in extensive pipeline networks serving the petrochemical and petroleum refining industries along the U.S. Gulf Coast of Texas and Louisiana, and serving the steel and chemical industries in northern France, the Benelux countries, and in the Chicago area in the United States. Nitrogen with oxygen is produced by numerous cryogenic air separation plants located along the pipeline networks (see CRYOGEMIC TECHNOLOGY). The U.S. Gulf Coast network is one of the world's longest with a total length of over 1200 km with 25 air separation plants supplying nitrogen and oxygen with a total capacity of over 20,000 t/d to over 70 companies.

Moderate quantities of nitrogen are shipped in liquid form in vacuum-insulated tanker trucks with typical capacities of 19 t liquid nitrogen (6200 gal) or 15,300 m^3 (580,000 SCF) when vaporized. The nitrogen is delivered to vacuum-insulated storage vessels at user sites with capacities ranging from 5,700 to 50,000 L (1,500 to 13,000 gal), containing from 3,700 to 31,500 m^3 (140,000 to 1,200,000 SCF) gaseous nitrogen upon vaporization. Liquid nitrogen is consumed directly from the vessels or gaseous nitrogen is produced as needed by vaporization in heat exchangers heated by free convection or forced ambient air, steam, or electricity. Heat leakage through the vessel insulation evaporates up to 0.5% of the vessel volume per day. Storage vessels are typically maintained at pressures up to 1700 kPa (250 psig) and pressure relief valves divert any excess pressure into the user's pipeline, eliminating loss of nitrogen to the atmosphere. Higher pressure liquid storage vessels (up to 4000 kPa (600 psig)) are available. Figure 5 shows a typical liquid nitrogen storage vessel and vaporizer.

Smaller quantities of liquid nitrogen are shipped in liquid cylinders, which are pressurized stainless steel vacuum-insulated containers with capacities of 160–180 L of liquid nitrogen, producing 100–120 m^3 (3800–4600 SCF) gaseous nitrogen when vaporized. Moderate quantities of high pressure gaseous nitrogen are shipped in tube trailers, which contain a number of horizontal steel cylinders the length of a truck trailer. Tube trailers contain from 1160 to 3860 m^3 (44,000–147,000 SCF) gaseous nitrogen at a pressure of 18,200 kPa (2640 psig). Very small quantities of gaseous nitrogen are shipped in individual steel cylinders ranging in capacity from 0.5 to 13 m^3 (20 to 490 SCF) at pressures from 18,200 to 41,400 kPa (2640–6000 psig).

6. Economic Aspects

In 2003, the United States remained the world's second largest producer of elemental and fixed types of nitrogen. China was first (4).

Total nitrogen gas produced in 2003 was $937{,}856 \times 10^6$ ft^3 and $860{,}262 \times 10^6 ft^3$ was shipped. The value of his shipment was ca $\$1{,}405 \times 10^6$. The quantity produced and consumed in plants was $9{,}803 \times 10^6$ ft^3. In 2003, liquid produced for merchant shipment was $280{,}035 \times 10^6$ ft^3; consumption in same plant was $11{,}235 \times 10^6$ ft^3, total for other shipments was 31,046 ft^3 (24).

Nitrogen solutions are used exclusively for nitrogen fertilizer materials. There is little or no industrial market. Nitrogen fertilizer use is largely confined to the countries that have highly developed agricultural economies. Although nitrogen solutions account for 5.5% of the world's nitrogen fertilizer market, they account for 30–35% of the market in the United States. World nitrogen solution production in 2001 was about 4.6×10^6 t with an estimate fob value of $\$2 \times 10^9$ (25).

World consumption of nitrogen solutions has been fluctuating around 5×10^6 t (of nitrogen) per year. A cyclical decline began in the United States in the period 1999–2001. A moderate upward growth is expected, however, in the forecast to 2007, resulting in a recovery to the highest consumption level of the past decade (25).

7. Specifications, Standards, and Quality Control

In the United States, the Compressed Gas Association lists nine grades of nitrogen, differentiated by oxygen content, dew point, total hydrocarbon content, and other contaminant levels (26). These grades, more often specified in government than commercial contracts, are shown in Table 3. Commercial cryogenically produced liquid nitrogen usually meets or exceeds Type II, Grade L. Higher purity Class II liquid nitrogen meets Type II, Grade M specifications. Commercially available compressed gaseous nitrogen, always produced from vaporized liquid nitrogen, usually meets or exceeds Type II, Grade L requirements. There are several specialty grades of compressed nitrogen typically available, eg, zero-grade which contains <0.2 ppm total hydrocarbons and a minimum nitrogen purity of 99.995%, ultra high purity (UHP) which contains <1 ppm water and a minimum nitrogen purity of 99.999%, oxygen-free which contains <0.5 ppm oxygen and a minimum nitrogen purity of 99.995%, and pre-purified which contains a minimum nitrogen purity of 99.998%.

