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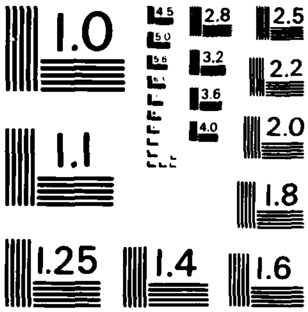

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# ON-BOARD OXYGEN AND NITROGEN GENERATION SYSTEMS FOR SURFACE VESSELS

PREPARED FOR
THE U.S NAVAL RESEARCH LABORATORY
WASHINGTON D.C. 20375
UNDER CONTRACT NO. N00014-81-C-2307

PREPARED BY
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320 NEEDHAM STREET
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| OXYGEN-GASEOUS | PRODUCT SAFETY ENGINEERING |
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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

Most ~~of the~~ Navy surface vessels are equipped with cryogenic (LOX and LN) storage-evaporator gas supply systems to produce oxygen and nitrogen for life support, flight service, and other system-applications. Increased mobility and independence of land-base logistic support requires new, on-board $O_2$ and $N_2$ generation systems, to be installed on existing and future Navy ships.

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This study summarizes existing industrial candidate systems, and overviews some new processes under development. ~~In-depth~~ analysis ~~has been~~ conducted on gaseous oxygen and nitrogen generation systems, of the most likely candidates, and particular attention was focused on molecular sieve gas separators.

The second part of this report concentrates on engineering design guidelines for constructions of on-board gas generators of confined scales. Safety, maintenance, and standard (industrial and MIL) requirements are summarized to help, construct, test, and evaluate a scaled prototype on-board $O_2/N_2$ generation system in the future.

The study ~~has~~ identified two types of presently available industrial gas generation systems suitable for confined on-board applications. However, significant modifications and development are necessary to meet filtration, protection and stress-prevention requirements.

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## 1. INTRODUCTION

In the modern technological weapons systems environment there is an ever increasing need for large capacity, reliable gaseous and liquid, nitrogen and oxygen supplies. Traditional cryogenic and chemical supply systems currently in use in Navy surface vessels may no longer be adequate to supply nitrogen and oxygen required for such applications as:

- Personnel life support systems
- Gas turbine starters
- Weapons systems
- Welding for maintenance and repair
- Medical oxygen

In addition to the increased volume demand, there are also special applications that require unusually high purity of the gases, e.g. fuel tank inerting, gas supply purging, pneumatic starters, etc. In addition to volume and purity, further requirements include:

- A necessity to eliminate or minimize land-base logistics and service support and to increase mission duration.
- Provide a more flexible, on-demand, automated on-board gas supply while minimizing the space and weight penalty.

For several applications, the new gas supply systems represent retrofits and there are prior space constraints.

The research reported here represents an overview of both current and state-of-the-art gas generation approaches. Specific attention is placed upon molecular sieve technology used to simultaneously generate high purity nitrogen and oxygen. A previous report examined the use of on-board cryogenic storage of oxygen for life support applications (1). The basic elements of the present report are outlined as follows:

- Review the range of technologies for gaseous and liquid oxygen generation and storage.
- Examine in detail the promising molecular sieve technology for use on surface vessels.
- Establish a set of design review criteria to aid in the selection of a "best" system.
- Outline requirements for a new, prototype gas generator for construction and evaluation purposes.

In establishing these requirements and criteria, a combination of military and industrial standards, as well as accepted engineering practices, was considered. As there are several alternate approaches advocated by different offerors, this survey seeks to be independent and generic in approach. While the guidelines and selection criteria are quantitative, there is no detailed description of any preferred or recommended system.

## 1.1 TECHNICAL SURVEY

According to recent statistics the annual commercial consumption of oxygen in the United States is approximately 20 million short tons. This figure is projected to increase, despite the decline in production by the steel industry - the single largest consumer to date.

Of this 20 million tons of oxygen production, 98% is generated by air separation methods, principally cryogenics; only 1-2% is produced by electrolysis or chemical methods.

Commercial requirements for oxygen include more than 10 major industrial sectors; among them are steel and oil production, environmental protection, and high technology and space applications.

More recently, the requirement for nitrogen has dramatically increased to more than 9 million short tons, annually. Major applications include chemical processing, electronic fabrication and aerospace engineering.

The increased demand for both oxygen and nitrogen, coupled with additional constraints imposed by the newer applications, has led to the development of alternate or modified technologies for oxygen/nitrogen production. Among the new constraints are included:

(a) Wide range of volumes ranging from microliters/day to thousands of tons/day.

(b) Availability in both gaseous and liquid form.

(c) Local production capability to offset increasing transportation costs or logistics constraints.

The developing technologies, or new combinations of old technologies, offer favorable alternatives for non-commercial applications, e.g. military. Often these military applications for both nitrogen and oxygen have severe space and/or weight restrictions, coupled with demanding reliability requirements. Obviously, failure of an on-site production capability could negate the mission of an aircraft, submarine or surface vessel with subsequent dire consequences. The specifications and selection of a system configuration is therefore of major concern.

A further consideration is the issue of safety; in addition to the possibilities of accidents induced by a hostile environment, the record shows an inordinately high number of accidents caused by human error. Design and operational criteria should seek to minimize these occurrences.

Therefore, any new or revised technology must be applied carefully, and an in-depth analysis performed to obviate potential errors. In particular, when a nitrogen/oxygen system is to be incorporated into an integrated complex of an aircraft or ship system, design activity must involve consideration of non-related, but co-located systems or subsystems.

This new generation of gas production systems will offer many options to future consumers, but those who wish hardware on a short time frame will likely be forced to utilize a variation or modification of a less innovative technology. For the retrofitting or new engineering into a vessel with an already established footprint, this modification/variation approach is most likely. Nonetheless, a detailed design review is necessary.

## 2.0 OVERVIEW OF OXYGEN AND NITROGEN GENERATION PROCEDURES

### 2.1 CRYOGENIC TECHNOLOGY

The most commonly used industrial process for the generation of nitrogen and oxygen from air has been cryogenic liquification and subsequent separation distillation. In spite of the relative complexity of equipment and high operating costs, it is still the method of choice for large scale operations.

The technical processes are based upon the Joule-Thompson isenthalpic expansion of a compressed gas, i.e. an adiabatic isentropic expansion of a compressed gas in a reciprocating or a turbine engine. A typical system consists of a filter-air compressor-cooler unit. Utilizing dry air, the system also contains heat exchangers and distillation columns and operates at approximately $90^{o}K$. By liquifying and distilling in a double column, the air is separated into components. The heat exchangers perform the dual role of (1) conserving plant refrigeration by discharging products at near ambient temperatures, and (2) removing moisture and $CO_2$.

The refrigeration unit is usually a turboexpander or a "Stirling" unit with a high efficiency (70-85%) using the cold feed air as a working fluid. The energy requirements for a cryogenic system are dictated primarily by the power needs of the compressor unit. The theoretical relationship between compressor work input and heat transfer to the refrigerant is given by:

$$\left(\frac{W}{Q}\right)_c = \frac{RT_1 \ln(P_1/P_5)}{M(H_4-H_3)}$$

where M is the molecular weight of air, H is the enthalpy of air between the temperatures $T_4$ and $T_3$, Q is the heat absorbed, and $P_1/P_5$ is the pressure ratio during the cycle. A schematic of a cryogenic system with liquid oxygen storage/vaporization is shown in Figure 1. Cryogenic plants are capable of delivering wide ranges of oxygen and nitrogen varying from two to two thousand tons per day. Normal pressure requirements are in the 70-80 psig range. Typical speeds of the turboexpander range from 25,000 to 400,000 RPM depending upon size.

Simple in concept, commercial units are complex and not free of operational, maintenance, and safety problems. A summary of potential hazards, covering both liquid and gaseous phases of $O_2$ and $N_2$, is presented in Appendix A.

In addition to these safety considerations and the constraints of size and weight, there are two generic recommendations for improvement for prospective cryogenic systems considered for shipboard use: cryogenic tank support and turboexpander bearings.

A. Cryogenic Tank Support System: Land-based cryogenic systems are designed for operation under readily predictable thermal and mechanical stresses. A travelling or shipboard unit, however, would be subject to additional vibration and shock loads. Modification to the solid tank support would be required to isolate the unit from these vibrations and loads. A combination of swing links between the tank and main frame with spherical bearings would allow the tank to free float about two axes and isolate the tank from these loads and vibrations. The main elements of such a modification are shown in Figure 2.

B. Turboexpander Bearings: The single most critical element in a cryogenic system is the turboexpander, and any malfunction results in immediate system shutdown. At present, turboexpander bearings are lubricated with oils and feature a sophisticated lubrication and control system (see Figure 3). Recent technological developments now offer promising alternatives. The first is

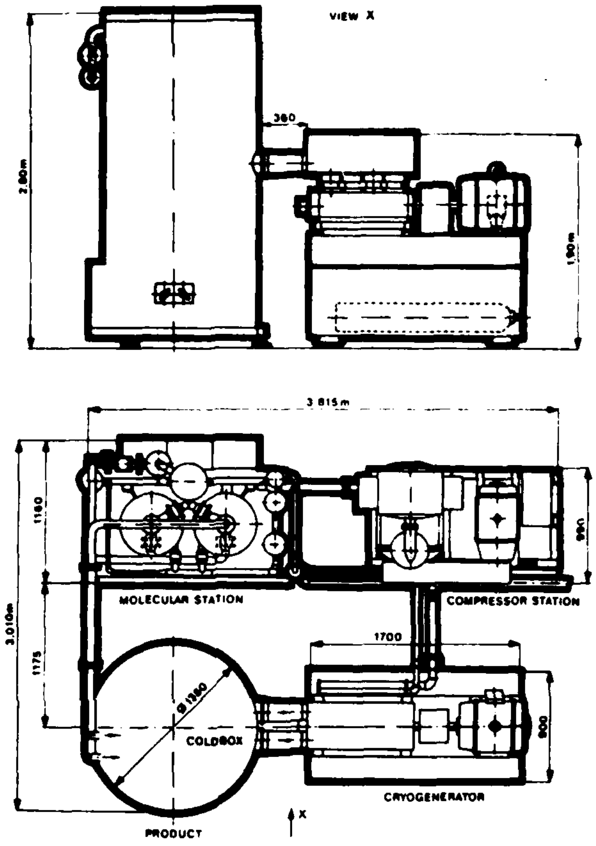


Figure 1. Schematic of a Cryogenic Oxygen Generator.

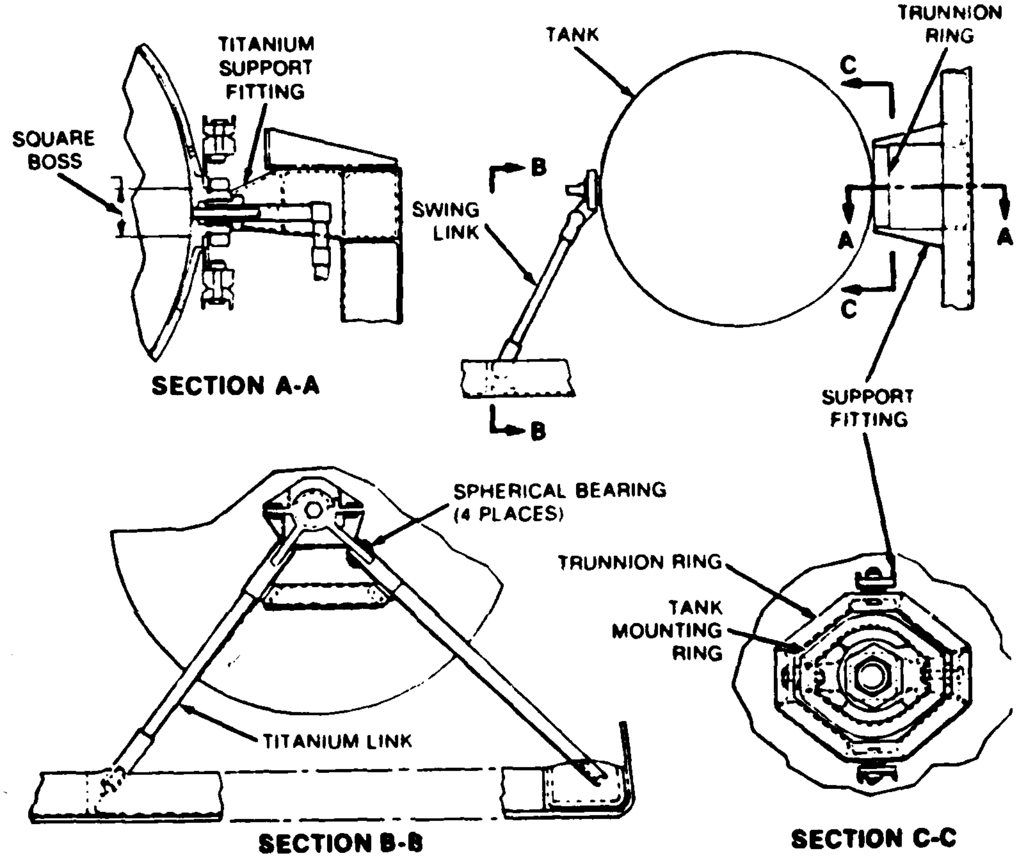
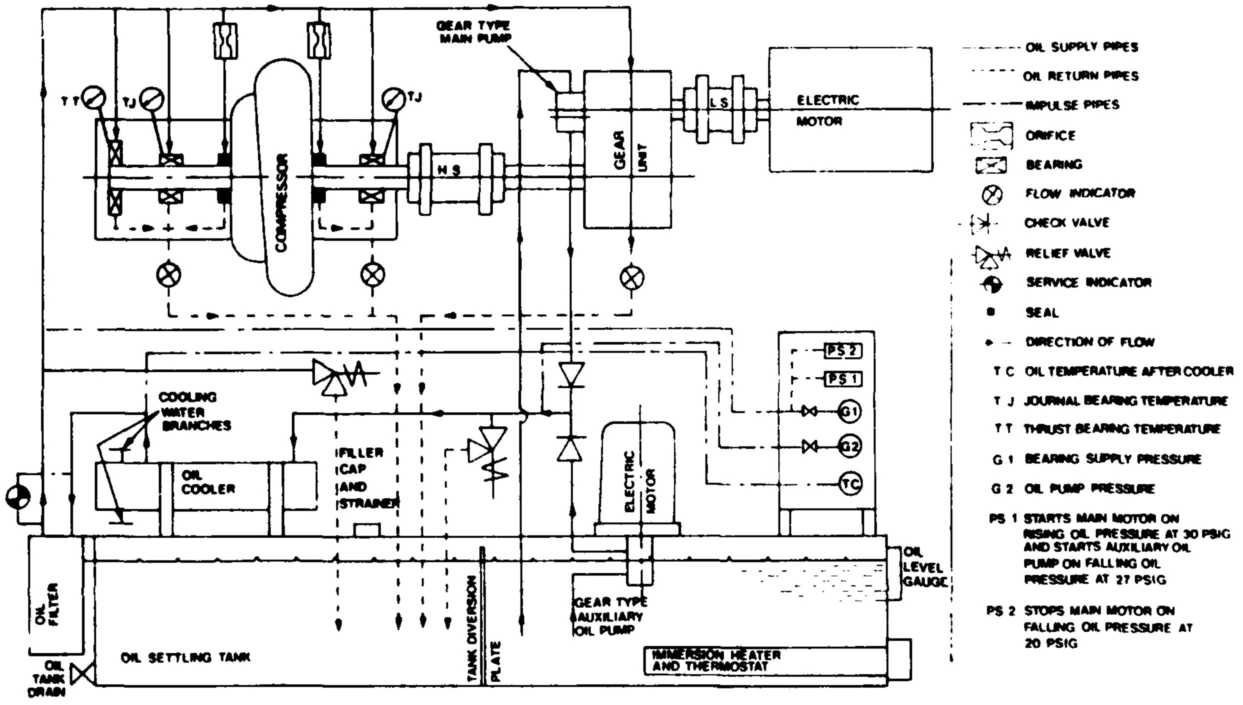


Figure 2. Cryogenic Tank Support System.



LUBRICATION DIAGRAM FOR S 50C TURBO BOOSTER

Figure 3. Lubrication and Control System for Turboexpander.

a well-tested foil air or gas bearing system, eliminating oil lubrication, its control system, and the latter's inherent maintenance requirements. Foil air and gas bearings are further unaffected by power shutdowns, a major problem for cryogenic systems with liquid lubricants. A typical design for a foil air bearing is shown in Figure 4. A second alternative, under development by the aerospace community, utilizes a flexible bearing support to relax axial deformation of a roller bearing unit. This has the effect of extending the lifetime of the bearing and decreases the risk of failure caused by fluctuating loads.

## 2.2 CHEMICAL AND ELECTROCHEMICAL PROCESSES

Utilization of cryogenic oxygen and nitrogen production methods for aircraft and shipboard applications has long been recognized as a potential source of operational and support problems. For this reason, several small scale chemical and electrochemical concepts have been developed under several joint Navy/Air Force efforts for use on aircraft, undersea vehicles, and spacecraft. These systems fall into five main categories:

(A) Generation by alkali-metal halates

(B) Reversible Barium oxide-dioxide concept (Brin process)

(C) Water electrolysis (Hoffman process)

(D) Fluomine sorbent process

(E) Electrochemical concentrator process

Process A, the use of chlorate candles, is currently utilized to generate breathing air in submarine vehicles. This process is generally considered as impractical for generating oxygen for any other use. Likewise, the Brin process (B) has been rejected by the Navy (2).

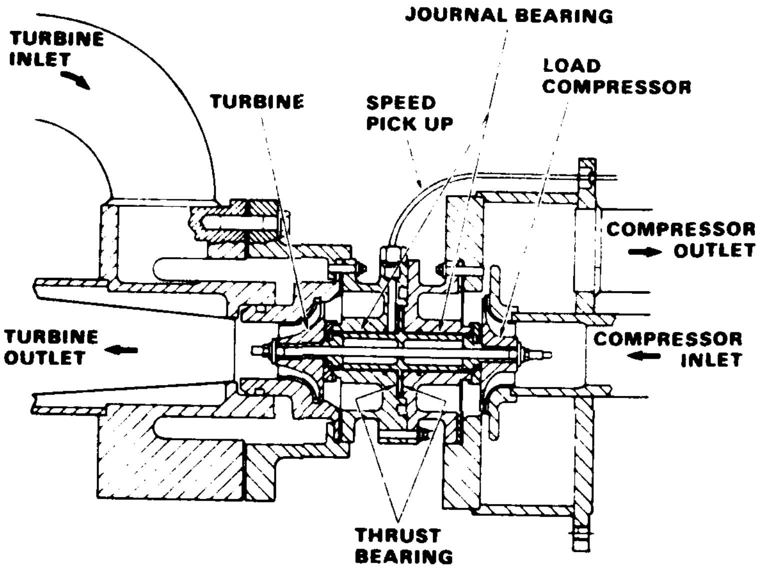


Figure 4. Foil Air Bearing.