8. Health and Safety Factors

Gaseous nitrogen is nontoxic and nonflammable but does not support life. Nitrogen should be stored and used only in well-ventilated areas. Special care must be taken entering an enclosed area which may be enriched in nitrogen. Deaths occur every year when personnel enter confined spaces in which nitrogen has displaced oxygen. Portable air packs or an air-fed mask must be used when working in an area with oxygen content below 19.5% by volume. Oxygen level analyzers with low level alarms should be used whenever the possibility of an oxygen-deficient atmosphere exists.

In high concentrations it is a simple asphyxiant. The release of nitrogen from solution in the blood is the cause of most of the symptoms and changes found in compressed air illness (caisson disease). It is a narcotic at high concentration and high pressure (27).

Liquid nitrogen and its vapor are extremely cold and can rapidly freeze human tissue. Liquid nitrogen spills should be flushed with water to accelerate evaporation. When exposed to liquid nitrogen, carbon steel, rubber, and plastic become embrittled and may fracture under stress. Copper, brass, bronze, Monel, aluminum, and 300 series austenitic stainless steels remain ductile and are acceptable for cryogenic service. Liquid nitrogen in poorly insulated containers can concentrate and condense atmospheric oxygen on the exterior surfaces which may cause a serious fire hazard. One volume of liquid nitrogen produces 696.5 volumes of gaseous nitrogen at atmospheric pressure and room temperature so extreme pressures can be generated if liquid nitrogen vaporizes in a confined space. Storage vessels or handling equipment should be provided with multiple pressure relief devices to prevent the buildup of high pressure. A pressure relief valve for primary protection and a frangible disk for secondary protection are commonly provided on commercial liquid nitrogen storage vessels (28).

9. Uses

Applications for nitrogen are widespread in both its gaseous and liquid phases. Gaseous nitrogen is usually used as an inert blanketing or carrier gas. Liquid nitrogen is used as an expendable nonreactive, nontoxic refrigerant. Very few applications, excepting the large-scale synthesis of ammonia from atmospheric nitrogen, use nitrogen as a reactant.

9.1. Chemical Process Industry. Gaseous nitrogen is used extensively in the chemical process industry as a blanketing, inerting, or purging agent to prevent oxidation of sensitive materials or to prevent the formation of an explosive mixture. Chemical storage tanks are frequently maintained under a slight positive pressure of nitrogen. During withdrawal of product from the storage tank, nitrogen is injected into the tank to maintain headspace pressure; during filling of the storage tank, nitrogen is vented from the tank to atmosphere, a flare system, or a solvent recovery system. Process vessels, piping, and storage vessels are purged with nitrogen to remove oxygen or control reactant levels. Purging is performed by one of three methods, ie, displacement, pressurization, or dilution. Displacement purging is often used to purge piping systems. The volume of nitrogen required corresponds to the volume of the pipe. Pressurization purging involves the repeated pressurization with nitrogen and venting of a vessel to remove the contaminant. Dilution purging assumes complete mixing of the vessel contents and the injected nitrogen, and the contaminant concentration is slowly reduced through time.

For blanketing flammable liquids or solids, considerable oxygen concentrations can be tolerated in the blanketing nitrogen without risk of formation of an explosive mixture. Table 4 shows the maximum permissible oxygen levels in nitrogen that can be used to blanket a number of common substances (29). Noncryogenically produced nitrogen is often used in such applications because of its economy and residual oxygen content (30).

Much nitrogen is utilized during polymerization operations where oxygen is a polymerization inhibitor. Nitrogen is often used for the pressure transfer of hazardous or flammable liquids and as a drying agent for oxidation-sensitive materials such as nylon resins and fibers (see DRYING). Nitrogen is used to agitate and deoxygenate liquids and solid–liquid mixtures. It is also used as a carrier gas for other reactants such as oxygen in the regeneration of spent reforming catalyst in petroleum (qv) refining. Nitrogen is used as a blowing agent in foamed plastic production and in blow molding of plastic containers. It can be used as a stripping agent to remove volatile organic compounds from process wastewater.

Liquid nitrogen is used in cold traps to remove and recover solvents or volatile organic compounds from gas streams to reduce atmospheric emissions. Liquid nitrogen can be used to accelerate the cooldown time for process reactors (31).

9.2. Food Industry. Large volumes of liquid nitrogen are used in the food industry for cryogenic freezing, where it competes with liquid carbon dioxide and mechanical freezing technologies. Cryogenic freezing of frozen foods reduces cell damage which results in reduced thawed product quality. By freezing the food very rapidly, inter- and intracellular ice crystal growth is minimized, avoiding rupture and damage of the cell walls of the food product. Concentration of water-soluble components between ice crystals during the freezing process is also reduced. Both effects reduce syneresis or drip loss due to release of cellular fluid, an effect which adversely impacts the texture, flavor, aroma, and nutritional value of the thawed product. Cryogenic freezing also reduces dehydration during the freezing process.

Types of cryogenic freezers include immersion freezers, in which the product is fed by conveyor belt directly through a bath of liquid nitrogen; in-line freezers, in which liquid nitrogen is sprayed onto the product traveling on a belt; and spiral freezers, in which an annular liquid nitrogen spray freezes the food product traveling on a space-conserving spiral conveyor. Immersion freezers provide the fastest freezing rates, at greater than 1000°C/min, but only utilize the latent heat of vaporization of liquid nitrogen. Efficiencies are less than 50% versus in-line freezers which use the additional cooling effect of vaporized nitrogen and have efficiencies approaching 90%. However, the capital cost of an immersion freezer is much less than that for in-line or spiral freezers (32). Liquid nitrogen consumption in food freezing applications is in the range of 1.0 to 2.0 kg/kg of product (33). Actual consumption is influenced by product and process variables.

Liquid nitrogen also finds application in pressurizing aluminum and plastic food and noncarbonated beverage cans and bottles. Several drops of liquid nitrogen are injected into the can or bottle prior to sealing. After sealing, the nitrogen vaporizes to provide internal pressurization which provides sidewall strength and allows the use of very thin sidewall materials. Nitrogen consumption is in the range of 0.12 to 0.25 g per can or bottle (34,35).

Other uses for liquid nitrogen include batch chilling of meat products and cookie dough, and cooling flour and sugar during warm season processing.

Gaseous nitrogen is used in controlled and modified atmosphere food storage and packaging to maintain the quality of fresh fruits and vegetables by retarding oxygen-dependent ripening and decay processes. Controlled atmospheres are extensively used in the storage of apples and pears to allow extended storage prior to sale without significant quality degradation. Controlled atmosphere storage rooms for apples and pears are typically maintained at 98–99% nitrogen concentrations with balance controlled amounts of oxygen and carbon dioxide. Nitrogen can be provided from vaporized liquid nitrogen, noncryogenic generators, or combustion-based generators.

Modified atmospheres that predominantly contain nitrogen are increasingly used in the packaging of fresh pasta, Nuts (qv), potato chips, dry goods (such as coffee), breads, and prepared salads to extend shelf-life.

9.3. Primary Metallurgy and Heat Treatment. In ferrous metallurgy (qv), nitrogen is typically provided by pipeline as a coproduct with oxygen to steel producing facilities for use as a scavenging, stirring, and inert blanketing gas during steel processing and casting operations. Nitrogen can be used to replace more expensive argon in the argon–oxygen decarburization (AOD) process during the manufacture of austenitic stainless steels. In nonferrous metallurgy, nitrogen finds application in degassing of aluminum melts to remove hydrogen and reduce oxide formation. Nitrogen is used to shroud and cool aluminum extrusion dies to reduce surface oxidation and increase die life. The use of PSA nitrogen generators in this application has been reported (36).

In most heat treatment processes for metal fabricated parts, nitrogen serves as a nonreactive, passive constituent of the furnace atmosphere. It can be used alone for the annealing of aluminum, copper, and some low carbon steels. Most often it is used in combination with other gases such as H_2 and CO to produce reactive atmospheres for sintering, carburizing, and carbonitriding ferrous parts. Nitrogen reacts with some stainless steels and cannot be used in their heat treatment. At high temperatures, atomic nitrogen combines with iron to form finely divided nitrides, producing a hardened nitrided or carbonitrided surface layer (37).