While the Hoffman (C) process is widely used in the chemical industry for photoelectric processing, metal recovery, electroplating, etc., it has several disadvantages for other applications. Among these are:

- Large electrical energy requirements
- Low production rates
- Continuous operation required

As a result of long term research and development efforts, the fluomine sorbent process (D) has been utilized in aircraft. The process, which is illustrated in Figure 5, is based on the capability of a cobalt chelate (fluomine) to adsorb oxygen on a basis of 1 molecule per two atoms of cobalt. The process requires 1.1 kw electrical power to produce 1.0 lb/hr oxygen (pressurized at 1800 psig).

Figure 6 shows a typical fluomine sorbent oxygen generating system. The laser energy requirements inherent in the system, and resultant large size, make it impractical for large scale operations. It is feasible as an additional shipboard life support device, but will still need refining, even after more than ten years of development.

The electrochemical oxygen concentrator process (E) should also not be considered for large scale utilization for two reasons:

- Extremely low oxygen productivity rate compared to electrical power consumption (0.7 lb/hr oxygen for 7.0 kw electricity).
- High external heat loads produced by the system result in severe environmental problems.

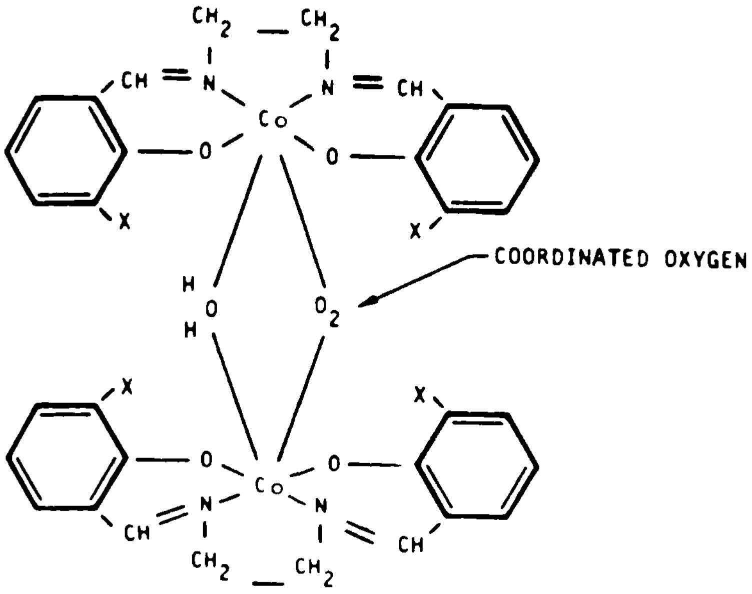


Figure 5. Metallic Fluomine.

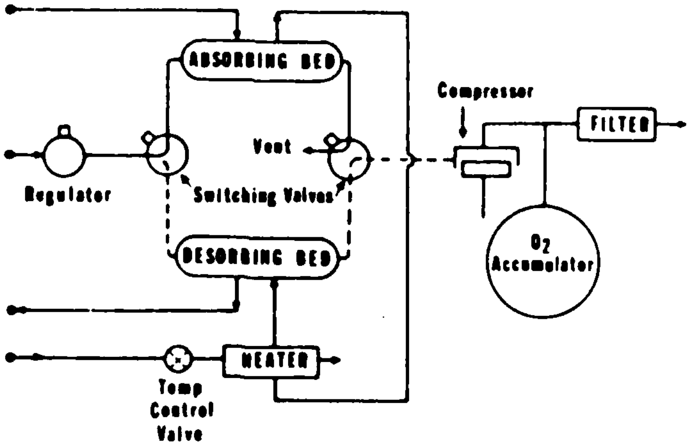


Figure 6. Schematic of a Fluomine Sorbent Oxygen Generating Process.

## 2.3 COMPONENT SEPARATION OF GASEOUS AIR

New technologies have been adopted from the fields of chemical and biochemical separation techniques to produce oxygen and nitrogen from ambient air. These technologies are based on (a) molecular, or particle separation capabilities of thin film membranes, or (b) crystalline structures of certain materials. The latter are utilized as molecular sieves. Both techniques are very promising for various sizes of gas separation/generation plants. However, they will require further research and development to be competitive in volume and reliability with cryogenic technologies.

### A. LIQUID MEMBRANE TECHNOLOGY

The membrane separation process is generally a type of microfiltration, combined with a capability of a molecular-sized reaction vessel and ion exchanger. Utilization of membrane filters varies from microfiltration to separation of metal particles from solutions. The largest volume applications are presently used in water desalinization plants, ranging from $10^5$ gallons/day to $3 \times 10^6$ gallons/day. A new oxygen-carrier system is under development, with liquid membranes capable of producing oxygen gas of 85% purity. In earlier systems, a liquid semi-permeable membrane could provide only 30-35% purity oxygen, or enrich the oxygen in breathing air to that level.

The new oxygen-carrier liquid membrane system is a promising candidate for future $O_2$ generators. The system is illustrated in Figure 7. The structure consists of multilayer composites, with a combination of a semi-permeable membranes (selective layer) and a supporting layer. They are produced in flat sheets, or in hollow fiber forms of polymers (polyphenil oxide-phosphonate ester, polysulphur, acrylonitrile). Depending on the application, the supply pressure can vary from atmospheric up to 900 psi.

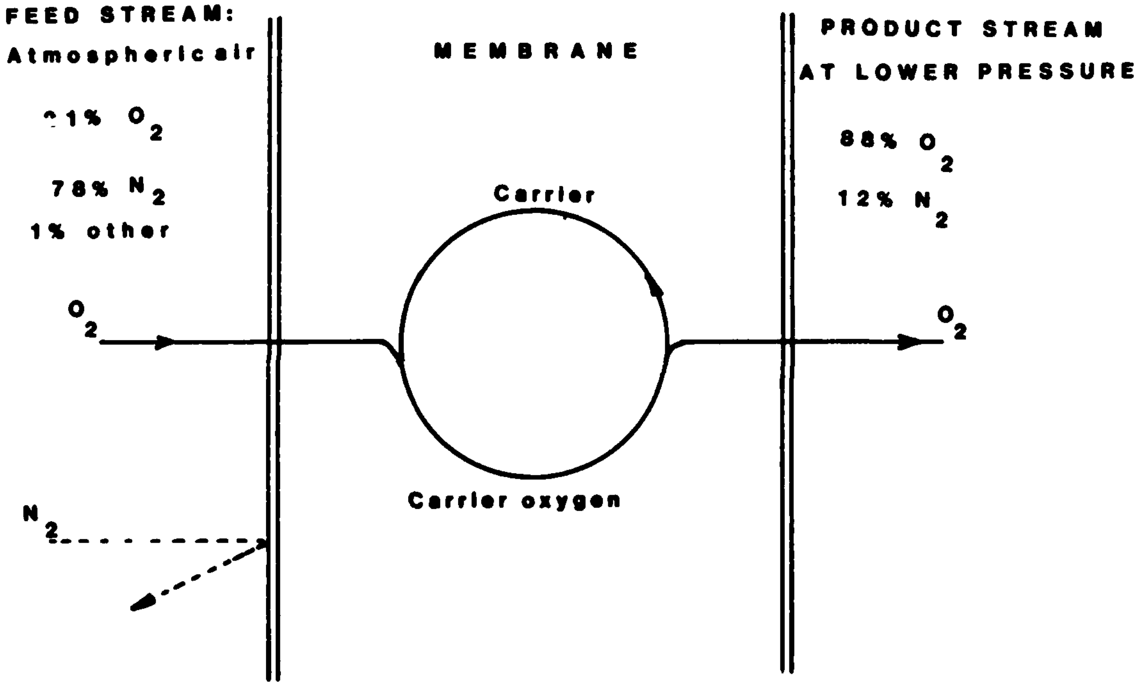


Figure 7. Theory of Operation of Liquid Membrane, Producing Oxygen from Air.

## B. MOLECULAR SIEVES

The newest industrialized methods in oxygen and nitrogen generation have originated from catalytic and filtration science. Separation of air components (oxygen, nitrogen, argon, water vapor, etc.) via molecular sieve became possible after the discovery of certain physical and chemical properties of natural and (later) synthetic materials. More specifically, their physical structure and special electro-static and Van Der Walls forces enable these materials to perform a controlled adsorption and desorption procedure.

For $O_2$ and $N_2$ production and purification purposes, there are two types of materials presently used in industrial applications of various sizes:

- Carbon based materials (carbo-gel, carbonex)
- Framework silicates: Zeolites (e.g. Na-Al silicates)

In both cases, pressurized air (20-100 psi depending on the application) is forced through a molecular sieve bed, where the crystalline structure of the sieve material, combined with ion exchange will adsorb one component (e.g. oxygen), retain it in its molecular cavities, allowing the other component (e.g. nitrogen) to flow through. At this point, either fresh air or a purge gas can be flowed through the bed in the reverse direction, to extract the retained gas from the molecular sieve by a desorption process. This process regenerates the bed at the same time.

Other gas separation procedures, such as those used in catalytic industries, are <u>excluded</u> from this study. These require extensive heat (e.g. chemical adsorption via palladium/Ni-Ca converters) or external energy supply (e.g. burning <u>LNG</u> to produce nitrogen). Such systems are impractical for any mobile design-concept for shipboard production of oxygen or nitrogen.

## B.1 CARBON-BASED MOLECULAR SIEVES

Carbon materials are widely used for gas and liquid filtration, disinfection, and purification. The carbon-based molecular sieve has been developed from filter/purification systems to improve oxygen purity or breathing air clarity for life-support equipment. In addition, a carbon-based dryer/filter unit has been designed for elimination of air contamination and water vapor from air.

To overcome certain limitations of a simple granular charcoal filter, new procedures have been developed and tested (3). The essence of this new type of filter is a fine charcoal particle covered with a thin layer of silica (carbo-gel) gel. During this development work, different types of silica gel, sodium silicate, and hydrogen chloride combinations were tested, finally resulting in a semi-solid filter-sieve structure with improved filtration performance as compared to conventional charcoal. In spite of some difficulties, this effort represents an improved test base for carbon molecular sieves, utilizing materials such as MCB SC 144 L 1083 silica gel and Barneby-Cheny AC and MI type charcoal.

Large scale production of a solid, durable carbon molecular sieve became possible by changing the molding structure to support carbon molecules. This modification was required because the "carbo-gel" procedure resulted in a statically strong, but dynamically fragile filter media (after mixing and drying). This type of newly developed carbon molecular sieve can be used to form any desired size of molecular cage of charcoal-purity carbon and a supporting polymer-type frame.

In this molecular carbon sieve, not only the inter-molecular distance is an important factor, but also the position of localized molecular orbitals. In the case of this new carbon sieve system, a typical physical adsorption process takes place as a result of forces between the solid surface and the adsorbate (in this case oxygen) molecules, which are similar to Van Der Walls forces between molecules. The energy of adsorption ranges from 8 x $10^{-2}$ to 1 x $10^{-3}$ cal/mol. Another important factor is that high pressure can be used to increase adsorption on the surface of the sieve. Since physical adsorption is generally reversible, by decreasing the pressure the adsorbed gas will be released from the structure of the molecular sieve. The energy required will follow the same isothermal curve as during adsorption (Figure 8). This method (carbon structure) has a better efficiency than other high temperature sieves. Another advantage is the homogeneous structure of the adsorption bed, allowing only a 33-35% pressure drop across the system (110 psi inlet air, and 85-80 psi outlet nitrogen gas), which is a result of the moderate flow resistance of the bed.

Since the above discussion is based on a patent application from a scientific institution of an allied country, no further details can be published without authorization.

In Chapters 4 and 5, design and testing recommendations will cover this molecular sieve nitrogen production system as an alternative to cryogenic devices. Both carbon-type systems and the zeolite sieve discussed below will be considered.

### B.2 ZEOLITE MOLECULAR SIEVES

In various chemical industries, zeolites, in both natural, and now dominatively synthetic forms, are utilized as adsorbents, cracking catalysts, filters, and desiccants.

To characterize a growing use of these materials in industrial applications, it is sufficient to point out that 115 million pounds of zeolites are expected to be produced for the above purposes in 1985, in addition to 495 million pounds production for

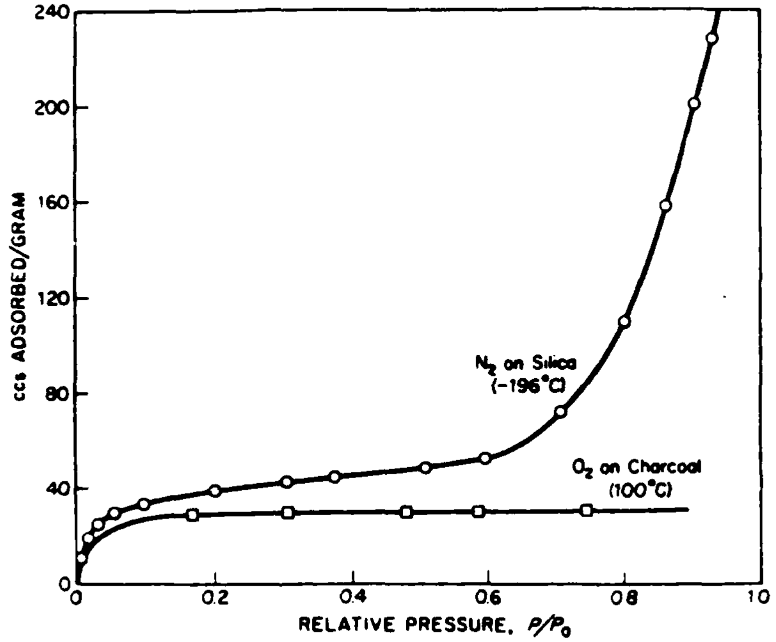


Figure 8. Adsorption Isotherm for Silica Gel.

detergents by 1985. The theory of operation and limitations of zeolites for $O_2$ and $N_2$ generation will be described in detail in Chapter 3.

As an air component separator, synthetic zeolites were first used for nitrogen production (80-85% purity), and also for oxygen generation in sewage treatment plants requiring 60-70% $O_2$ purity in large quantities.

Regardless of the final product ($N_2$ or $O_2$), the synthetic zeolite molecular sieve was utilized as an adsorption/desorption bed in a Pressure Swing Adsorption system (PSA). The procedure is also known as a Rapid Cycle Pressure Swing Adsorption system (RPSA), or as a Molecular Sieve Adsorption system (MSA). The distinction depends upon the inlet pressure, the gas flow process, and the specific system structure.

Synthetic zeolite molecular sieves adsorb not only nitrogen and oxygen, but also hydrocarbons, water, and carbon dioxide. They therefore assure a dry and contamination-free end product, separated from ambient air. As a $CO/CO_2$ and moisture separator, three types of molecular sieves serve as components in cryogenic air liquification plants (see Figure 1).

The structural topology, crystallography, and wide variety of ions which can be incorporated into a synthetic zeolite cage structure have made it feasible to produce seven different major groups of synthetic zeolites which can be tailored to material separation ranging from argon to heavy hydrocarbons (see Table I).

The most common used synthetic zeolites for $O_2$ and $N_2$ separation are the type "A" zeolites, commercially known as 4A or 5A LINDE molecular sieves. By the addition of light metallic atoms such as Na, Ca, K, the sieving capability of the Na-Al silicates can be enhanced, thereby increasing selectivity, accelerating regeneration, and expanding adsorbent capacity.

TABLE I.

**Synthetic materials (dominant)**

| | | |
|---|---|---|
| Type-A | $Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$ | Isometric |
| Type-X | $Na_{86}Al_{86}Si_{106}O_{384} \cdot 264H_2O$ | Isometric |
| Type-Y | $Na_{56}Al_{56}Si_{136}O_{384} \cdot 250H_2O$ | Isometric |
| Type-L | $K_9Al_9Si_{27}O_{72} \cdot 22H_2O$ | Hexagonal |
| Type-$\Omega$ | $(Na, etc.)_8Al_8Si_{28}O_{72} \cdot 21H_2O$ | Hexagonal |
| Type-ZK5 | $Na_{30}Al_{30}Si_{66}O_{192} \cdot 98H_2O$ | Isometric |
| Type-ZMS5 | $M_xAl_{1.1}Si_{94.9}O_{192}$ (anhydrous) | Orthorhombic (?) |

## 3.0 ANALYSIS OF THE PSA MOLECULAR SIEVE GAS SEPARATION SYSTEM

### 3.1 THEORY OF OPERATION

The pressure swing adsorption process is based on the capability of synthetic zeolites to adsorb nitrogen or oxygen from pressurized inlet air. Whether nitrogen or oxygen is the first component retained in the first adsorbent bed is a function of pressure, bed composition, and molecular sieve structure. The basic configuration of the process is shown in Figure 9. The process is cyclic, and each adsorber bed is subject to sequentially repeated operational steps.

First, air is introduced into the system, and then pressurized, dryed, and cooled. The air then enters into the selected adsorbent bed. Depending upon the end product orientation and configuration, 3-6 different beds are utilized. (The more units used, the higher degree of purity attained; however, electric power requirements are also increased.) The selected bed adsorbs nitrogen (in this case) and also retains $CO_2$ and moisture. The gas leaving this adsorbent column will contain roughly 85-90% oxygen.

As the air flows through the adsorbent bed, the pressure forces the nitrogen to move further into the bed, until the peak capacity is reached, at which point the bed is fully filled with nitrogen. When this occurs, a rotary valve switches the air flow to the number 2 adsorbent bed with minimum time delay. Because of the almost continuous air flow through the second bed, oxygen will be continuously produced, and flowed to a third bed. In the meantime, by reducing the pressure in the first bed, the retained nitrogen will leave, either as a free flow or as a pre-pressurized product. Thus, by "swinging" pressures and changing flow directions, a small part of the nitrogen will be used to purge the

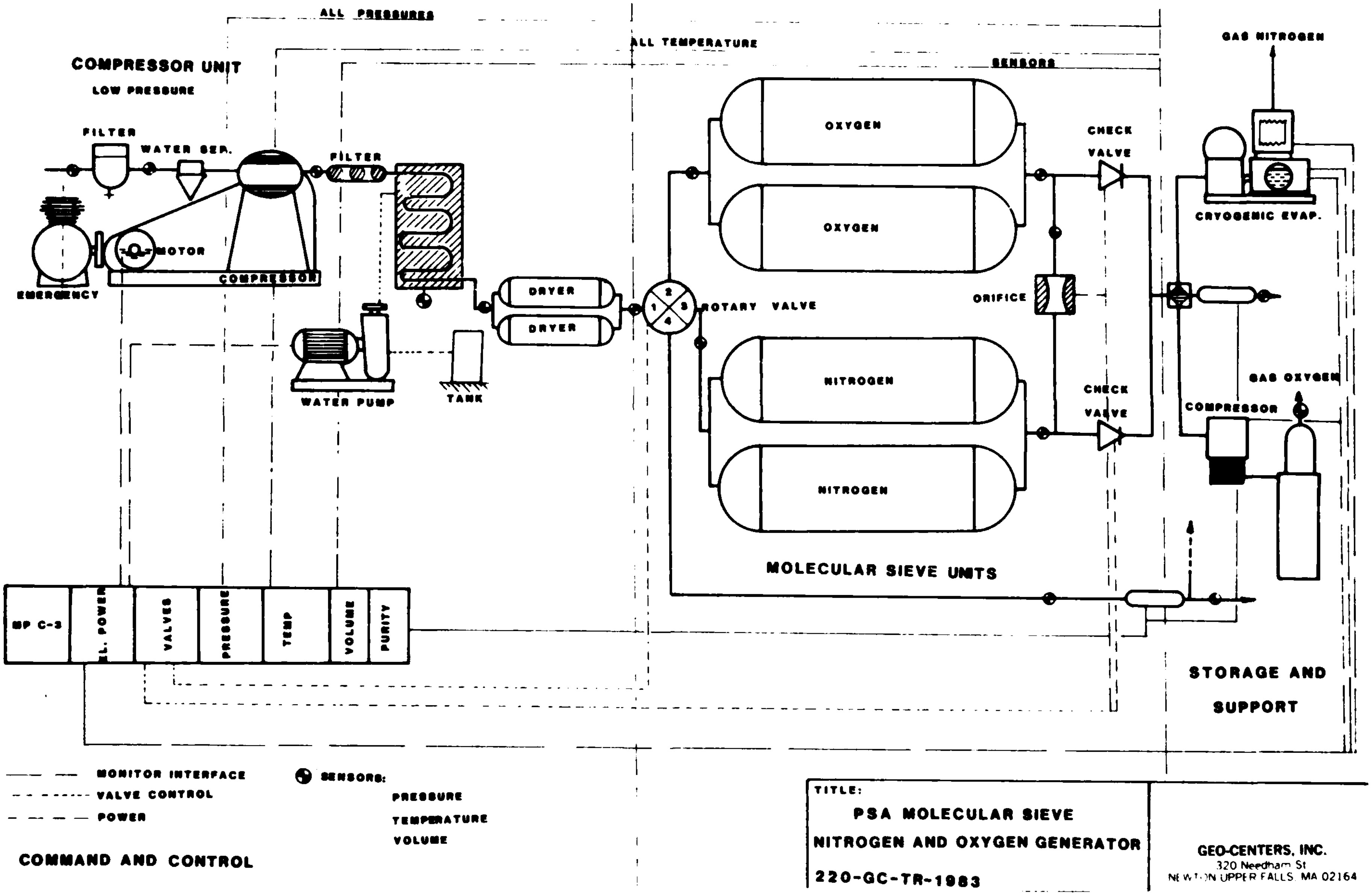


Figure 9. PSA Nitrogen and Oxygen Generator.

oxygen from the third bed, where it was retained during the process. The final step is the bed regeneration by pressure release prior to readmitting the new air stream.