9.4. Electronics Manufacturing. In the manufacture of semiconductors, gaseous nitrogen is used in the largest quantity of any gas as an inert carrier in epitaxy and diffusion processes, ion implantation, chemical vapor deposition, annealing, and plasma etching. Nitrogen purity requirements are extremely rigorous, reaching 1 ppb contaminant levels. On-site cryogenic nitrogen plants are often used as the supply mode. If delivered liquid nitrogen is used, careful purging of transfer lines is required to maintain purity. Facility piping is usually electropolished stainless steel.

In electronic component assembly operations, standard purity nitrogen finds uses in atmospheres for wave soldering and infrared reflow soldering machines. This application has grown because manufacturers are converting soldering operations from older technologies, that required post-cleaning with chlorofluorocarbons, to no-clean technologies, that require nitrogen atmospheres. Nitrogen is also used extensively in various utility applications such as dry box storage of work-in-process components, blanketing of process chemicals, burn-in oven atmospheres, and nitrogen-driven pneumatic tools.

9.5. Oil and Natural Gas Production. Nitrogen is used in oil and natural gas well completion and stimulation applications as well as oil and natural gas enhanced recovery. Applications in well completion and stimulation include use as a foaming agent for fracturing, acidizing, cementing, and gravel packing fluids. Nitrogen up to 95% by volume is used in these fluids to reduce density and hydrostatic gradient in the wells, thereby reducing the amount of energy required to return the fluid to the surface after the operation (38). Nitrogen for these applications historically has been delivered in liquid form by tanker truck and vaporized on-site. In the 1990s, portable on-site membrane generators had begun to find application.

Nitrogen is used for pressure maintenance in oil and gas reservoirs for enhanced recovery. It is sometimes used as a miscible agent to reduce oil viscosity and increase recovery in deep reservoirs. Other applications include recovery of oil in attic formations, gas cap displacement, and a sweep gas for miscible CO_2 slugs. Nitrogen competes with CO_2, a more miscible gas with hydrocarbons (qv), in most of these applications. The production mode is typically by on-site cryogenic separation plants.

Two applications well suited to noncryogenic nitrogen production technologies include the replacement of cushion gas with nitrogen in underground natural gas storage reservoirs, pioneered by Gaz de France (39,40), and the use of nitrogen to displace natural gas in underground coal seams (41).

9.6. Other Applications. Other applications for gaseous nitrogen include use as a blanketing agent for float glass manufacture, pressurizing agent in aerosols, inflation agent in aircraft tires and landing struts, purging agent for electrical cabinets, and pressurization agent for autoclaves used in the production of composite materials (42).

A significant application for liquid nitrogen is the cryogenic grinding of plastic or heat-sensitive materials. Plastic materials become brittle at cryogenic temperatures enabling easier grinding or deflashing operations. Cryogenic grinding is performed on both thermoplastic and thermosetting resins, old rubber tires for recycling, spices, coffee, coloring agents and pigments (qv), and wax.

Other liquid nitrogen applications include freezing biological specimens such as livestock semen and whole blood, cryosurgery, shrink fitting metal parts, and paint removal. Liquid nitrogen can be used for ground freezing to allow excavation in unstable wet soils (43), freeze plugging pipe sections to allow repairs while the rest of the pipeline remains pressurized (44), and cooling concrete in hot weather (45).

Uses for nitrogen described in current patent literature include in phase changeable memory devices (46), a nitrogen injection assembly for use in optical fiber coloring and curing (47), and nitrogen blow molding to enhance oxygen scavenger shelf life (48).

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Table 1. **Physical Properties of Molecular Nitrogen**

Property	Value
molecular weight	28.0134
N−N bond length, pm	109.8
first ionization energy, eV	15.58
critical point	
T_{crit}, K	126.2
P_{crit}, MPa[a]	3.39908
Q_{crit}, g/L	314.03
boiling point,[b] K	77.35
weight of liquid at boiling point,[b] kg/m^3	808.5
heat of vaporization, kJ/kg[c]	199
triple point	
T, K	63.15
P, kPa[a]	12.463
Q_g, Q_l, Q_s, g/L	0.6803, 867.7, 947
heat of fusion, kJ/kg[c]	25.8
Q,[d] g/L	1.2505
relative density (air)[d]	0.967
specific heat capacity,[d] J/(g·K)	1.039
dynamic viscosity,[d] mPa·s(=cP)	15.9×10^{-3}
thermal conductivity, mW/(m·K)	23.86
compressibility factor (PV/RT)	0.9995

[a] To convert MPa to psi, multiply by 145.