The described method is used if oxygen is the desired end product, and the nitrogen is used only for purge and regeneration. In the opposite case, when nitrogen is required, the oxygen will be retained in the first bed, allowing nitrogen to pass through towards the outlet. Through a combination of the flow orientation, and utilizing more frequent pressure changes via a rotation valve, check valve units, and a low pressure/high pressure compressor combination, both gases, oxygen and nitrogen, can be produced in one gas separation unit.

As will be described in Chapter 4, it should be recognized that in most industrial applications, only one of the gases ($O_2$ or $N_2$) is primarily produced, so that a combined system with a double gas production task should be considered as an additional development, which is still in the prototype stage. However, it is technically feasible to produce both oxygen and nitrogen continuously by utilizing one combined gas separation unit.

In the design of such a double-role system, there are certain limitations with which to be concerned:

- Decide which is to be the primary product ($N_2$ or $O_2$), because delivery rate will be a function of component percentage in ambient air (78.5/21%).
- Internal structure of the selected sieve materials should be determined and tailored to the primary gas production rate and first stage purity.
- Increased electric power demand.
- Increased weight and dimensions.

- Install a reserve, back-up supporting storage system for the secondary product, to overcome cyclic delivery.
- Increased vulnerablity of the system as a single source for both gases.

## 3.2 CHEMICAL AND PHYSICAL CHARACTERISTICS OF ZEOLITE MOLECULAR SIEVES

In a selective gas separation system, the key components are the adsorbent beds, which contain the molecular sieves. In the case of nitrogen and oxygen separation, these are composed of synthetic zeolites, which have basic characteristics similar to their natural counterparts, but with an improved (more homogeneous and balanced) structure.

The zeolites consist of a complex three-dimensional framework originating from alumino silicates. This framework is a logical extension of simple $SiO_4$ ions, but is now in an extended structure, where some silicone atoms are replaced by aluminum atoms. The framework is negatively charged, having other cations uniformly distributed throughout it. In order to utilize this characteristic, other anions and cations are added to the structure during synthetic zeolite production to balance the negative charge of the original framework. Since the ionic bonds of the additional elements are less cohesive than the others in the framework, it will create a potential for ion exchange for those gases or liquids having a stronger ionic potential than those of the added ions. Also, adding Ca atoms to the framework allows one to block (decrease) channels and cavities by means of physical restriction, so that selectivity can be increased.

The general composition is always symbolized by a form of

$$M_{x/n} [(AlO_2)_x(SiO_2)_y] \ x \ ZH_2O$$

where n is the charge of the metal cation $M_n$+, which is usually $Na^+$, $K^+$, or $Ca^{++}$ and the 'Z' is the number of moles of water of hydration - a highly variable characteristic. The ion exchanging potential of zeolites is based on an equilibrium ion distribution, which is rapidly achievable because the structure of the framework allows an equalized fast passage of ions in and out.

The construction of a tailored synthetic zeolite requires a slow crystallization process of a sodium-alumino silicate gel of a balanced composition under definite, well controlled conditions to obtain a stabile $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \times 27H_2O$ format.

As a further processing step, the zeolite should be dehydrated by heating in vacuum to 350°C, to get a crystalline substance of cubic symmetry. The basic elements, e.g. $AlO_4$ and $SiO_4$, will be linked together to form a ring of 8 oxygen atoms on each face of the unit cube, and an irregular ring of six oxygen atoms across each corner (see Figure 10).

The restricted transition-state selectivity depends on the cavity and unit cell sizes, and also the electrostatic and Van Der Walls forces in the framework. In the case of a 4A or a 5A type synthetic zeolite, the largest size cavity of a unit cell is 11.4Å, and the connecting diameter of the 8 oxygen atom-rings is 4.2Å. The six irregularly formatted oxygen atoms form a ring with a diameter of about 2-2.5Å. The larger (corner coordinated) rings also form eight smaller cavities with a largest central opening of 6-7Å.

To design (or calculate) a potential separation capability of a 4A or 5A type molecular sieve, the following basic data and equations are required:

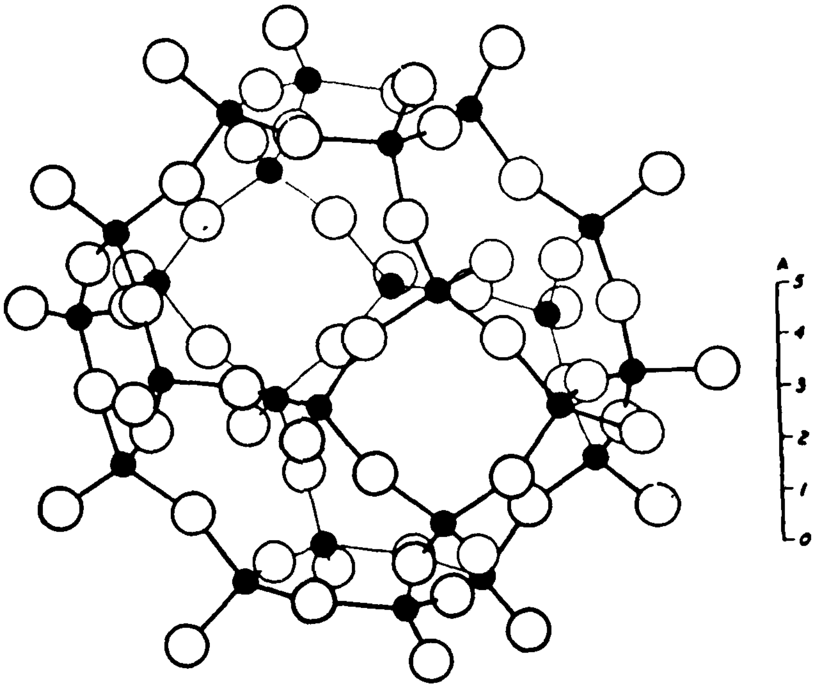


Figure 10. Basic Element of a 4A Type Synthetic Zeolite.

- Physical and thermodynamic properties of a selected gas ($O_2$ or $N_2$) (P, V, T, 2s and 2p orbitals, m, n, σ, τ, d)

  n = $(2.68719 \pm 0.0001) \times 10^{19}$ $cm^{-3}$; Loschmidt number; the number of molecules per unit volume of an ideal gas at 0°C and normal atmospheric pressure (CRC F-111)

  d = diameter of the largest size cavity of a unit cell (in Angstrom) (Inorganic Chemistry Group VI)

  m = molecular volume: volume occupied by one mole, numerically equal to the molecular weight divided by the density (CRC F-113)

  τ = temperature gradient (influence of temperature increase)

  σ = surface tension of an absorbent material

- Determination of the compressability of the product (Born-Lande Method)

- Determination of the intermolecular energy constants (MIE's equation)

- Computation of restricted gas flow (two-dimensional)

- Integer 'n' from viscosity of gases (Rayleigh-Chapman Method)

- Calculation of gas flow in an unsteady-state thermal condition

- Determination of a designated output volume of the selected gas at a given condition of elevated pressure/ normal temperature)

- Physical characteristics of a unit molecular sieve bed

For design variations and basic determination of cage dimensions, two general computer calculation methods have been studied (4):

(1) Equilibrium theory for oxygen enrichment of breathing air

(2) Two-dimensional dynamic model simulation of pressure swing adsorption

Both methods are utilized for theoretical evaluation purposes only, since some of the equations used for calculating internal potential forces inside of the 4A structure are empirical, and a minor structural change could invalidate them.

Another uncertainty factor is the use of the ideal gas law, even though the authors have attempted to compensate for non-ideal processes. Also, the calculation of the molecular energy and electrostatic charge distribution is also more of a theoretical model than a practical design format for a final evaluation.

In spite of all the idealizations contained in the model of a molecular sieve-pressure swing adsorption process, during the study-stage of a prototype design, it would be worthwhile to conduct a size-modeling study and compare it with engineering calculations. This modeling will probably provide some explanations for discrepancies between actual and predicted performance in previously built PSA models. In some cases, experimenters have found that the gas flow volume and pressure are lower than the calculated value (apparently due to flow restriction), and that product purity is also below predicted levels. These effects are thought to result from decreased selectivity due to inadequate or deteriorated molecular dynamic forces caused by unfilterable contaminants in the inlet gas.

In spite of considerable development efforts in the past 5 years, the molecular sieve PSA system still exhibits some deficiencies, especially when compared with cryogenic systems. For example:

- Anticipated purity of 99.5%/stage has not yet been attained. 90-95% purity appears to be a more reasonable estimate.
- Adsorption/desorption cycle varies from 40-45 sec/cycle to 2 1/2 min/cycle. The lower figure corresponds to the rapid PSA systems.

- Heavy gas pulsations require damping vessels.
- Non-linear operating characteristics can result in very high electric power requirements at high volumetric flow rates (see Chapter 4).

## 3.3 OVERVIEW OF SYSTEM COMPONENTS

A molecular sieve pressure swing adsorption system consists of the following modules, regardless of the material utilized in the molecular sieve:

(a) Primary compressor unit with filter(s), dryer and aftercooler

(b) Molecular sieve beds, connected with rotational valves, check valves and regulators

(c) A catalytic afterdryer for secondary refining (to increase purity)

(d) A pressure booster/compressor unit with aftercooler (if the outlet gases require increased pressure)

(e) Control, analyzer and safety instrumentation, incorporating electric and electronic connections and wiring

(f) Supporting framework with an option of insulation, enclosure, and transportation joints

(g) Tubing and coupling

(h) A storage and reservoir system (options: high pressure storage or cryogenic reservoir)

(i) Emergency power supply (electric generator or secondary powerlines)

(j) Automatic fire protection system (only if the ambient enclosure is not so equipped)

The components listed in h, i, and j are only additional, or proposed portions of a PSA system, and presently not listed by any candidate manufacturer.

Unlike cryogenic systems, the PSA construction has a flexible module advantage; it is feasible to locate module units in separate places without serious flow or pressure loss penalties.

As it will be demonstrated in Sections 4.1 and 4.2, the module packaging concept will allow one to operate system components in different, remote enclosures, eliminating the necessity of total replacement in case of fire or other destruction of the containing units.

### PRIMARY COMPRESSOR UNIT

Compressors which are utilized for nitrogen or oxygen production are required to provide:

- Air free of oil and water contamination (50 ppm or less water)
- Stable air flow rate
- High volumetric efficiency
- Relative moderate pressure pulsation
- Preferable high lifetime and relative low maintenance ratio
- Low resonance and vibration level

The compressor cooling system is preferably a closed-loop water cooler, although an air cooler could be utilized if necessary. Regular air supply systems are usually equipped with reciprocating type compressors with valves and other components non-lubricated; however, large volume (and moderate pressure) could be provided by multi-stage turbocompressors. The following equations are used to calculate basic power requirements.

Product Volume:

$$\Sigma = [(KR_c)^{\sigma} - 1]46/\sigma$$

where

$\sigma = \frac{(k-1)}{k}$ and k = ratio of specific heats
k = 1.40 for dry air at 14.4 psi and 60°F

K = 1.13 (loss factor for valves)

Compressor:

Compressor efficiency will be determined by the power losses between the inlet and discharge stations. For compressor cylinder sizing:

$$V(ft^3/min) = 9.1 \times 10^{-4} [D^2 - (d/2)^2] LN$$

where

N = rpm
L = stroke
D = cylinder bore
d = piston rod diameter

If the compressor is a closed-loop, water cooled unit, the cylinder heat rejection can be calculated as

$$H = 4(t_{ag} - t_{aw}) + 100 \quad Btu/bhp\text{-}hr$$

$t_{ag}$ = average gas temperature (°F)
$t_{aw}$ = average water temperature (°F)

Compressor accessories will require 5-8% of the electric energy used for the compressor. For the cases of nitrogen production examined in Sections 4.1-4.3, the designer should consider a 60-110 psig suction pressure requirement. With an intake volumetric air flow rate of 150 SCFM to 800 SFCM, design parameters in an oxygen or nitrogen gas production system should follow ANSI B31.1 and ANSI B16.5 standards.

For preliminary design purposes, the following safe practice calculations can be used:

If $D_1$ and $D_2$ are the compressor inlet and outlet diameters, $D_2 = 1.25D_1$

For line connectors $D_3 = \frac{D_1}{1.75}$ For vents $D_v = \frac{D_1}{6.3}$

For bypass lines $D_4 = \frac{D_1}{4.5}$ For relief ports $D_p = \frac{D_1}{9}$

AFTERCOOLERS

The aftercoolers are usually tube/shell component coolers with a design temperature of 15-25°F (for water, measured on return side). If the compressor is supplied with adequate pre-filtering and a separator, the aftercooler will consist of only a moisture removal filter.

REQUIREMENTS FOR DRYERS AND SEPARATORS

To remove all particles over 3 μm size, and for the flow resistance not to exceed 0.5 psi pressure drop across the unit, contamination-free, dry air feed is important, and generally it must be in a range of -40°F - 50°F dew point. If the moisture content of the feed air exceeds this value, the PSA molecular sieve bed could be damaged, and will lose its filtering and selective capability.

Other contaminants, having higher chemical or electric potential than does nitrogen or oxygen, could "block" zeolite (or carbon) molecules in the sieve bed, can also drastically reduce the filter/selection functions of the unit below design levels.

## PRESSURE FLUCTUATIONS

To compensate for pressure fluctuation effects caused by the compressor, designers have to provide reservoir capacity sufficient to compensate for variation in air density and also to dampen pressure waves. A simple method is to utilize a damping chamber with volume equal to the compressor cylinder swept volume plus the volume of the largest nominal pipeline. A more efficient method is to calculate the pressure surge wavelength and build a Helmholtz type resonator.

## ROTARY VALVES

Proper and safe connections and metering of gases to the PSA beds, as well as an after treatment unit, will require high quality valve units. In the case of a double function design (simultaneous oxygen/nitrogen generator), the selective rotary valve has primary importance. Design specifications for a rotary valve are:

(a) $6 \times 10^4 \rightarrow 10^6$ lifetime rotation cycles, over a temperature range of $-40^{\circ}C \rightarrow +125^{\circ}C$.

(b) Chemically resistant valve housing, closing elements and seals (e.g. a combination, like a 316SS body/valve, "fluorosent" seal ring, neoprene or silicone back-up ring is preferable).

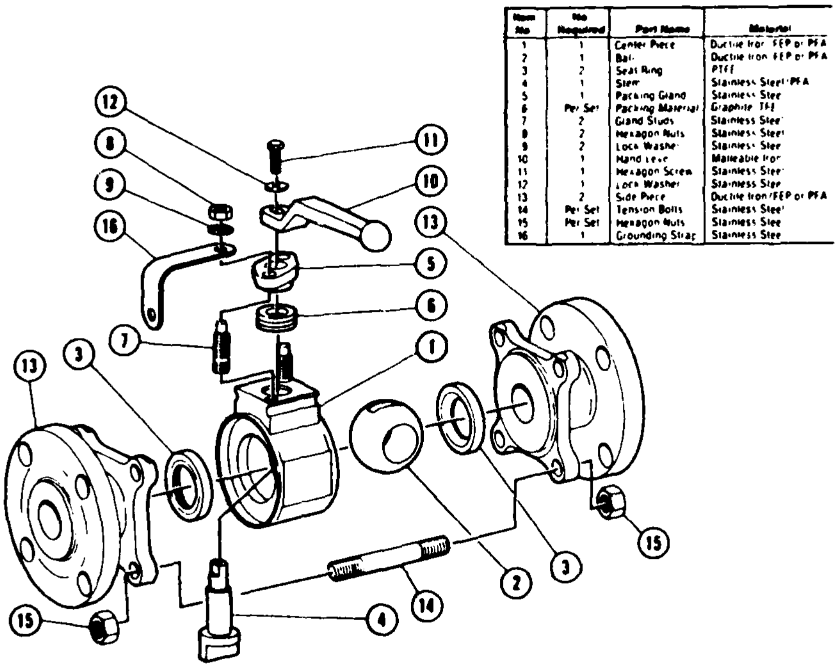
(c) High reliability, and fast reaction with minimum delay time (e.g. motorized butterfly valve output speeds from open to close): 0.5 - 2 sec.

Electromagnetic solenoid valves: 15-18 msec to open
21-25 msec to close

Pneumatic valves: 10-12 msec to open
15-19 msec to close

(d) Leak tight up to $5 \times 10^{-13}$ STD $cc^3$ sec measured vacuum. If the system is subdivided into modules at different locations, flexible interconnector piping, or pipe resonance dampers could be attached to the system.

Figure 10/A shows a simplified version of rotary valve, explaining components and structural material requirements.



| Item No | No Required | Part Name | Material |
|---|---|---|---|
| 1 | 1 | Center Piece | Ductile Iron/FEP or PFA |
| 2 | 1 | Ball | Ductile Iron/FEP or PFA |
| 3 | 2 | Seat Ring | PTFE |
| 4 | 1 | Stem | Stainless Steel/PFA |
| 5 | 1 | Packing Gland | Stainless Steel |
| 6 | Per Set | Packing Material | Graphite/TFE |
| 7 | 2 | Gland Studs | Stainless Steel |
| 8 | 2 | Hexagon Nuts | Stainless Steel |
| 9 | 2 | Lock Washer | Stainless Steel |
| 10 | 1 | Hand Lever | Malleable Iron |
| 11 | 1 | Hexagon Screw | Stainless Steel |
| 12 | 1 | Lock Washer | Stainless Steel |
| 13 | 2 | Side Piece | Ductile Iron/FEP or PFA |
| 14 | Per Set | Tension Bolts | Stainless Steel |
| 15 | Per Set | Hexagon Nuts | Stainless Steel |
| 16 | 1 | Grounding Strap | Stainless Steel |

Figure 10/A. Simplified Version of Rotary Valve.