[b] At 101.3 kPa = 1 atm.

[c] To convert kJ to kcal, divide by 4.184.

[d] At 273.15 K and 101.3 kPa = 1 atm.

Table 2. **Physical Properties of Solid Molecular Nitrogen**

Form[a]	Temperature range, K	Crystal structure	Q, g/L	Vapor pressure, kPa[b]
β	35.6–63.15	hexagonal	948[c]	6.3[c]
α	0–35.6	cubic	1027[d]	1.47×10^{-11}[d]

[a] Heat of transformation (α–β): 228.9 kJ/mol (54.71 cal/mol).
[b] To convert kPa to mm Hg, multiply by 7.5.
[c] Measured at 60 K.
[d] Measured at 21.2 K.

Table 3. **Grades of Industrial Nitrogen**

Gaseous and liquid nitrogen	Nitrogen, min% (mol/mol)	Oxygen[a]	Water, ppm (v/v)	Dew point, °C	Total hydrocarbon content[a]
B[b]	99.0				
E[c]	99.5	0.5%	26	−63	58
F	99.9	0.1%	32	−60	
G	99.95	500	26	−63	
H[c]	99.99	50	11	−75	5
K	99.995	20	16	−70	
L	99.998	10	4	−90	
M	99.999	5	2	−100	5
Q[d]	99.999	1	2	−100	1

[a] Units in ppm (mol/mol) unless otherwise noted.
[b] 10 ppm CO.
[c] Type II <1.0 mg/L permanent particulates.
[d] 5 ppm each of Ar, Ne, He, and CO.

Table 4. **Maximum Permissible Oxygen Concentrations for Various Substances**[a]

Gas or vapor	Oxygen,%
methane	12
ethane	11
propane	11.5
ethylene	10
benzene	11.4
toluene	9.5
styrene	9.0
gasoline	12
acetone	11.5
carbon disulfide	5
hydrogen	5
methanol	10
dust	
soy flour	15
charcoal	17
aluminum	2
magnesium	0
sulfur	12
butadiene–styrene	13

[a] Percent of oxygen in nitrogen above which combustion can take place.

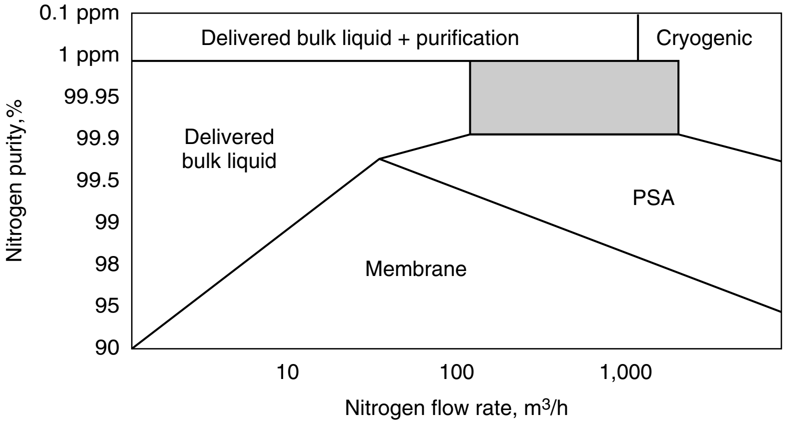

Fig. 1. Approximate economic range of nitrogen supply technologies (at median site conditions). Shaded area represents bulk liquid or PSA membrane plus deoxo or liquid assist cryogenic. To convert m^3/h to SCFH, multiply by 40.