## MOLECULAR SIEVE PSA BEDS

In spite of several design attempts to calculate flow resistance, efficiency, and structural stability of molecular sieves, the designer still has to rely on empirical knowledge for flow and pressure losses:

(a) For carbon molecular sieves utilized for nitrogen production, pressure losses average 28-38% (inlet/outlet pressure ratio).

(b) Synthetic zeolite molecular sieves experience slightly higher pressure losses across the system, about 30-40% (measurements and calculations were based on SAE 1145a, 244, and SAE 177a).

(c) Some control over pressure losses can be obtained by varying flow rate and inlet pressure. Again, experiment and empiricism are required to establish the best operating point.

(d) A lower flow rate would also result in higher nitrogen (or oxygen) purity; however, either the size (volume) of the molecular sieve bed, or a compressor characteristic should be adjusted to achieve the originally designed delivery rate.

(e) Minimum <u>inlet</u> pressure to feed a <u>PSA</u> system:

For a <u>4A</u> or <u>5A</u> type zeolite molecular sieve bed: 40 psig
For a <u>carbon</u> molecular sieve bed: 110 psig (max)
The recommended inlet pressure at a given flow rate should be provided by either a compressor or a pressurized air network. (If the supply air is available from some other source, the low pressure compressor can be eliminated.)

## 3.4 EVALUATION OF THE SYSTEM

Regardless of the type of molecular sieve system utilized, there are several points which should be emphasized as follows:

(1) There are only a limited number of existing high purity production (95% or above) nitrogen and oxygen plants with the desired flow capacity of 50 lb/hr ($N_2$) and 40 lb/hr ($O_2$). Only 4 nitrogen plants using synthetic zeolite molecular sieves were available for this study. The oldest model has been in operation only since 1979, which is far too short a time period in which to judge the lifespan and long time reliability of those plants.

(2) For oxygen as a primary product, we found 11 operating plants, with a capacity of 20-90 lbs/hr. (These all utilized 4A type zeolite molecular sieves.)

(3) According to the plant operators and researchers, the failure rate was moderate (an average of 22-27 recorded failures per operating $O_2$ production unit). It is remarkable that most of the malfunctions were consequences of breakdowns involving smaller components (oxygen pressure regulator unit, rotary valves, flow monitoring and regulating units, filters, electric failure in solid state monitoring and handling units). Molecular sieve failures were not observed, which is not unexpected since synthetic zeolites have a long lifespan, and no significant damage occurs to them as long as adequate filtration and demoisturization is provided to protect the molecular sieve beds. Some detailed maintenance observations are listed in Section 4.5.

(4) Nitrogen production plants, utilizing carbon molecular sieves, have been in operation only since 1981. At present, less than 10 are in operation by domestic consumers. Since these nitrogen plants are connected with chemical process plants, they assure a high purity (99.5% when not equipped with a catalytic converter, and 99.995% with a catalytic converter) nitrogen gas output. In cases of on-board, or on-site gas production, 10-15 years are allotted for return on investment, maintenance contracts, and expected lifespan as a regular practice between supplier and user. Therefore, 1-1.5 years operation experience may not be sufficient to evaluate these systems.

In order to compare cryogenic systems with non-cryogenic gas plants, we considered the following factors:

(a) Electric energy requirements vs. production rate

(b) Air supply demand vs. output request

(c) Cooling water recommended vs. production rate

(d) Predicted service requirements vs. production rate (maintenance, shut down time, start time)

(e) Other dimensions vs. production rate

(f) Estimated monthly operational cost vs. monthly production rate

Based upon these factors, we attempted to reach conclusions relative to predicting an "optimum" operational system for selected nitrogen and oxygen outputs. For the purposes of this study, the nominal system output was selected to be 40-50 lb/hr (gaseous) oxygen.

In addition, both low and high off-design operation was examined at 10 lb/hr to 20 lb/hr, and 80 to 90 lb/hr gaseous oxygen. For gaseous nitrogen production, 50 lb/hr, 20 lb/hr and 10 lb/hr were compared. Among possible applications of cryogenic $O_2$ and $N_2$ supplies, for oxygen 1, 5, 40 and 125 lb/hr outputs were calculated. Liquid nitrogen generators were selected at ranges of 5, 20, 50, and 250 lb/hr.

It must be emphasized that in each of the above design cases either oxygen or nitrogen will be considered as the primary product, and the other will be considered as a by-product only.

As was discussed in Chapters 2 and 3, there are tendencies in the gas production industry to design and build single plants for both applications. However, assurance of adequate gas purity and delivery time/volume sequences are still in the development stage. It is also questionable to estimate the economic consequences of producing both gases in one composite plant, since all system component expenses will be significantly increased over those designed for a single product.

For Navy ship applications, specifically in a retrofit, lack of utility area for a new system installation will cause many design problems, and compromises between system complexity and packaging will undoubtedly be necessary. This factor was not considered in this study.

On the basis of the comparison factors (a-f) above, size and performance specifications were developed for a PSA and cryogenic gas supply system. Comparisons among specifications are shown in Figures 11 (a-f). The following conclusions can be drawn from the parametric study:

(a) For gaseous nitrogen production in a lower range (5-20 lb/hr) all factors indicated that an improved cryogenic installation is preferable. Cryogenic systems in this production range require lower energy input, less space, and produce higher purity.

(b) In medium range nitrogen production, (40-80 lb/hr) of gas, molecular sieve systems are superior for a production purity of 98% or higher, and provided the system is equipped with a supporting storage system for intermediate operational shutdowns.

(c) In higher nitrogen production ranges (200-250 lb/hr and up) cryogenic gas generation has the advantage of optimized performance/expense ratio. However, there are some dimensional limitations, and increased electric power demand which may be serious objections to installation as a shipboard system.

(d) For gaseous oxygen production at lower production requirements (4-5 lb/hr) cryogenic plants could be installed, since at this size there appears to be no potential safety hazards.

(e) In medium ranges (20-80 lb/hr) a molecular sieve system is preferable, because little or no liquid oxygen is stored. In this situation, operation is less hazardous than for a cryogenic plant operating in the same output range.

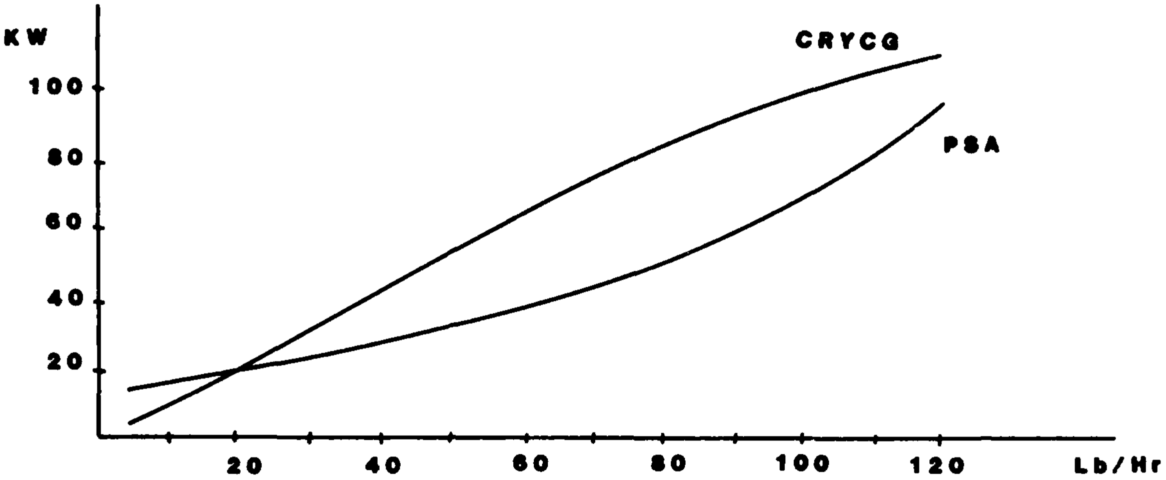


FIG.11A POWER REQUIREMENTS vs. PRODUCTION RATE

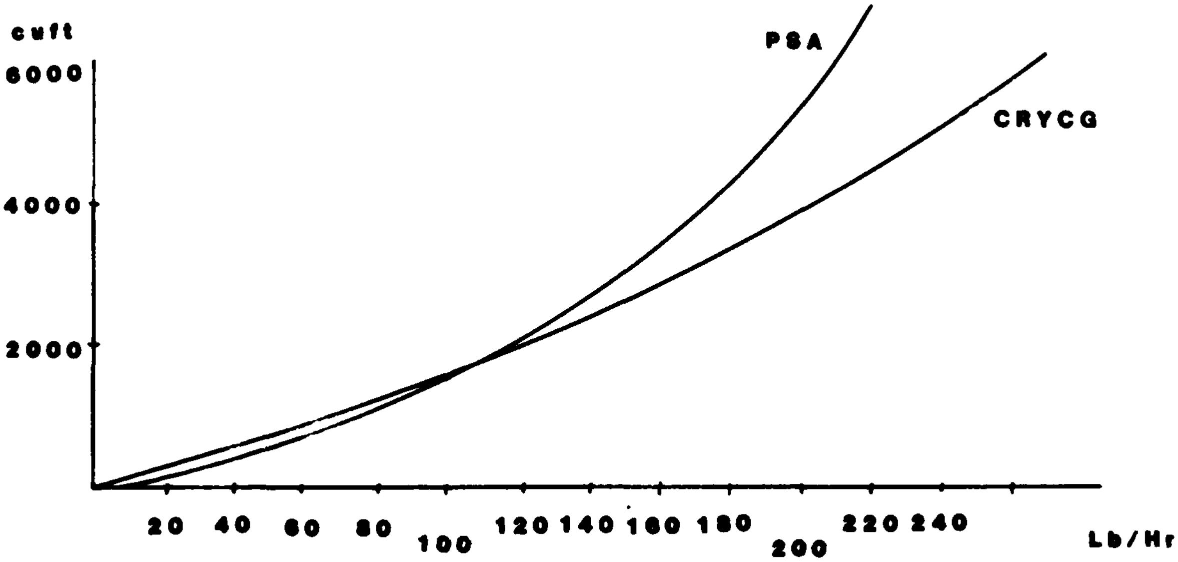


FIG.11B. SYSTEM SPACE REQUIREMENTS vs. PRODUCTION RATE

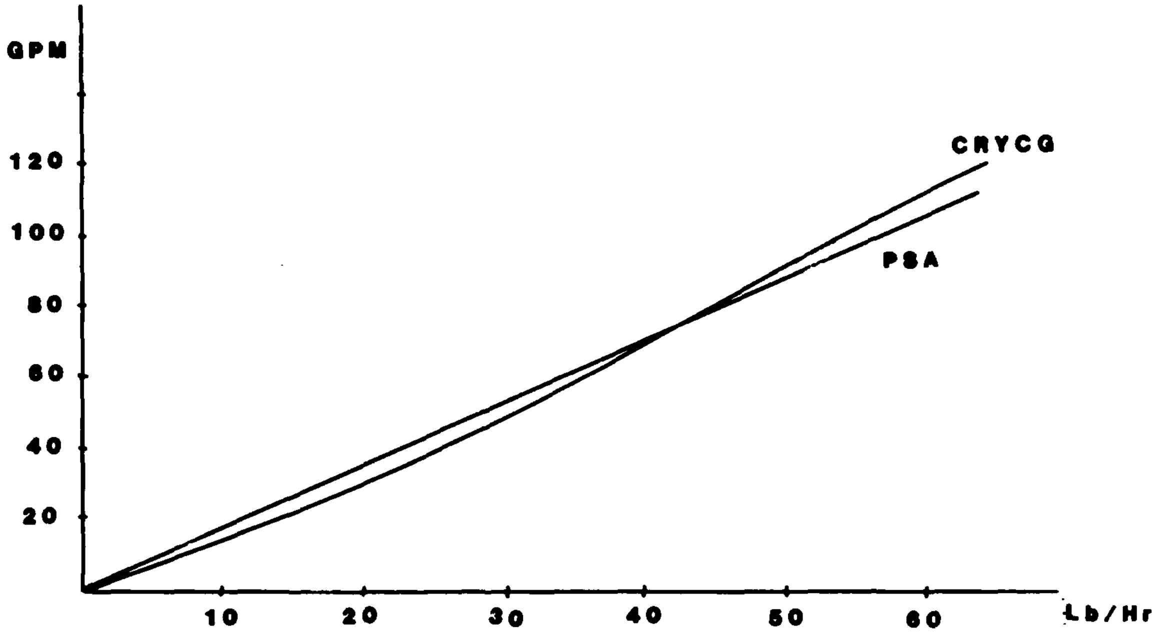


FIG.11C. COOL WATER REQ. vs. PRODUCTION RATE

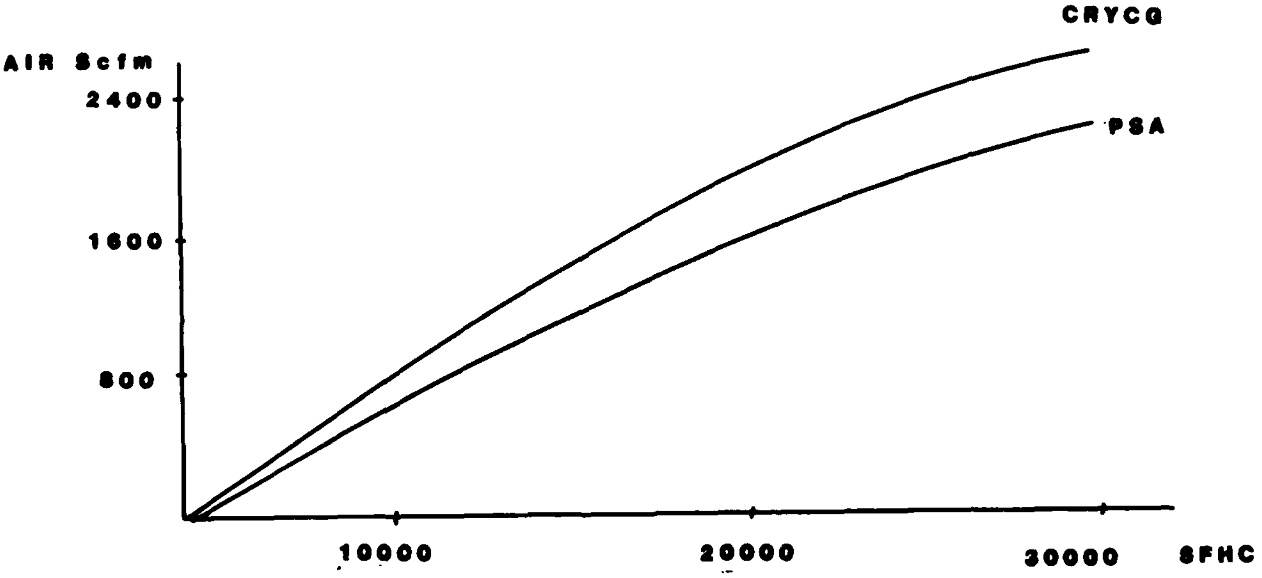


FIG 11D AIRSUPPLY vs. PRODUCTION RATE

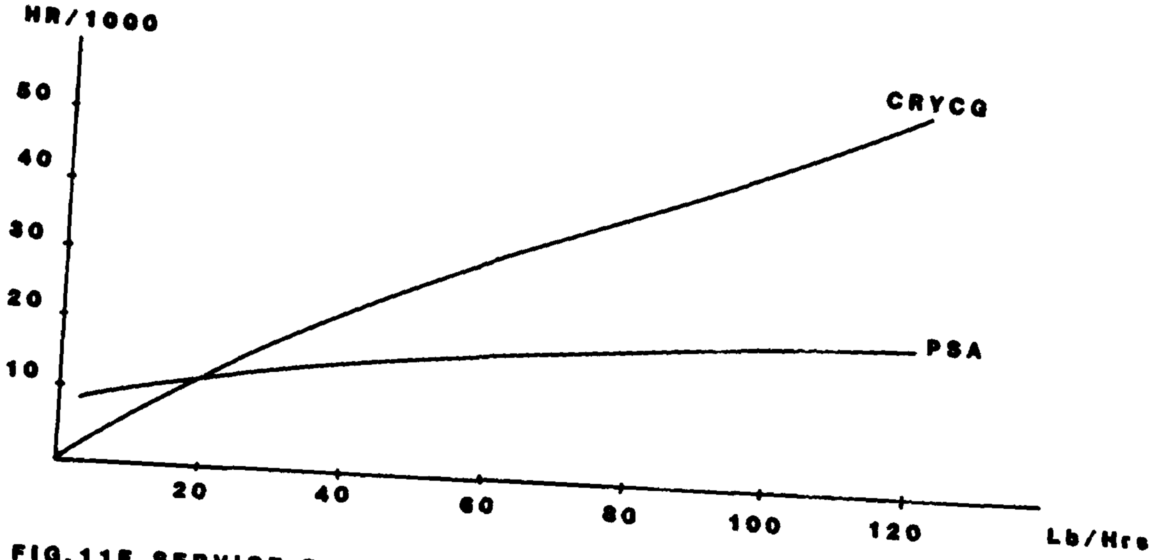


FIG.11E SERVICE REQUIRED HR/1000 HOURS PRODUCTION RATE

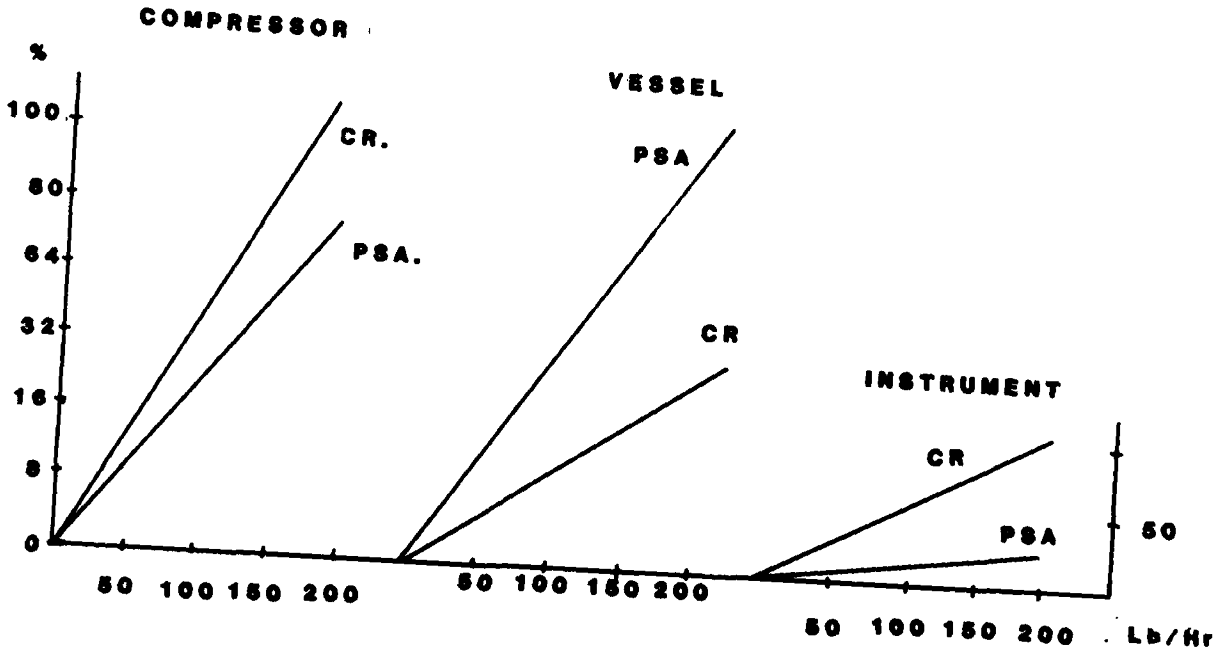


FIG.11F COMPONENT SIZE vs. PRODUCTION RATE

(f) In a higher output-case (125 lb/hr and up) cryogenic plants for oxygen still have advantages, particularly if production should be as high as 250-500 lb/hr liquid oxygen.

Beyond the listed factors, in the selection of a nitrogen or oxygen gas generation unit, there are other limitations which also should be considered:

- Liquid cryogenic plants can provide 99.5-99.7% purity ($O_2$ or $N_2$).
- PSA 4A and 5A plants perform: 94-96% purity as a first step, and require further purification.
- PSA carbon sieve plants perform: 99.5% purity nitrogen only, as a first stage, 99.995% purity is available, with 10-15% additional power requirement.
- PSA molecular sieve gas generators should be provided with a storage system (liquifier or pressurizer).
- PSA systems are best built in the form of a vertical gas adsorber column, requiring 10 feet or more head clearance (see Sections 4.2 and 5.5 for other comparative factors). Additional information describing the high efficiency of vertical units can be obtained from the manufacturer (reference 9, Appendix C).
- If a PSA system is the sole source of nitrogen, any shutdown longer than 3 hours will force the shutdown of any system requiring nitrogen gas.
- In an oxygen system, shutdown of a PSA supply will require a second life support system to be installed, since there would be no emergency medical oxygen supply available without such a back-up system (oxygen shutdown period could not exceed 0.5-1.0 minutes without automatic switchover to an emergency life support network).

In the higher production ranges, where the cryogenic production is preferable over PSA systems, the following observations should be considered:

(a) Upgrading of existing cryogenic systems currently onboard surface vessels is feasible.

(b) It is preferable to use a number of smaller units whose combined output meets required production.

(c) If structural conditions allow, the cryogenic units should be changed to a "Stirling" type in order to eliminate problems inherent with turboexpanders.

(d) If it is not feasible to change the turboexchangers, improvements in the bearing and connection sections are necessary.

(e) Tank supports and joints should be changed to assure a uniform stress/load configuration.

(f) Review maintenance records of all cryogenic systems, and overhaul piping and valves where required.

(g) Since most of the electrical system controls and gauges are technologically outdated, these should be replaced with upgraded equipment.

(h) The designer should consider relatively high shutdown and recuperation times (e.g. 12-20 hours/7 days of operation) for deiceing, cleaning, and repeated cool-off sequences.

## 4.0 DESIGN CONSIDERATIONS FOR NITROGEN AND OXYGEN GENERATORS OF CONFINED SCALE

### 4.1 OPERATIONAL AND SUPPLY REQUIREMENTS

This section of this report will serve as a guideline for selection of components, focusing attention largely to PSA systems, since cryogenic technologies and their associated machinery have well developed design practices.

### BASELINE DATA FOR SYSTEM SELECTION

(a) Total volume of required gas (nitrogen or oxygen or using by-product as an auxiliary supplement). (For this study: 50 lb/hr oxygen, 40 lb/hr nitrogen).

(b) Required outlet pressure, measured at exit point of the PSA bed.

40 psig/15 psig for a 4A/5A type zeolite bed
85 psig/75 psig for a carbon based sieve

(c) Required operating schedule: (operating hours/day, number days/week, expected shutdown periods) Case by case, determined by the type of ship and nature of mission.

(d) Peak gas delivery rate and its time/sequencing (4-6 hours per day, 80-100% available delivery).

(e) Purity requirements (measured at user interface with the system)

99.5% purity required for oxygen
99.995% purity for nitrogen
Maximum oxygen content in nitrogen: 10 ppm
Maximum allowable hydrogen content in nitrogen: 2000-3000 ppm
Maximum allowable hydrogen content in oxygen: 1000-2000 ppm
Water vapor (dew point in both): -40°F - 60°F at 80 psig
Output gas temperature: 90-110°F

NOTE: To monitor gas purity, either system ($O_2$ and $N_2$) should be equipped with a contamination monitor (e.g. $ZrO_2$ type $O_2$ monitor) connected with an emergency warning signal and, if necessary, operation shutdown switch.

(f) Required electrical supply: all utilities (filter, heater, cooler, compressor, valves, solid state electronics, monitor/command, converters, firefighting) are assumed to add 25-30% to required compressor energy. Standard NEC or NEMA 3Ø 440V or 3Ø 230V (60 Hz) supply for compressors. NEMA 1Ø 115V supply for controls.

(g) Service and maintenance expectations: (General) The gas supply system is required to run fully automatically, either by demand/command on the user's side, or by on-off remote control switch. The system must be equipped with automatic switch-over valves in case of emergency.

(h) Molecular sieve adsorbent beds: All selected bed materials should have a maximum flow resistance resulting in no more than a 30% pressure drop across the bed. Life expectancy should be certified by the supplier and provisions should be made for a removable bed structure to facilitate on-board rebuilding in case of heavy contamination (removable vessel cleaning covers, or tops).

(i) Pressure vessel design should follow ASME code for 200 psig. Non-pressurized vessel design should follow ASME VIII.11. Connecting pipes conform to ANSI B 31.1 (minimum). Connecting flanges conform to ANSI B16.5 or better. If the PSA bed is allocated to a separate enclosure, all connecting elements should comply with MIL-STD-167 or equivalent for shock and wear resistance. To estimate the expected natural resonance frequency of a multi-component system, the following equation can be used:

$$F_n = 3.13\left(\frac{1}{S_{st}}\right)^{1/2} \quad \text{or} \quad F_n = 3.13\left(\frac{k}{w}\right)^{1/2}$$

where $S_{st}$ = static deflection

k = stiffness

w = weight

## 4.2 SELECTION OF SYSTEM COMPONENTS

Any PSA nitrogen or oxygen production system will be a composite of elements obtained from different manufacturers. For this reason, design of a new system which is expected to deliver the same high reliability as that provided previously by cryogenic equipment will require considerable care and effort. To ensure adequate reliability, the following guidelines for lifetime should be observed:

Life expectancy of NL-1 and NL-2 non-lubricated compressors: Minimum 7 years

- Scheduled maintenance: every 80 hours based on 16 hours/ day continuous operation.
- Fatigue rate expectancy for valves: $10^6$ combined openings and closings with minimum leak rate below $5 \times 10^{-3}$ psi/hr.

Molecular sieve beds: Minimum 7 years for contamination free air.

Solid state electric components: 12,000-14,000 hours at 60% load (2.45 years, for 16 hours/day operating schedule).

If the PSA system supplier will perform vendor evaluation tests, an extended lifespan/fatigue test is required as indicated below.

- For compressors: 5000 hours pre-run test
- For valves: accelerated fatigue test in conditioned enclosure (99.5% oxygen atmosphere in -40°C + 115°C temperature range)

After evaluation tests, the supplier should adjust predicted maintenance and repair schedules, and also prepare spare parts lists which include identification of component manufacturers.

## 4.3 ELECTRIC POWER SUPPLY

Unlike cryogenic systems with a reserve capacity, PSA systems are highly sensitive to unscheduled power failures. To prevent a system loss caused by loss of power, the following regular preventive procedures should be considered:

(a) Parallel electric supply-wire attachment from other than main electric power source.

(b) Emergency batteries/power generator set, coupled to solid state connectors with automatic switch-over devices.

(c) Utilize emergency power/generator set, preferable with internal combustion on-site power source. (Automatic, semi-automatic, or mechanically activated mechanisms are all feasible).

(d) The system monitoring network should have automated connections for warning, system stop, or system-reactivating functions.

## 4.4 INDUSTRIAL AND MILITARY STANDARDS

Any PSA or cryogenic system is a composite of many subsystems with designated functions, and is not generally a standardized product. As a result, approximately 150 different industrial (e.g. ASME, ANSI), military (e.g. MIL-STD, MIL-E, MIL-T, etc.), and manufacturers's own internal (Air Product, LINDE) standards can be applied to the various components. As is shown in Appendix B, this study gives a sample of standards which should be utilized in the design, construction, testing, and operation of gaseous and cryogenic (liquid) nitrogen and oxygen production devices and plants.

## 4.5 SYSTEM RELIABILITY AND MAINTENANCE

Beyond the requirements described in Chapter 3 and Sections 4.1 and 4.2, there are other desirable system characteristics to be considered during prototype design. Of particular concern is the monitoring system, which should be designed to control all pressure levels in the system (e.g. inlet, valve, sieve in/out, piping, outlet; generally, before and after each restriction in the gas flow). Flow volume monitoring units should be mounted upstream and downstream of both the compressor unit and molecular sieve beds, and at the final outlet point. Oxygen, nitrogen, hydrogen, and moisture monitors are needed for outlet gases (supply side). The compressor should be supplied with the following monitors:

- Oil pressure and temperature (if lubricated/equipped with oil separator)
- Cylinder head temperature sensor
- Cylinder wall outer skirt temperature sensor
- Cooling water temperature sensor
- RPM monitor
- Supply voltage sensor on driving electric motor

For bench-test and prototype evaluation purposes: stress and vibration measurement on all mechanical elements and electric connecting wires.

## MAINTENANCE REQUIREMENTS

When considering the average lifetime of a Navy ship, there are three possible design and manufacturing concepts:

(a) Design and manufacture an oxygen-nitrogen system, with a minimum (maintenance) lifetime which is equivalent with the ship's life expectancy (minor component replacement).

(b) Design and manufacture a system where each component will be subject to replacement within the lifespan of the most expensive unit or building block (equivalent fatigue strategy). In this case, the whole system will require a packaged unit building strategy, with an option for a quickly replaceable container-type enclosure.

(c) Construct a PSA system with divided building blocks, where each unit has a lifespan step, and where this step is determined by the technical vulnerability of the whole system, and maintenance repair availability (e.g. remote control electric and electronic devices, with an automatic trouble-shooting capability, quick pipe connectors, divided building blocks). It is also feasible to carry compact building blocks as maintenance kits, without duplicating a whole PSA system.

## 4.6 SYSTEM SAFETY AND OPERATIONAL HAZARD - PROTECTION OF THE SYSTEM

A PSA nitrogen or oxygen generator system should have a limited capacity-gas liquifier or pressurized gas storage back-up system. As was mentioned previously, certain hazards could exist due to the presence of liquid oxygen (fire, explosion), liquid nitrogen (suffocation, cold temperatures, etc.). A comprehensive analysis of expected hazards caused by the presence of LOX, LN, GOX and GN is shown in Appendix A. It is necessary to mention that the majority of the listed materials probably exist only in a testing laboratory. However, for prototype testing, the researcher should be aware of potential dangers. The Appendix shows in detail the regular safety procedures which must be followed in handling gaseous and liquid $O_2$ and $N_2$. This is an attached example from a gas manufacturer, and therefore it will not supersede any industrial or military standards for hazardous material transportation or handling.

Considering the special missions of a gas generation system, with the major task of providing ships with an on-board supply, the following protection features should be analyzed and added to the system:

(a) Separate fire and thermal protection, possibly with self contained and automated sensors and fire extinguishers.

(b) If the gas generator is not built into any deck enclosure on the ship, an adequate protective armor should be provided to prevent piercing by 30/50 mm projectiles.

(c) Utilize a double filtration system ahead of the compressor or air inlet to protect the unit from chemical, biological or nuclear contamination.

(d) Prevent unauthorized or unexpected starting or shutdown operations.

# 5.0 PROTOTYPE MANUFACTURING AND TESTING

## 5.1 SELECTION OF SYSTEM COMPONENTS

Since most of the present or contemplated oxygen/nitrogen production plants will utilize existing components, there are only two ways to create prototypes:

- By selecting proper size components, assembly of a real size system
- Calculate a functional mathematical/mechanical model, to analyze gas production trends as a function of plant size, and assemble a down sized demonstrator model (scaling is a comparison between the requested gas production rate and the delivery rate of the test model).

The second procedure has a cost advantage over the first one.

Once the size of the prototype model is set, the designers should calculate or estimate predicted tolerance ranges for each component and for the whole system. This is important for further calculations to determine electric power and space requirements. As it was indicated in Chapter 4, each subcontractor should certify production and dimensional tolerances, and submit data about life expectancy of the component.

Since maintenance and repair is also an important point, it is advisable to decide an average life cycle of a particular component. This is necessary in the case of any later changes, in order to guarantee the exchangeability of a component with a newer one, without forcing the user to change other connecting components in the system.

For every component, the subcontractor or manufacturer should supply replacement parts and a maintenance schedule, to be integrated into the system maintenance scheme.

## 5.2 PRE-ASSEMBLY COMPONENT EVALUATION

Among all the components of an oxygen or nitrogen generation system, usually the compressor is the only unit tested for resonance and vibration. Some manufacturers resonance test the whole assembly; however, an externally applied vibration (using a vibration table) will not adequately represent an internally amplified resonance.

It is important to calculate or measure the resonance "avalanche" effect, e.g. if the compressor or pump unit generates a vibration, how will the other components within the same assembly frame be effected, and what magnitude of amplified resonance could occur.

Since most components are tested under ANSI, ASME, or the manufacturer's own standards, it is necessary for the system designer to extend testing procedures to include other, non-standard tests such as:

- Accelerated fatigue (higher/lower temperature)
- Moderate shock resistance (e.g. non-linear pressure increase for pipes and valves)
- Chemical and temperature test for molecular sieve materials
- Piercing or penetration test for vessels
- Repeated temperature increase/decrease test (chamber test) for determination of temperature effects on component performance (4).
- Fire resistance tests for valves, instruments and electric/or electronic assemblies to determine fire protection and fire prevention procedures
- Test for component maintainability

## 5.3 MANUFACTURING A BENCH MODEL

Beyond the consequences of prototype scaling (5.1), the prototype bench model should follow assembly and system layouts of the final model design as closely as possible. If it is feasible for testing purposes, both a compact (dense) packaged model and a modular (divided) model should be built to study the consequences of model separation for performance-changes or potential hazards.

Since a real-time fatigue test is unlikely, the manufacturer and potential user have to decide on accelerated test sequences and conditions to demonstrate system breakdowns and rebuilding (or partial component replacements). Temporary line and component connections should be avoided, since such practice could influence measurement tolerance and reliability. Also, the use of non-design connections would void any real resonance and vibration tests.

During bench model tests, a double instrumentation philosophy is advisable, i.e. the originally designed sensors and monitoring devices should be parallel mounted with higher precision laboratory test equipment.

## 5.4 OPERATIONAL AND EVALUATION TESTS

The following main groups of test procedures should be designed:

- Determine product (gas) flow and volume at user interface
- Gas purity and continuity for both shorter and extended service time
- System reliability (repeated stop/restart, lifespan and fatigue, tolerances in product delivery)
- System response time sequences (start-up time, regeneration times for molecular sieves)

- Monitoring equipment reliability
- Command module response (reliability and time)
- Simulated emergency situation tests (partial/total breakdown, repairability, preventive maintenance)

## 5.5 SYSTEM/ENVIRONMENT COMPATIBILITY

During the design period, the manufacturer must analyze all environmental impacts on the gas generation system. The most unfavorable scenario is ship retrofitting, since the system designer will be limited by other on-board equipment, and for this reason flexible packaging is probably essential. Figure 12 shows a conceptual container package of on-board oxygen generation system.

Another important factor is a bilateral resonance situation, e.g. how vibrations from the gas generator influence other close by equipment, and also how vibrations from the surrounding environment influences the gas generator system.

Another important consideration is establishing methods and equipment for fire protection. If it is feasible, a self contained, automated fire protection network should be used in order to assure survivability of the gas generator, even if the central fire fighting equipment should fail.

By learning from previous design problems with PSA systems, the prototype model should utilize a more flexible (variable) flow management to allow a module building block approach, free from major component changes in case of failure. Potential fire, exposure, and explosion hazards should be analyzed at every interface point. In the case of nitrogen production, both the designer and the user should review the application environment (e.g. open or in enclosure) to avoid a potential suffocation hazard. (Appendix A gives examples of handling oxygen and nitrogen.)

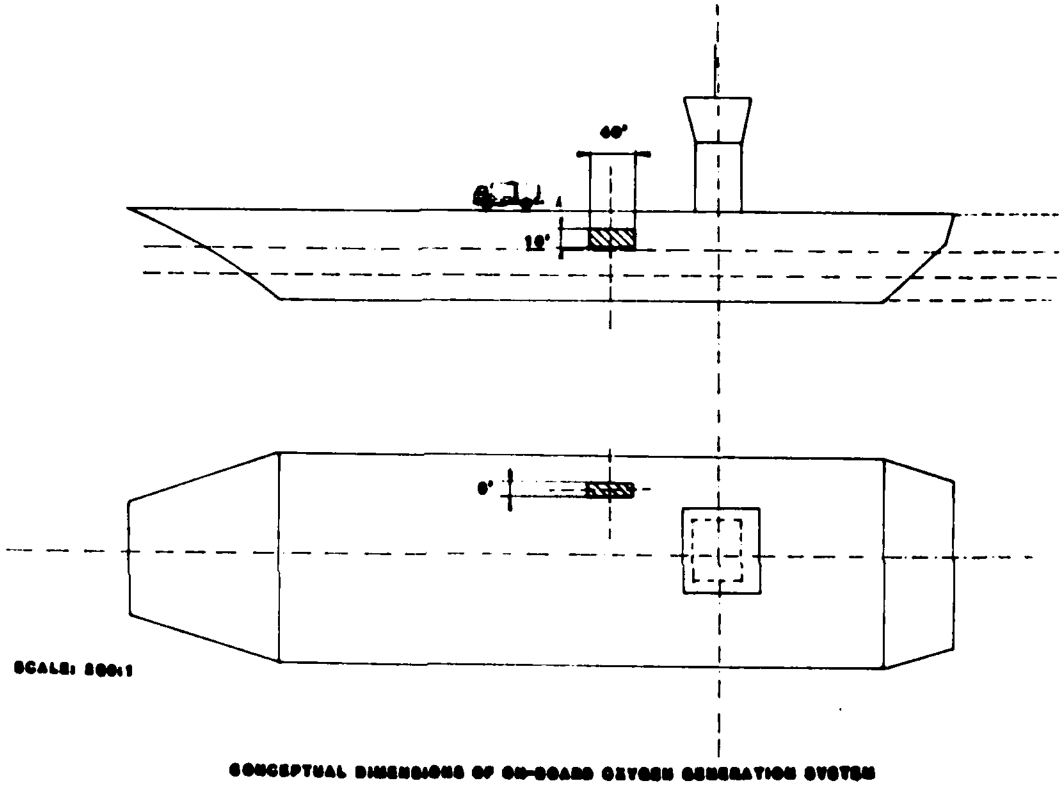


Figure 12. Conceptual Container Package of On-Board Oxygen Generation System.