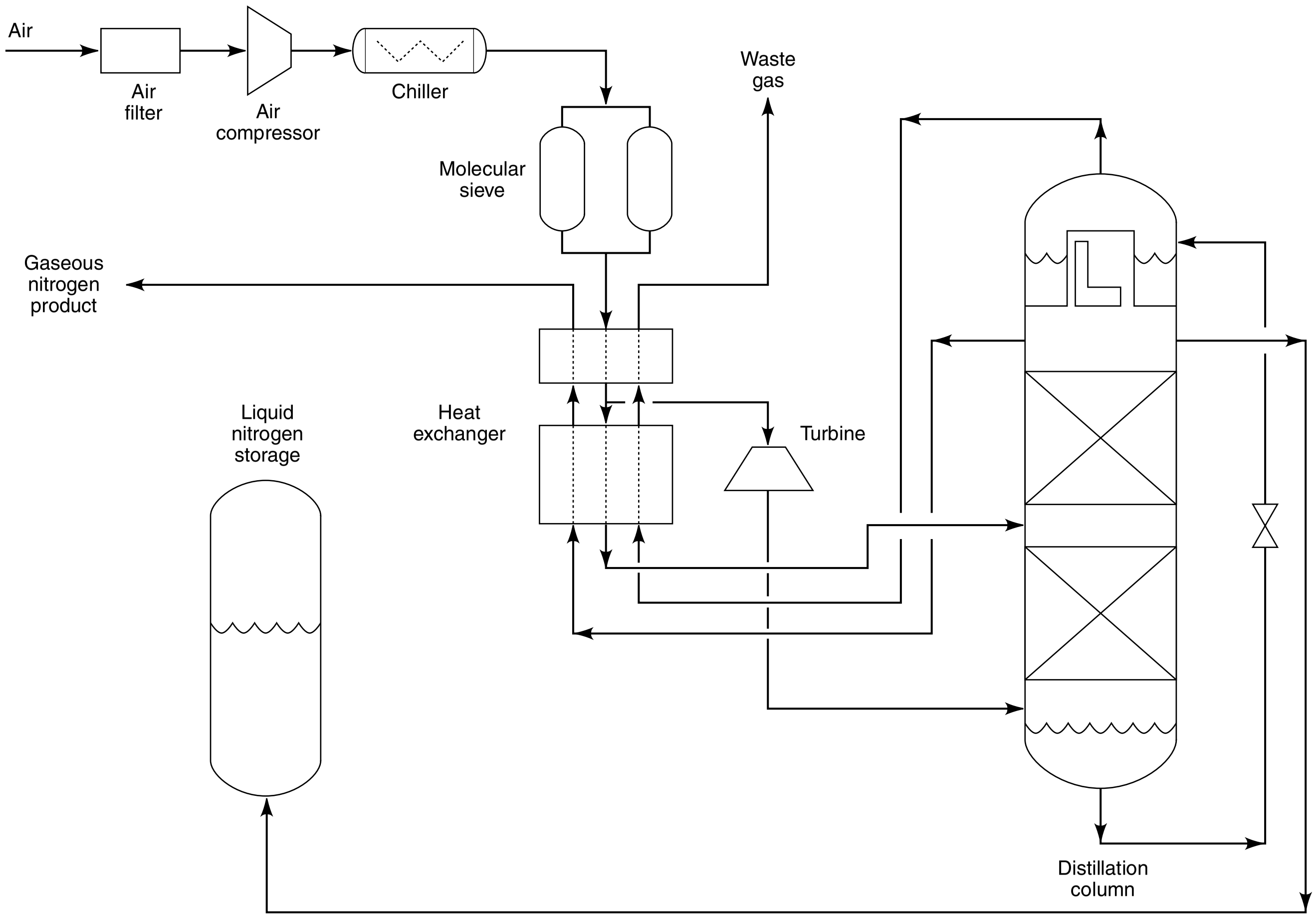

Fig. 2. Cryogenic nitrogen generation process.