## 6.0 SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Several types of oxygen/nitrogen generating systems have been examined for possible Navy shipboard applications. Major emphasis was placed on cryogenic (liquid phase) and pressure swing adsorption (gas phase) systems, as these are the most highly developed. Other technologies were also considered, however. The cryogenic and PSA systems were evaluated for their economic and performance benefits under low (10-20 lb/hr), moderate (40-50 lb/hr), and high (up to 250 lb/hr) production rates. The following conclusions were reached in this study.

(1) The present situation of having LOX and LN storage/evaporator systems in service on Navy surface vessels needs to be changed. To increase mobility and decrease the high degree of dependence on expensive and difficult land-based support, on-board oxygen and nitrogen generation systems need to be developed for both existing ships and future ship designs.

(2) Among all of the candidate systems we studied, only two types of gas generation systems were found reliable enough to meet our criteria.

  (a) Gas separation, which utilizes pressure swing adsorption (PSA) via molecular sieves, and

  (b) On-board cryogenic oxygen/nitrogen plants which combine absorbent beds and turboexpanders, or Stirling generators.

(3) For the moderate oxygen/nitrogen production rates envisioned for shipboard use (40-50 lb/hr), PSA systems are superior and preferable to cryogenic systems on the basis of power and space requirements, complexity of the system, and safety. The advantages are likely to remain for production rates perhaps as high as 80 lb/hr.

(4) For future ship designs, other $N_2/O_2$ production methods, such as gas separation by liquid membranes and large volume solid oxygen concentrators, appear to be feasible. These methods are still in the research and development stages, however, and the technology has not yet been significantly developed to warrant serious consideration at this time.

Based on the above conclusions, a detailed analysis was made of requirements for design, construction, and testing of a full scale prototype PSA unit for shipboard use. Included in this effort are specific recommendations and guidelines for meeting industrial and military specifications, obtaining high reliability and low maintenance costs, reducing operational hazards, and providing adequate protection for the system. This material is presented in detail in Chapters 3, 4, and 5 of this report. A few generalized recommendatons deserve special emphasis:

(1) For a PSA-molecular sieve type gas generator, the following areas of the system should be redesigned in order to upgrade the unit for shipboard use:

  (a) Improve the purity of the oxygen and nitrogen produced up to 99.5% through either a multi-stage absorption process or modification of the delivered volume/delivery speed ratios.

  (b) The system should be coupled with an emergency gas storage area in order to supply gases during system re-start periods, power failures, or other emergency situations.

  (c) Beyond regular safety precautions, separate heat and fire protection is advisable. This is necessary because certain types of molecular sieves could be damaged by extensive heat radiation.

(2) PSA systems have two inherent areas of vulnerability:

  (a) Contamination of the ambient air, which serves as the sole source of oxygen and nitrogen for the unit. By the use of proper filtration techniques, any possible inlet air contamination problem can be eliminated. The designer should consider developing an effective system for an ABC type of attack.

  (b) Electric power failure or loss which stops operation of compressors. To prevent system shutdown by power failure, it is necessary to couple the electric supply with an independent power source. This can be an electric generator-set with automatic starters.

(3) For safety and retrofit considerations on existing ships, it is a better alternative to employ two or more smaller $O_2/N_2$ generators with a total capablity of the required gas volume, rather than one centralized system.

(4) During the period of system-design, the contractor(s) should pay special attention to compatibility of the gas generator with its environment. Beyond the questions of power supply, gas delivery, operational safety, location of the gas generator vs. farthest gas delivery point, other considerations include frame dimensions vs. mounting and service requirements, and environmental shock and vibration compatibility.

(5) Before an actual prototype system is constructed, a detailed design plan of the candidate system should be examined and analyzed by independent experts.

(6) In certain instances, a cryogenic $O_2/N_2$ generating system may be preferable to a PSA system. In order to upgrade these systems for shipboard use, the following modifications are necessary:

   (a) Redesign the supports for the cryogenic tanks, making them resistant to vibration and moderate shock loads.

   (b) Noise and vibration isolators are required for the turboexpanders to prevent damage to their internal structures and decrease excessive vibration to the surrounding machinery.

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Discharge of a Liquid or Vapor From a Ruptured Container, DTIC-AD-B068-541L, R. Saucier, et. al. (August 1982).

## APPENDIX A

TABLE A-1. List of Materials of Potential Hazard with Mixing or React with GOX + $N_2$

| | Potentially Hazardous Material | Physical or Chemical Condition, Could Lead to Explosion |
|---|---|---|
| 1. | Acetaldahyde<br>Acetylene | Uncontrolled mixing with $O_2$, 1 atm or higher pressure. Presence of open flame or spark, heat, or exposure. |
| 2. | Secondary alcohols (i.e. 2-Propanol) | Exposed to sunlight or heat |
| 3. | Alkali metals (lithium, caesium, potassium, rubidium) | Absence of moisture, and exposure on oxygen |
| 4. | Alkaline earth metals (lithium, potassium, caesium, rubidium) | Exposure and heat 300°C or more |
| 5. | Ammonia | Mixing and intensive vaporization |
| 6. | Diethyl ether | Mixing and heat 100°C or more |
| 7. | Benzoic acid | Mixing, pressure |
| 8. | Carbon disulphide | Mixing, 1 atm overpressure, presence of mercury |
| 9. | Hydrogen disulphide | Mixing, and presence of copper |
| 10. | Diborane and diborane tetrafluoride | Mixing and pressure |
| 11. | Dimethoximethane | Mixing and pressure |
| 12. | Dimethil sulphide | Heat at or above 210°C |

TABLE A-1 (continued)

| Potentially Hazardous Material | Physical or Chemical Condition, Could Lead to Explosion |
|---|---|
| 13. Fibrous fabrics | Absorption more than 21% volume |
| 14. Oils, mineral and synthetic | Oxygen pressure at or below 150 psi |
| 15. Halocarbons (Trichloroethane) | Heat 100°C or more and pressure over 54 atm |
| 16. Hydrocarbons* | Various temperature and pressure conditions, extremely hazardous potentials |
| 17. Hydrogen* | Stoichiometric, or leaner mixtures, 17-82 bar prressure |
| 18. Metal hydrates and complex hydrates | 230°C or over, various pressure conditions, accelerated reaction in moist air |
| 19. Non-metal hydrates (tetraborane, sihydrates) | Mixing at reduced pressure atmosphere |
| 20. Polymers (neoprene, foam rubber) | Adiabatic compressive heating, friction with metal fibers, in high speed and pressure $O_2$ stream |
| 21. Rhenium | Mixing and high temperature 300°C or over |
| 22. Metals and Alloys* | Various temperature and pressure conditions, due to heavy oxidation effects |
| 23. $N_2$ (gas) Lithium: Atmospheric gases + metal chlorides; Titanium | The explosive oxidation of gaseous nitrogen in admixture + with ozone |

*The materials, listed in 16, 17 and 22, are the most common cause of accidents, therefore, require individual evaluation for compatibility and material selection before manufacturing and spacing $O_2$ generating systems.

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CABLE AIRPROD · TELEX 84-7416

Air Products

Industrial Gas Division

# Nitrogen Material Safety Data Sheet

| | | |
|---|---|---|
| EMERGENCY PHONE 800—523-9374<br>IN PENNSYLVANIA 800—322-9092 | TRADE NAME AND SYNONYMS<br>Nitrogen, LIN (Liquid only) | CHEMICAL NAME AND SYNONYMS<br>Nitrogen |
| ISSUE DATE AND REVISIONS<br>Issued: 13 April 1977<br>Rev: 16 February 1981 | FORMULA<br>$N_2$ MW: 28.01 | CHEMICAL FAMILY<br>Inert gas |

## HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE

Nitrogen is a simple asphyxiant and has no threshold limit value (TLV).

SYMPTOMS IF INGESTED, CONTACTED WITH SKIN OR VAPOR INHALED

Nitrogen is odorless and nontoxic, but may produce suffocation by diluting the concentration of oxygen in air below levels necessary to support life. PERSONNEL, INCLUDING RESCUE WORKERS, SHOULD NOT ENTER AREAS WHERE THE OXYGEN CONCENTRATION IS BELOW 19%, UNLESS PROVIDED WITH A SELF-CONTAINED BREATHING APPARATUS OR AIR LINE RESPIRATOR. Exposure to oxygen-deficient atmospheres may produce dizziness, nausea, vomiting, loss of consciousness, and death. Death may result from errors in judgement, confusion, or loss of consciousness which prevents self-rescue. At low oxygen concentrations unconsciousness and death may occur in seconds without warning. Extensive tissue damage or burns can result from exposure to liquid nitrogen or cold nitrogen vapors.

TOXICOLOGICAL PROPERTIES

Nitrogen is a simple asphyxiant and constitutes 79% of the air we breathe. Nitrogen does not support life and may produce immediately hazardous atmospheres through the displacement of oxygen. Nitrogen under high pressure can produce narcosis even though oxygen sufficient for life is present.

RECOMMENDED FIRST AID TREATMENT

Persons suffering from lack of oxygen should be moved to areas with normal atmospheres. SELF-CONTAINED BREATHING APPARATUS MAY BE REQUIRED TO PREVENT ASPHYXIATION OF RESCUE WORKERS. Assisted respiration and supplemental oxygen should be given if the victim is not breathing. If cryogenic liquid or cold boil-off gas contacts a worker's skin or eyes, frozen tissues should be flooded or soaked with tepid water (105-115F; 41-46C). DO NOT USE HOT WATER. Cryogenic burns which result in blistering or deeper tissue freezing should be seen promptly by a physician.

## FIRE AND EXPLOSION HAZARD DATA

| | | | | |
|---|---|---|---|---|
| FLASH POINT (Method used)<br>N/A | AUTO IGNITION TEMP<br>N/A | FLAMMABLE LIMITS<br>N/A | LEL<br>N/A | UEL<br>N/A |

EXTINGUISHING MEDIA
N/A

ELECTRICAL CLASSIFICATION
GROUP N/A

SPECIAL FIRE FIGHTING PROCEDURES
N/A

UNUSUAL FIRE AND EXPLOSION HAZARDS
N/A

## PHYSICAL DATA

| | | | |
|---|---|---|---|
| BOILING POINT (°F.)<br>@ 1 atm. -320.5F (-195.8C) | | FREEZING POINT (°F.)<br>@ 1 atm -346.0F (-210.0C) | |
| VAPOR PRESSURE (psia)<br>N/A | | SOLUBILITY IN WATER<br>@ 68F (20C), 1 atm 1.52% by volume | |
| VAPOR DENSITY (lb/cu ft)<br>@ 68F (20C), 1 atm 0.07273 | SPECIFIC GRAVITY (AIR = 1)<br>@ 68F (20C), 1 atm 0.967 | LIQUID DENSITY (lb/cu ft)<br>@ boiling point, 1 atm 50.45 | SPECIFIC GRAVITY ($H_2O$ = 1)<br>@ boiling point, 1 atm 0.808 |

APPEARANCE AND ODOR

Both liquid and gaseous nitrogen are colorless and odorless.

## DISCLAIMER

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Since the Company shall have no control of the use of the product described herein, the Company assumes no liability for loss or damage incurred from the proper or improper use of such product.

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## REACTIVITY DATA

|  |  |  |  |
|---|---|---|---|
| STABILITY<br>Relatively Inert | UNSTABLE |  | CONDITIONS TO AVOID<br>None |
|  | STABLE | X |  |

INCOMPATIBILITY (Materials to avoid)
None

HAZARDOUS DECOMPOSITION PRODUCTS
None

|  |  |  |  |
|---|---|---|---|
| HAZARDOUS POLYMERIZATION | MAY OCCUR |  | CONDITIONS TO AVOID<br>None |
|  | WILL NOT OCCUR | X |  |

## SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Avoid contact of skin with liquid nitrogen or its cold boil-off gas. Flush liquid nitrogen spill with water to disperse. Ventilate enclosed areas to prevent formation of oxygen-deficient atmospheres caused by the evaporation of liquid nitrogen or the release of gaseous nitrogen.

WASTE DISPOSAL METHOD
Allow liquid nitrogen to evaporate in a well ventilated outdoor location remote from work areas. Vent nitrogen gas slowly to a well ventilated outdoor location remote from work areas. Do not attempt to dispose of residual nitrogen in compressed gas cylinders. Return cylinders to Air Products with residual pressure, the cylinder valve tightly closed and valve caps in place.

## SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
Use self-contained breathing apparatus in oxygen-deficient atmospheres. Caution! Respirators will not function. Use may result in asphyxiation.

|  |  |  |
|---|---|---|
| VENTILATION<br>Natural or mechanical where gas is present. | LOCAL EXHAUST | SPECIAL |
|  | MECHANICAL (General) | OTHER<br>Vents should be situated to avoid higher than normal concentration of nitrogen in work areas |

PROTECTIVE GLOVES
(LIN) Loose-fitting gloves of impermeable materials such as leather. Leather work gloves are recommended when handling compressed gas cylinders.

EYE PROTECTION
(LIN) Chemical goggles or safety glasses. Safety glasses are recommended when handling high-pressure cylinders.

OTHER PROTECTIVE EQUIPMENT
None

## SPECIAL PRECAUTIONS*

SPECIAL LABELING INFORMATION
Nitrogen shipments must be in accordance with Department of Transportation (DOT) regulations using DOT "NON-FLAMMABLE GAS" label. Consult DOT regulations for details on the shipping of hazardous materials.

SPECIAL HANDLING RECOMMENDATIONS
Prevent contact of liquid nitrogen or cold boil-off gas with exposed skin. Prevent entrapment of liquid in closed systems. Use only in well ventilated areas. Compressed gas cylinders contain nitrogen at extremely high pressure and should be handled with care. Use a pressure-reducing regulator when connecting to lower pressure piping systems. Secure cylinders when in use. Never use direct flame to heat a compressed gas cylinder. Use a check valve to prevent back flow into storage container. Avoid dragging, rolling, or sliding cylinders, even for a short distance. Use a suitable hand truck. For additional handling recommendations on compressed gas cylinders, consult Compressed Gas Association Pamphlet P-1.

SPECIAL STORAGE RECOMMENDATIONS
Store liquid containers and cylinders in well ventilated areas. Keep cylinders away from sources of heat. Storage should not be in heavy traffic areas to prevent accidental knocking over or damage from passing or falling objects. Valve caps should remain on cylinders not connected for use. Segregate full and empty cylinders. Storage areas should be free of combustible material. Replace the cylinder cap when the cylinder is not in use. Avoid exposure to areas where salt or other corrosive chemicals are present. See Compressed Gas Association Pamphlet P-1 for additional storage recommendations.

SPECIAL PACKAGING RECOMMENDATIONS
Gaseous nitrogen containers meet DOT specifications or American Society of Mechanical Engineers (ASME) codes. Liquid nitrogen is stored in vacuum-insulated containers meeting DOT specifications or ASME codes.

OTHER RECOMMENDATIONS OR PRECAUTIONS
Liquid nitrogen is a cryogenic liquid. Materials of construction must be selected for compatibility with extremely low temperatures. Avoid use of carbon steel and other materials which become brittle at low temperatures. Compressed gas cylinders should not be refilled except by qualified producers of compressed gases. Shipment of a compressed gas cylinder filled without the permission of the owner is a violation of Federal Law. If oxygen-deficient atmospheres are suspected or can occur, use oxygen monitoring equipment to test for oxygen deficient atmospheres.

*Various Government agencies (i.e., Department of Transportation, Occupational Safety and Health Administration, Food and Drug Administration and others) may have specific regulations concerning the transportation handling, storage or use of this product which will not be reflected in this data sheet. The customer should review these regulations to ensure that he is in full compliance.

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**Air Products**

Industrial Gas Division

# Oxyge
# Material Safet
# Data Shee

| | | |
|---|---|---|
| EMERGENCY PHONE 800—523-9374<br>IN PENNSYLVANIA 800—322 9092 | TRADE NAME AND SYNONYMS<br>Oxygen, LOX (Liquid only), GOX (Gas only) | CHEMICAL NAME AND SYNONYMS<br>Oxygen |
| ISSUE DATE AND REVISIONS<br>Issued: 13 April 1977<br>Rev: 16 February 1981 | FORMULA<br>$O_2$ MW: 32.00 | CHEMICAL FAMILY<br>Oxidizing gas |

## HEALTH HAZARD DATA

THRESHOLD LIMIT VALUE
N/A

SYMPTOMS IF INGESTED CONTACTED WITH SKIN, OR VAPOR INHALED
Oxygen is nontoxic under most conditions of use and is necessary to support life. Liquid oxygen or cold gas will freeze tissues and can cause severe cryogenic (extremely low temperature) burns.

TOXICOLOGICAL PROPERTIES
Oxygen is nontoxic under usual conditions of use. Breathing pure oxygen at one atmosphere, however, may produce cough and chest pains within 8-24 hours. Concentrations of 60% may produce these symptoms in several days. At two atmospheres symptoms occur in 2-3 hours.

Partial pressure of oxygen in excess of two atmospheres may produce a variety of central nervous system manifestations including tingling of fingers and toes, visual and hearing disturbances, abnormal sensations, impaired coordination, confusion, muscle twitching, and seizures resembling those of epilepsy. Severe hazards may be present when confusion and impaired judgment lead to operational errors.

Infants exposed to oxygen levels in excess of 35-40% may suffer permanent visual impairment or blindess due to retrolental *fibroplasia.*

RECOMMENDED FIRST AID TREATMENT
If cryogenic liquid or cold boil-off gas contacts a worker's skin or eyes, frozen tissues should be flooded or soaked in tepid water (105-115F; 41-46C). DO NOT USE HOT WATER. Burns which result in blistering or deeper tissue freezing should be seen promptly by a physician.

## FIRE AND EXPLOSION HAZARD DATA

| FLASH POINT (Method used) | AUTO IGNITION TEMP | FLAMMABLE LIMITS | LEL | UEL |
|---|---|---|---|---|
| N/A | N/A | N/A | N/A | N/A |

| EXTINGUISHING MEDIA | ELECTRICAL CLASSIFICATION |
|---|---|
| N/A | GROUP N/A |

SPECIAL FIRE FIGHTING PROCEDURES
Oxygen is nonflammable, but supports and VIGOROUSLY ACCELERATES COMBUSTION of flammables. To fight fires, shut *off sources of oxygen and fight like conventional fire.*

UNUSUAL FIRE AND EXPLOSION HAZARDS
Oxygen is nonflammable, but supports and VIGOROUSLY ACCELERATES COMBUSTION of flammables. Some materials which are noncombustible in air will burn in the presence of oxygen.

## PHYSICAL DATA

| BOILING POINT (°F) | FREEZING POINT (°F) |
|---|---|
| @ 1 atm. -297.3F (-183.0C) | @ 1 atm -361.8F (-218.8C) |

| VAPOR PRESSURE (psia) | SOLUBILITY IN WATER |
|---|---|
| N/A | @ 77F (25C), 1 atm 3.16% by volume |

| VAPOR DENSITY (lb/cu ft) | SPECIFIC GRAVITY (AIR = 1) | LIQUID DENSITY (lb/cu ft) | SPECIFIC GRAVITY ($H_2O$ = 1) |
|---|---|---|---|
| @ 68F (20C), 1 atm 0.08309 | @ 68F (20C), 1 atm 1.10 | @ boiling point, 1 atm 71.21 | @ boiling point, 1 atm 1.14 |

APPEARANCE AND ODOR
Gaseous oxygen is colorless and odorless. Liquid oxygen is pale blue and odorless.

## DISCLAIMER

Information contained in this data sheet is offered without charge for use by technically qualified personnel at their discretion and risk. All statements, technical information and recommendations contained herein are based on tests and data which we *believe to be reliable, but the accuracy or completeness thereof is not guaranteed and no warranty of any kind is made with* respect thereto. This information is not intended as a license to operate under or a recommendation to practice or infringe any patent of this Company or others covering any process, composition of matter or use.

Since the Company shall have no control of the use of the product described herein, the Company assumes no liability for loss or damage incurred from the proper or improper use of such product.

Printed in U.S.A 310-8

## REACTIVITY DATA

| | | | |
|---|---|---|---|
| STABILITY | UNSTABLE | | CONDITIONS TO AVOID<br>Materials which burn in air will burn violently in atmosphere richer than approx 25% oxygen. Some materials will burn in pure oxygen which are nonflammable in air. |
| | STABLE | X | |

INCOMPATIBILITY (Materials to avoid)
All flammables, especially petroleum products, asphalt, other volatile flammables.

| | | | |
|---|---|---|---|
| HAZARDOUS POLYMERIZATION | MAY OCCUR | | CONDITIONS TO AVOID |
| | WILL NOT OCCUR | X | None |

## SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED
Prevent liquid oxygen from contacting grease, oil, asphalt or combustibles. Ventilate area to evaporate and disperse oxygen. Flush area with large quantities of water. DO NOT ENTER areas of high oxygen concentration, which can saturate clothing and increase its flammability. Avoid smoking and contact with sources of ignition after exposure to concentration of oxygen higher than the normal atmosphere.

WASTE DISPOSAL METHOD
Allow liquid oxygen to evaporate in a well ventilated outdoor area. Vent oxygen gas to outside location. Disposal site should be remote from work areas, open flames or sources of ignition and combustibles. Flushing with water will increase the vaporization rate of the liquid. Do not attempt to dispose of residual oxygen in compressed gas cylinders. Return cylinders to Air Products with residual pressure, the cylinder valve tightly closed and valve cap in place.

## SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION (Specify type)
N/A

| | | |
|---|---|---|
| VENTILATION<br>Prevent accumulation with natural or forced air. | LOCAL EXHAUST | OTHER<br>Vents should be situated to avoid higher than normal concentration of oxygen in work areas. |
| | MECHANICAL (General) | |
| | SPECIAL | |

PROTECTIVE GLOVES
(Liquid) Loose-fitting gloves of impermeable material, such as leather. (Gas) Leather work gloves are recommended when handling compressed gas cylinders.

EYE PROTECTION
(Liquid) Chemical goggles or safety glasses. (Gas) Safety glasses are recommended when handling high pressure cylinders.

OTHER PROTECTIVE EQUIPMENT
N/A

## SPECIAL PRECAUTIONS*

SPECIAL LABELING INFORMATION
*Oxygen shipment must be in accordance with Department of Transportation (DOT) regulations* using DOT "OXIDIZER" label. Consult DOT regulations for details on the shipment of hazardous materials.

SPECIAL HANDLING RECOMMENDATIONS
Prevent contact of liquid oxygen with exposed skin. Prevent entrapment of liquid in closed systems. Use only in well ventilated areas. Cleanliness and compatibility of materials in contact with oxygen are essential especially internal parts of piping systems. Some elastomers (o-rings, valve seats, etc.) are not compatible with oxygen. Open oxygen valves slowly. Compressed gas cylinders contain oxygen at extremely high pressure and should be handled with care. Use a pressure-reducing regulator when connecting to lower pressure piping systems. Secure cylinders when in use. Never use direct flame to heat a compressed gas cylinder. Use a check valve to prevent back flow into storage containers. Avoid dragging, rolling, or sliding cylinders, even for a short distance. Use a suitable hand truck. For additional handling recommendations on compressed gas cylinders, consult *Compressed Gas Association Pamphlet P-1*.

SPECIAL STORAGE RECOMMENDATIONS
Store liquid containers and cylinders in well ventilated areas. Do not store cylinders of oxygen within 20 ft. of flammable or combustible materials, especially oil or grease. Keep cylinders away from source of heat. Storage should not be in heavy traffic areas to prevent accidental knocking over or damage from passing or falling objects. Valve caps should remain on cylinders not connected for use. Never lubricate valves or cylinder caps. Segregate full and empty cylinders. Storage areas should be free of combustible material. Avoid exposure to areas where salt or other corrosive chemicals are present. See Compressed Gas Association Pamphlet P-1 for *additional storage recommendations*.

SPECIAL PACKAGING RECOMMENDATIONS
Gaseous oxygen containers meet DOT specifications or American Society of Mechanical Engineers (ASME) codes. Liquid oxygen *is stored in vacuum-insulated containers meeting DOT specifications or ASME codes*.

OTHER RECOMMENDATIONS OR PRECAUTIONS
Oxygen is not to be used as a substitute for compressed air. Applications such as cleaning, dusting, powering pneumatic tools, etc., are not safe due to lubricating oils and other materials present. Use only with equipment specifically designed and cleaned for oxygen service. Consult Compressed Gas Association Pamphlet G-4.1, "Cleaning Equipment for Oxygen Service," for details. Liquid oxygen is cryogenic liquid. Materials of construction must be selected for compatibility with extremely low temperatures. Avoid use of carbon steel and other materials which become brittle at low temperatures. Compressed gas cylinders should not be refilled except by qualified producers of compressed gases. Shipment of a compressed gas cylinder filled without the permission of the owner is a violation of Federal Law. If oxygen concentrations exceeding 25% are suspected or can occur, use oxygen monitoring equipment to test for oxygen-enriched atmospheres.

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*Various Government agencies (i.e., Department of Transportation, Occupational Safety and Health Administration, Food and Drug Administration and others) may have specific regulations concerning the transportation, handling, storage or use of this product which will not be reflected in this *data sheet*. The customer should review these regulations to ensure that he is in full compliance.

# Gaseous Nitrogen

## General

Gaseous nitrogen is inert, colorless, odorless, tasteless, noncorrosive, and nonflammable.

Nitrogen is inert except when heated to very high temperatures, when it is combined with metals to form nitrides, oxygen to form oxides of nitrogen, and when combined with hydrogen in the presence of catalysts to form ammonia.

Since nitrogen is noncorrosive, special materials of construction are not required. Vessels and piping should be designed to the American Society of Mechanical Engineers (ASME) or Department of Transportation (DOT) codes for the pressure and temperatures involved.

Nitrogen may be compressed into cylinders by water lubricated, oil lubricated, or dry compression systems. The amount of nitrogen in a cylinder is determined by the pressure and temperature capacity chart for a specific size cylinder. The higher the pressure, the more nitrogen contained in the cylinder.

The molecular symbol for nitrogen is $N_2$.

## Toxicity

Nitrogen is nontoxic but can act as an asphyxiant by displacing the necessary amount of oxygen in the air to sustain life.

## Manufacture

Nitrogen is produced by the fractional distillation of liquefied air.

## Uses

Nitrogen is used as an inert gas in electrical systems, the chemical industry, and the food packaging industry. Nitrogen also finds extensive use as an inert atmosphere, and in the filling of some incandescent lamps.

## Containers

Gaseous nitrogen is shipped and stored in hollow, steel cylinders or tubes.

The cylinder has a concave base, which allows the cylinder to stand upright, and is tapered to a small opening at the top. The small opening on the top. The tapered or open end is threaded to receive a cylinder valve or another suitable outlet connection. Safety relief devices are part of the cylinder valve or the outlet connections. A threaded neckring is secured to the tapered end of the cylinder to allow a protective cylinder cap to be installed.

The tube is tapered on both ends. Each end has threaded openings to which connections, valves, or safety devices are attached. The amount of nitrogen that can be contained in a tube is dependent on the water volume and service pressure of the tube.

Cylinders may be used individually or in groups. When in groups, the cylinders should be piped together, for stationary storage or to form portable banks. Tubes are generally mounted on truck-trailer chassis, railroad car beds, or placed at stationary locations when large amounts of nitrogen are needed.

## Cylinders and Tubes

Cylinders and tubes are manufactured according to Department of Transportation-3A or DOT-3AA specifications (formerly Interstate Commerce Commission ICC specifications). Cylinders and tubes in nitrogen service are hydrostatically tested upon manufacture, and every ten years thereafter, at 5/3 times the service pressure.

## Valves

The Compressed Gas Association and the American National Standards Institute have adopted a thread size of 0.965 inch—14 internal right hand threads per inch designated as valve connection No. 580 (Figure 1) for nitrogen.

## Properties

| | |
|---|---|
| Molecular Weight | 28.01 |
| Boiling Point @ 1 atm | -320.5F (-195.8C) |
| Freezing Point @ 1 atm | -346.0F (-210.0C) |
| Critical Temperature | -232.4F (-146.9C) |
| Critical Pressure | 493 psia (33.5 atm) |
| Density, Liquid @ B.P., 1 atm | 50.45 lbs./cu.ft. |
| Density, Gas @ 68F (20C), 1 atm | 0.07273 lbs./cu.ft. |
| Specific Gravity, Gas (Air = 1) @ 68F (20C), 1 atm | 0.967 |
| Specific Gravity, Liquid @ B.P., 1 atm | 0.808 |
| Specific Volume @ 68F (20C), 1 atm | 13.75 cu.ft./lb. |
| Latent Heat of Vaporization | 2399 Btu/lb. mole |
| Expansion Ratio, Liquid to Gas, B.P. to 68F (20C) | 1 to 694 |

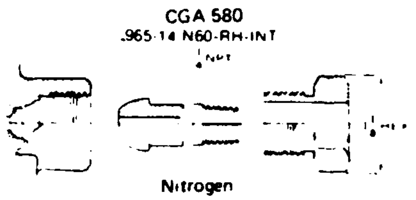


FIGURE 1

## Safety Devices

Safety devices help provide protection against excessive temperature and pressure in the container. Safety devices are usually part of the cylinder valves or attachments to the tubes. These devices take the form of frangible discs and frangible discs with fusible plugs.

## Identification

Each cylinder or tube is identified between the neckring and shoulder by:

(1) DOT-3A or DOT-3AA—the specifications controlling the manufacture of the container followed by the service pressure rating in pounds per square inch.

(2) Serial number of the container

(3) Manufacturer's symbol and the owner's symbol

(4) Month and year of the container manufacture

(5) Month and year of subsequent 5-year or 10-year hydrostatic retest of the container

(6) Original inspector's identification stamp

The neckring usually is identified by the owner's and manufacturer's symbol.

## Shipment of Nitrogen Cylinders

The shipment of nitrogen cylinders by surface transportation must conform to Department of Transportation Regulations as set forth in the Code of Federal Regulations Title 49, which describes the labeling and identification required. A DOT 4" x 4" green nonflammable label or tag is required for common carrier shipments. Figure 2 illustrates the label (black printing on green) that is required for shipment of nitrogen by common carrier.

FIGURE 2

Shipments by air must conform with Title 49 Code of Federal Regulations (FAA Regulations).

49 CFR is the official publication of the Department of Transportation concerning transport of hazardous materials by any mode. These regulations are also found in the Civil Aeronautics Board No. 82 Restricted Articles Tariff No. 6-D, but the designation of this tariff may change from time to time. The weight limitations for shipping on passenger or cargo aircraft remain the same.

### Sizes of Cylinders

| DOT or ICC Type | Dimensions<br>O.D. (In.) | Length (In.) | Water Volume (Cu. In.) | Capacity Std. Press. (Cu. Ft.) | Capacity at 10% Overpress.* (Cu. Ft.) |
|---|---|---|---|---|---|
| 3A2015 & 3AA2015 | 5 [illegible] | 32 | 678 | 51 | 57 |
| 3A2015 & 3AA2015 | 5³⁄₁₆ | 37 | 678 | 51 | 57 |
| 3A2015 & 3AA2015 | 7 | 32½ | 985 | 75 | 82 |
| 3A2015 & 3AA2015 | 7 | 43 | 1337 | 102 | 111 |
| 3AA2265 | 7 | 43 | 1337 | 115 | 125 |
| 3AA2015 | 7⅜ | 46⅛ | 1660 | 126 | 138 |
| 3A2015 & 3AA2015 | 9 | 51 | 2675 | 203 | 222 |
| 3AA2265 | 9 | 51 | 2675 | 230 | 251 |
| 3AA2400 | 9¼ | 55 | 3025 | 274 | 301 |

*DOT Regulation 173.302 (c)

## SAFETY CONSIDERATIONS

The hazards associated with nitrogen are asphyxiation and the high pressure of the gas in containers and systems.

### Buildings

(1) Provide adequate ventilation where nitrogen is being used.

(2) Test the atmosphere in confined work areas for oxygen

# Gaseous Oxygen

## General

Gaseous oxygen is colorless, odorless, tasteless, and nonflammable. Oxygen supports life and readily combines with other elements. It is a strong oxidizer, and an oxidizer is necessary to support combustion.

Oxygen will react with nearly all organic materials and metals. Materials which burn easily in air usually burn more vigorously in oxygen. Equipment used in oxygen service must be designed to utilize materials that have high ignition temperatures and are nonreactive with oxygen under the service conditions of the contemplated system. Vessels should be designed to American Society of Mechanical Engineers (ASME) or Department of Transportation (DOT) codes for the pressures and temperatures involved.

The amount of oxygen contained in a cylinder is determined by the pressure and temperature as referenced to a capacity chart for a specific-sized cylinder. Generally, the higher the pressure, the more oxygen is contained in the cylinder. The molecular symbol for oxygen is $O_2$.

## Toxicity

Oxygen is nontoxic under usual conditions. Breathing pure oxygen at one atmosphere, however, may produce coughing and chest pains within 8-24 hours. Concentrations of 60% may produce these symptoms in several days. At two atmospheres pressure, the above symptoms occur in 2-3 hours. Partial pressures of oxygen in excess of two atmospheres may produce a variety of central nervous system manifestations including tingling of fingers and toes, visual and auditory disturbances, abnormal sensations, impaired coordination, confusion, muscle twitching, and epileptiform seizures. Severe hazards may be present when confusion and impaired judgment lead to operational errors.

Infants exposed to oxygen levels in excess of 35-40% may suffer permanent visual impairment or blindness due to retrolental fibroplasia.

## Manufacture

The principal commercial source of oxygen is from the distillation of liquefied air.

[illegible]

Latent Heat of Vaporization [illegible]

Solubility in Water [illegible] (25°C) [illegible] atm [illegible] volume

## Uses

The principal uses of oxygen stem from its strong oxidizing and life sustaining properties.

Oxygen is used in metal industries in conjunction with acetylene and other fuel gases in metal cutting, welding, hardening, scarfing, cleaning, and dehydrating. Oxygen is also used extensively in the manufacture of steel and the treatment of wastewater.

In the chemical and petroleum industries, oxygen is used in the production of synthesis gas from coal, natural gas, or liquid fuels used to produce gasoline, methanol and ammonia, and in the OXO process for the production of aldehydes and alcohols. Oxygen is similarly used to produce acetylene by the partial oxidation of hydrocarbons. It is used in the manufacture of nitric acid by the catalytic oxidation of ammonia and in the production of ethylene and propylene oxides.

## Containers

Gaseous oxygen is shipped and stored in hollow, steel cylinders or tubes. The cylinder has a concave base which allows the cylinder to stand upright and is tapered to a small opening on the top. The tapered or open end is threaded to receive a cylinder valve or other suitable connection. Safety relief devices are part of the cylinder valve or the outlet connections. A threaded neckring is secured to the tapered end of the cylinder to allow a protective cylinder cap to be installed.

The tube is tapered on both ends. Each end has threaded openings to which connections, valves, or safety devices are attached. The amount of oxygen that can be contained in a tube is dependent on the water volume and service pressure of the tube.

Cylinders may be used individually or in groups. When in groups, the cylinders should be piped together for stationary storage or to form portable banks. Tubes are generally mounted on truck-trailer chassis, railroad car beds, or placed at stationary locations when large amounts of oxygen are needed.

## Cylinders and Tubes

Cylinders and tubes are manufactured according to DOT-3A or DOT-3AA specifications, although there are other DOT specifications that can be used for oxygen. Cylinders and tubes used in oxygen service are hydrostatically tested upon manufacture and every ten years thereafter, at 5/3 times the service pressure.

## Valves

The Compressed Gas Association and the American National Standard Institute have adopted a thread size of 0.903 inch - 14 external right-hand threads per inch, designated as valve connection No. 540 (Figure 1) for oxygen.

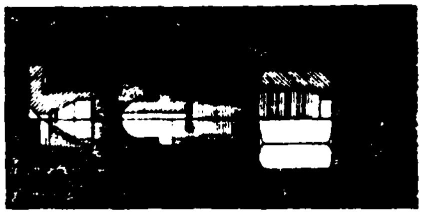


FIGURE 1

## Safety Devices

Safety devices provide protection against excessive temperature and pressure in the container. Safety devices are usually part of the cylinder valves or attachments to the tubes. These devices take the form of frangible discs and frangible discs with fusible plugs.

## Identification

Each cylinder or tube is identified between the neckring and shoulder by:

(1) DOT-3A, DOT-3AA or other DOT oxygen specifications that control the manufacture of the container, followed by the service pressure rating in pounds per square inch.

(2) Serial number of the container.

(3) Manufacturer's symbol and the owner's symbol.

(4) Month and year of the container manufacture.

(5) Month and year of subsequent hydrostatic retest of the container.

(6) Original inspector's identification stamp.

The neckring is usually identified by the owner's symbol or name.

## Shipment of Oxygen Cylinders

The shipment of oxygen cylinders by surface transportation must conform to Department of Transportation Regulations as set forth in the Code of Federal Regulations, Title 49, which describes the labeling and identification required. A yellow label (black printing on yellow) with the word Oxidizer is used for oxygen shipments. Figure 2 illustrates the label that is required for shipment of oxygen by common carrier.

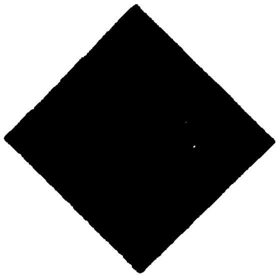


FIGURE 2

## Safety Considerations

Fire is the primary hazard associated with gaseous oxygen; oxygen is nonflammable but readily supports combustion. Explosions may occur in locations where a mixture of fuel gas and oxygen may collect. Clean and compatible materials are essential when using and storing oxygen. Eliminate sources of fuel and ignition from oxygen systems.

## Buildings

(1) Provide adequate ventilation.

(2) Keep work areas clear of combustible materials.

(3) Post signs in the work areas indicating hazards.