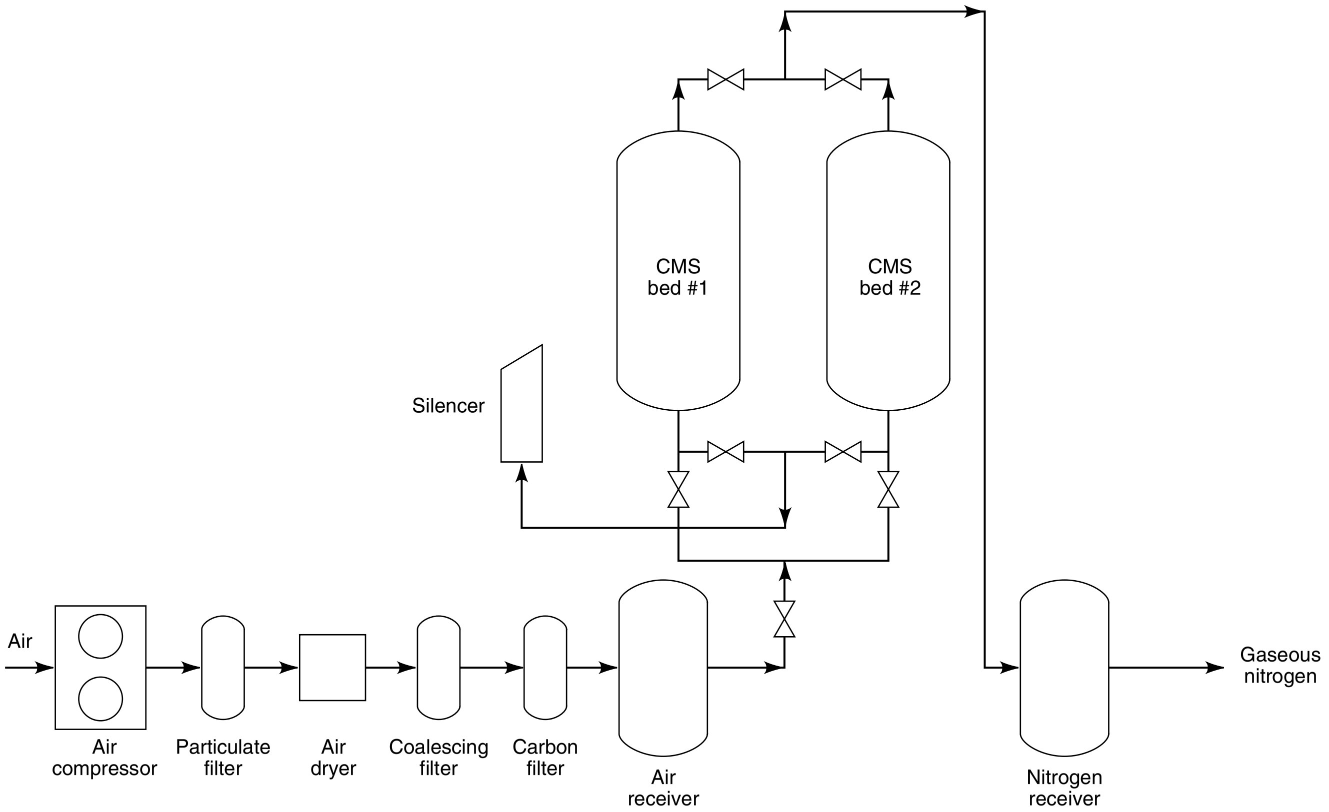

Fig. 3. Pressure swing adsorption nitrogen generation system. CMS = carbon molecular sieve.

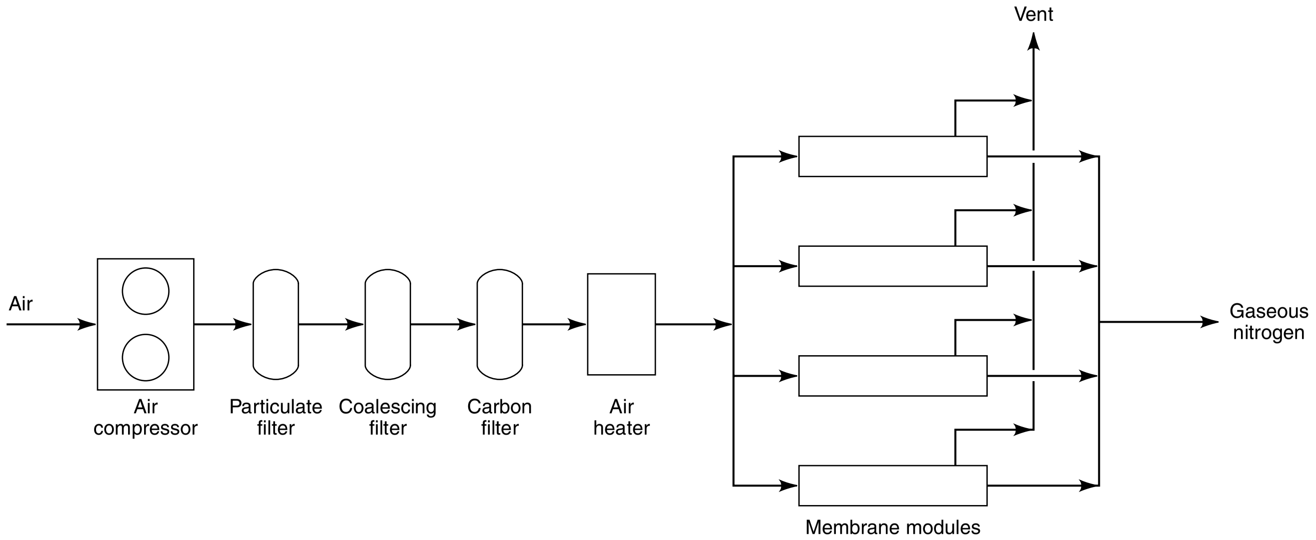

Fig. 4. Membrane permeation nitrogen generation system.