(4) Test the atmospheres in confined work areas for oxygen content. Materials which burn in air generally burn more violently and sometimes explosively in oxygen. Oxygen in excess of 25% concentration increases the hazard exposure to personnel and material.

## Handling and Storage

(1) Never drop cylinders or permit them to strike each other violently.

(2) Cylinders should be assigned a definite area for storage. The area should be dry, cool, well ventilated, and preferably fire resistant. Keep cylinders protected from excessive temperatures by storing them away from radiators or other sources of heat

# Oxygen

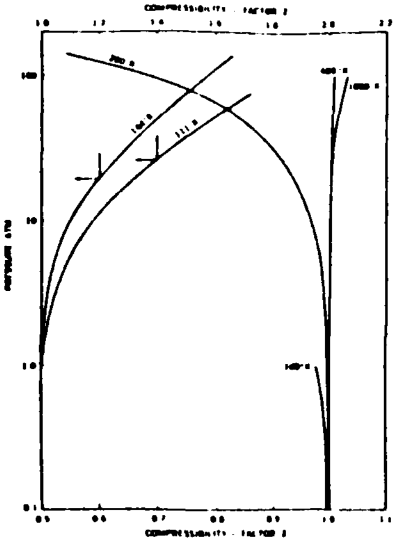
## Oxygen References

1. Thermodynamic and transport properties for the $N_2 + O_2$ system Roger A Svehla Lewis Research Center NASA-SP 3011 1964

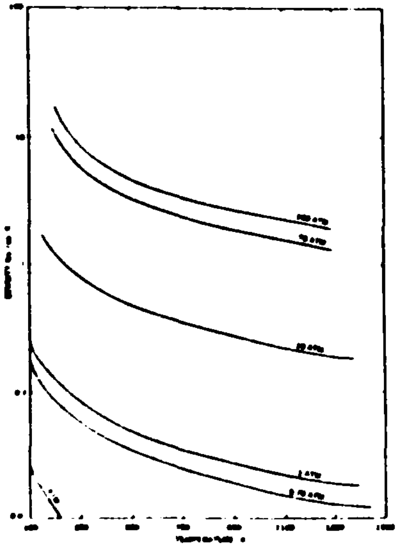
2. A compendium of the properties of materials at low temperatures Wadd Technical Report 60-56 Dec 1961 Richard B Stewart and Victor J Johnson National Bureau of Standards Boulder Colorado General Editors

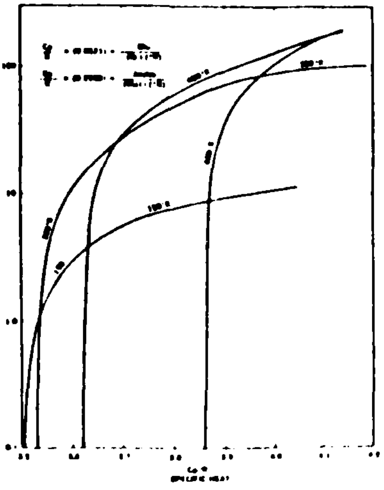
3. Tables of Thermodynamic and Transport Properties of air argon carbon dioxide carbon monoxide hydrogen nitrogen oxygen and steam Pergamon Press 1960 (was originally published as NBS Circular 564 1960)

4. Compressed Gas Handbook edited by J S Kunkle S D Wilson & R A Cota John F Kennedy Space Center-NASA-SP 3045



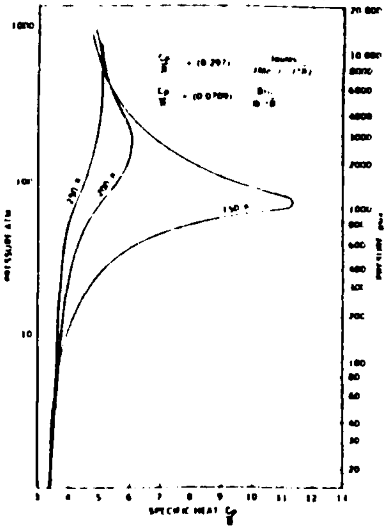
*Compressibility Factor - Oxygen*



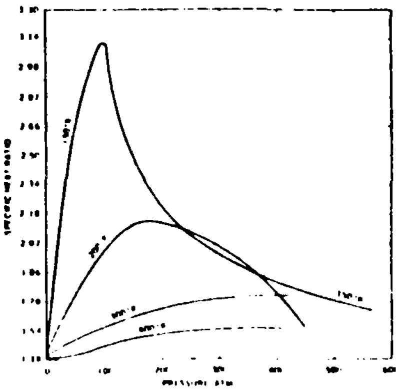


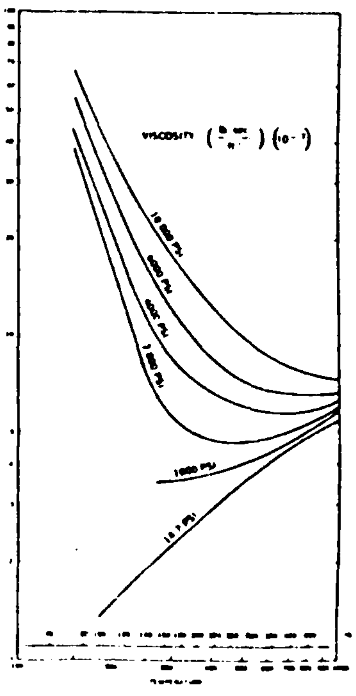
# Nitrogen

Ratio Specific heat-temperature Nitrogen



Ratio Specific heat ratio Nitrogen





Mass Viscosity-temperature Nitrogen

# FIXED POINT PROPERTIES OF OXYGEN

From NASA SP-3071, "ASRDI Oxygen Technology Survey, Thermophysical Properties", Volume I (1972), edited by Hans M. Roder and Lloyd A. Weber. This NASA publication contains an extensive bibliography and a discussion of basis for selection of these data for oxygen. The publication is available from the National Technical Information Service, Springfield, Virginia 22151.

| PROPERTIES ↓ | CONDITIONS → | Triple Point |  |  | Normal Boiling Point |  | Critical Point †† | Standard Conditions |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  | Solid | Liquid | Vapor | Liquid | Vapor |  | STP (0°C) | NTP (20°C) |
| Temperature (K) |  |  | 54.351 |  | 90.180 |  | 154.576 | 273.15 | 293.15 |
| Pressure (mmHg) |  |  | 1.138 |  | 760 |  | 37,823 | 760 | 760 |
| Density (mole/cm$^3$) x $10^3$ |  | 42.46 | 40.83 | 0.000336 | 35.65 | 0.1399 | 13.63 | 0.04466 | 0.04160 |
| Specific Volume (cm$^3$/mole) x $10^{-3}$ |  | 0.02355 | 0.02449 | 2975 | 0.028047 | 7.1501 | 0.07337 | 22.392 | 24.038 |
| Compressibility Factor, $Z = \frac{PV}{RT}$ |  | – | 0.0000082 | 0.9986 | 0.00379 | 0.9662 | 0.2879 | 0.9990 | 0.9992 |
| Heats of Fusion & Vaporization (J/mole) |  | 444.8 | 7761.4 |  | 6812.3 |  | 0 | – | – |
| Specific Heat | $C_s$, @saturation | 46.07 | 53.313 | -108.7 | 54.14 | -53.2 | (very large) | – | – |
| (J/mole-K) | $C_p$, @ constant pressure | – | 53.27 | 29.13 | 54.28 | 30.77 | (very large) | 29.33 | 29.40 |
|  | $C_v$, @ constant volume | – | 35.65 | 20.81 | 29.64 | 21.28 | (38.7) | 20.96 | 21.04 |
| Specific Heat Ratio, $\gamma = C_p/C_v$ |  | – | 1.494 | 1.400 | 1.832 | 1.446 | (large) | 1.40 | 1.40 |
| Enthalpy (J/mole) |  | -6634.4 | -6189.6 | 1571.8 | -4270.3 | 2542.0 | 1032.2 | 7937.8 | 8525.1 |
| Internal Energy (J/mole) |  | -6634.4 | -6189.6 | 1120.0 | -4273.1 | 1817.5 | 662.3 | 5668.9 | 6089.5 |
| Entropy (J/mole-K) |  | 58.92 | 67.11 | 209.54 | 94.17 | 169.68 | 134.42 | 202.4 | 204.5 |
| Velocity of Sound (m/sec) |  |  | 1159 | 141 | 903 | 178 | 164 | 315 | 326 |
| Viscosity, $\mu$ | (N-sec/m$^2$) x $10^3$ | – | 0.6194 | 0.003914 | 0.1958 | 0.00685 | (0.031) | 0.01924 | 0.02036 |
|  | (centipoise)‡‡ | – | 0.6194 | 0.003914 | 0.1958 | 0.00685 | (0.031) | 0.01924 | 0.02036 |
| Thermal Conductivity (mW/cm-K), k |  |  | 1.929 | 0.04826 | 1.515 | 0.08544 | (*) | 0.2428 | 0.2575 |
| Prandtl Number, $N_{pr} = \mu C_p/k$ |  | – | 5.344 | 0.7392 | 2.193 | 0.7714 |  | 0.7259 | 0.7265 |
| Dielectric Constant, $\epsilon$ |  | (1.614) | 1.5687 | 1.000004 | 1.4870 | 1.00166 | 1.17082 | 1.00053 | 1.00049 |
| Index of Refraction, $n = \sqrt{\epsilon}$ † |  | (1.271) | 1.2525 | 1.000002 | 1.219 | 1.00083 | 1.0820 | 1.00027 | 1.00025 |
| Surface Tension (N/m) x $10^3$ |  | – | 22.65 | – | 13.20 | – | 0 | – | – |
| Equiv. Vol./Vol. Liquid at NBT |  | 0.8397 | 0.8732 | 106.068 | 1 | 254.9 | 2.616 | 798.4 | 857.1 |

† Long Wavelengths
* Anomalously Large

Gas Constant: R = 62, 365.4 cm$^3$-mm Hg/mole-K$^1$
†† Values in parenthesis are estimates

Molecular Weight = 31.9988$^3$
"mole" = gram mole
‡‡ Units for poise are: g/cm-sec

## APPENDIX B

## PARTIAL LIST OF STANDARD REQUIREMENTS FOR DESIGN, BUILD AND TEST GAS GENERATION EQUIPMENT

The following list in numerical order is a sample of standards, to be considered in conjunction with construction and test/maintenance practice of gas generation systems. To complete a standard list, it is necessary to determine the type of a system (PSAG, Cryogenic, Etc.) will be employed. Before applying any of the listed standards, they should be checked and updated, if necessary.

| SPECIFICATION/STANDARD CODE | SHORT FORM OF THE TITLE |
|---|---|
| MIL-STD-167 (11) | Mech. Vibration of Shipboard Equipment |
| MIL-STD-721 | Definition of Effectivness |
| MIL-STD-781 | Distribution and Reliability Test |
| MIL-STD-882 | Safety Control Devices |
| MIL-E-917 D | Electric Power Equip. Basic Requirements |
| MIL-D-1000 A | Drawings, Engineering and Associated List |
| MIL-STD-1008 | Engineering Drawing Practices |
| MIL-B-5087 | Standard Tubing |
| MIL-T-5542 | Threaded Fittings |
| MIL-T-7003 | Cleaning Solvent |
| MIL-T-8506 | Corrosion Resistant Tubing |
| MIL-S-8805-3 | Press to Test |
| MIL-G-19053 | Quantity Indicators |
| MIL-C-19803 | Converter Mounting Bracket |
| MIL-H-22343 | Converter, Metal Housing |
| MIL-P-25508 C | Propulsion Oxygen |
| MIL-L-25567 | Leak Test Compound |
| MIL-V-25961 | Ventillation Valve |
| MIL-V-25962 | Drain Valve |
| MIL-D-26393 | Converter |
| MIL-H-26626 | Teflon Hose |
| MIL-O-27210 | Aviators Breathing Oxygen |

| SPECIFICATION/STANDARD CODE | SHORT FORM OF THE TITLE |
|---|---|
| MIL-T-27730 | Threaded Components |
| MIL-P-27401 A | 40 Micron Filter For Nitrogen |
| MIL-V-33650 | Internal Straight Threads |
| ASME Code VIII | Boiler and Pressure Vessel Code |
| SAE AIR 822 | Oxygen for General Aviation Aircraft |
| SAE AIR 825 | Oxygen for Aircrafts |
| SAE AIR 1059 | Transportation and Maintenance of Pressurized cylinders |
| SAE AIR 1176 | Oxygen System Components |
| SAE AIR 1892 | Oxygen System Maintenance Guide |
| AFTO 42-C-1-11 | Cleaning and Inspection for GOX and LOX |
| NFPA No. 410 B | Fire Protection for Oxygen Systems |
| NAVAIR 00-65-502 | Reliability Engineering Handbook |
| ASTM-P-10-11-12 | 1982 Annual Handbook of ASTM Standards |

# PROPERTIES OF LOW-TEMPERATURE STEELS*

| Grade | Temperature, °F °K=(5/9) (°F+459.7) | Yield Strength 0.2% Offset, psi 1 psi=700 kg/m² | Ultimate Tensile Strength, psi | Elongation in 2 in. % | Charpy Impact, V-notch, ft-lb. 1 ft-lb = 0.138 kg-m | Thermal Conductivity Btu ft/hr ft² °F Btu ft/hr ft² °F= 1.73 J/m s°K |
|---|---|---|---|---|---|---|
| 301 | + 70 | 50,000 | 110,000 | 40 | 95 | 8.6 |
| 302 | + 70 | 35,000 | 95,000 | 68 | 110 to 120 | |
| | −100 | 52,000 | 160,000 | 53 | 113 | |
| | −320 | 80,000 | 230,000 | 35 | 100 to 120 | |
| | −423 | 125,000 | 268,000 | 25 | — | |
| 303 | + 70 | 33,000 | 100,000 | 40 | 85 | 9.3 |
| 304 | + 75 | 33,000 | 85,000 | 60 | | 9.75 |
| | −320 | 57,000 | 205,000 | 43 | | |
| | −425 | 63,700 | 244,500 | 48 | 91 | |
| 304L | + 75 | 28,000 | 85,000 | 60 | | 9.75 |
| | −320 | 35,000 | 57,000 | 42 | 67 | |
| | −425 | 33,900 | 63,700 | 41 | 66 | |
| 310 | + 70 | 35,000 | 80,000 | 60 | 90 to 100 | 7.6 |
| | −100 | 40,000 | 100,000 | 55 | 90 | |
| | −320 | 70,900 | 150,500 | 54 | 85 | |
| | −413 | 95,500 | 180,500 | 56 | — | |
| 316 | + 70 | 35,000 | 84,000 | 70 | 110 | 7.87 |
| | −100 | 48,000 | 120,000 | 65 | 110 | |
| | −320 | 75,000 | 185,000 | 58 | 110 | |
| | −423 | 84,000 | 210,000 | 55 | — | |
| 321 | + 70 | 38,000 | 90,000 | 60 | 110 to 125 | 7.74 |
| | −100 | 50,000 | 140,000 | 49 | 120 to 170 | |
| | −320 | 68,000 | 210,000 | 43 | 110 | |
| | −432 | 92,000 | 238,000 | 35 | — | |
| 347 | + 70 | 38,000 | 91,000 | 62 | 85 to 110 | 16.0 |
| | −100 | 45,000 | 140,000 | 53 | 70 to 125 | |
| | −320 | 50,000 | 195,000 | 42 | 85 to 105 | |
| | −423 | 65,000 | 230,000 | 40 | 60 | |
| 203<br>2¼% Ni | + 70 | 40,000 | 70,000 | 23 | 80 | 22.2 |
| 3½% Ni | + 70 | 40,000 | 70,000 | 23 | 80 | 21.1 |
| A-353<br>9% Ni | + 70 | 65,000 | 95,000 | 20 | 110 | 15.7 |
| Full Hard 301 | + 78 | 183,000 | 205,000 | 6 | | |
| | −320 | 215,000 | 302,000 | 20 | | |
| | −423 | 250,000 | 340,000 | 15 | | |
| Full Hard 304L | + 78 | 158,000 | 176,000 | 6 | | |
| | −100 | 186,000 | 198,000 | 5 | | |
| | −320 | 187,000 | 251,000 | 33 | | |
| | −423 | 231,000 | 279,000 | 1 | | |
| Full Hard 310 | + 78 | 153,000 | 174,000 | 3 | | |
| | −320 | 205,000 | 233,000 | 17 | | |
| | −423 | 232,000 | 278,000 | 18 | | |

*Specific Heat at 70°F 0.012 to 0.08 Btu/lb °F
Density 0.29 lb/in³
Mean Coef. of Thermal Expansion 5.7 to 9.2 x $10^{-6}$ in/in °F

# APPENDIX C

## PARTIAL LIST OF MANUFACTURERS AND SUPPLIERS OF OXYGEN/NITROGEN GENERATING SYSTEMS

| | Company Name and Address | Phone Number |
|---|---|---|
| 1. | Gas Equipment Engineering Corporation<br>1240 Oronoque Road<br>Milford, Connecticut 06460 | (203) 874-6786 |
| 2. | Union Carbide Corporation Linde Division*<br>270 Park Avenue<br>New York, New York 10017 | (212) 551-2345 |
| 3. | Air Products & Chemical, Inc.*<br>P.O. Box 538<br>Allentown, Pennsylvania 18105 | (215) 481-8148 |
| 4. | Trane International Corporation<br>La Crosse, Wisconsin 54601 | (608) 787-2000 |
| 5. | Palley/s Corporation<br>2263 E. Vernon Avenue, Dept. CIG-63<br>Los Angeles, California 90058 | (213) 692-7501 |
| 6. | Rockwell International - Dept. G-314<br>400 N. Lexington Avenue<br>Pittsburgh, Pennsylvania 75208 | (412) 565-2000 |
| 7. | Air Research Manufacturing Company<br>2525 West 1903<br>Torrance, California 90509 | (213) 323-9500 |
| 8. | N. V. Philips Gloeilampenfabrieken<br>Cry-Dept. Building TQ III-2<br>Eindhoven, The Netherlands | |
| 9. | C. M. Kemp Manufacturing Company*<br>490 Baltimore-Annapolis Boulevard<br>Glen Burnie, Maryland 21061 | (301) 761-5100 |
| 10. | Normal Air Garrett, Ltd.<br>Yowille Sommerset, BE-20.2YD<br>United Kingdom | 44 935 5181 |
| 11. | Bendix (Litton) Corporation*<br>Lifesupport Division<br>Davenport, Indiana | (319) 383-6000 |

*Suppliers for PSA systems

APPENDIX C (continued)

| | Company Name and Address | Phone Number |
|---|---|---|
| 12. | AIRCO Corporation<br>1900 Main Street<br>Irvine, California 92664 | (714) 540-3010 |
| 13. | Applied Engineering Company<br>P.O. Box 1327<br>Orangeburg, South California 29114 | (803) 534-2424 |
| 14. | Stone and Webster Engineering Corporation<br>225 Franklin Street<br>Boston, Massachusetts 02107 | (617) 434-7950 |
| 15. | Sumitomo Shoji Kaisha, Ltd.<br>2-2 1-Chome Ciyoda-ku<br>Tokyo, Japan | 06 217 6043 |

Printed in U.S.A. 310-812

Number

540-3010

534-2424

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O-CENTERS, INC.

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