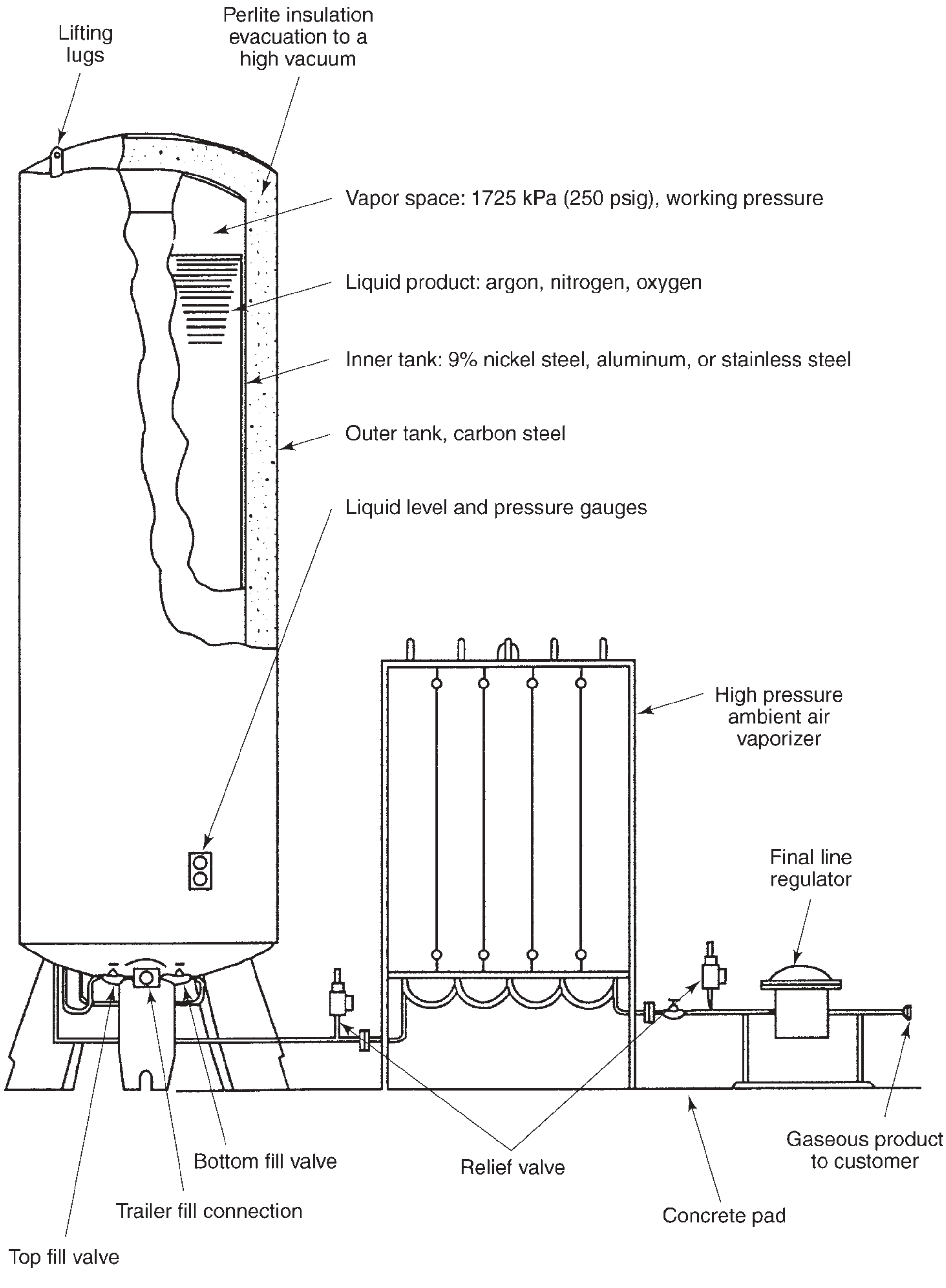

Fig. 5. Liquid nitrogen storage vessel and vaporizer.