CRYOGENS AND GASES:

TESTING METHODS AND STANDARDS DEVELOPMENT

ASTM STP 537

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CRYOGENS AND GASES: TESTING METHODS AND STANDARDS DEVELOPMENT

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Foreword

The Symposium on Cryogens and Gases: Testing Methods and Standards Development was given at the Seventy-fifth Annual Meeting of the American Society for Testing and Materials held in Los Angeles, Calif., 25–30 June 1972. Committee F-7 on Aerospace Industry Methods sponsored the symposium. R. W. Vance, Cryogenic Society of America, served as symposium chairman, and M. C. Miyaji, General Dynamics, was co-chairman. R. E. Biever, Cryogenic Distributors, presided at the two sessions.

Related
ASTM Publications

Fracture Toughness Tests at Cryogenic Temperatures (1971), $5.00 (04-496000-30)

Contents

Introduction

In the June and August 1971 issues of *Materials Research and Standards,* a forum was provided by the American Society for Testing and Materials (ASTM), in conjunction with the Cryogenic Society of America (CSA), so that cryogenic standards could be established. Nine papers describing the progress being made on solving problems in the cryogenic region, aimed essentially at work being conducted by Committee F-7, were published.

We have come a long way since the first attempt in 1967 in development procedures, and now this book describes the efforts being made, not only in support of the aerospace, but also in support of nondefense industries. ASTM and CSA are becoming the focal points for standards as they now impact on the entire cryogenic industry.

The need for standards is perfectly clear as the nation begins to solve the pollution and energy crises. The base for developing these necessary standards was provided by ASTM in their charter for Committee F-7. This has been expanded as described by the papers on "Cryogenics" in *Materials Research & Standards.*

Because of the favorable reaction to the special issues on cryogenics, it was decided to have a joint ASTM-CSA seminar at the Seventy-fifth Annunual Meeting of ASTM held in June 1972 in Los Angeles, Calif. The papers in this special technical publication (STP) were prepared not only to show the state of the art, which pointed out the lack of standards, but also emphasized the need for immediate action to develop usable enforceable standards.

This STP lucidly shows the problems in the food industry, which is now a major facet of cryogenics, stressing the need for standards with strict controls necessary for food handlers and processors. The controls now existing are inadequate but Appleman et al point out the urgency for closer cooperation between ASTM, the U. S. Department of Agriculture, and those industries providing cryogenic food processing equipment. Similarly, the impact of lack of standards on the shipment and use of liquefied natural gas (LNG) in motor vehicle systems, including regulations now in effect by the California State Highway Department, are described by R. K. Johnson. ASTM however, should not limit itself to LNG problems as compressed natural gas (CNG) is also an energy source for motor vehicles. This work is associated with air pollution controls.

Sometimes it is easy to overlook the implications of standards on design consideration and equipment. Some aspects of these problems have been provided by Leonard and McCarthy to give a complete picture showing how fluid standards impact on equipment and equipment testing.

As standards are developed, the sensitivity and reaction intensity of propellant or combustible combinations such as liquid oxygen (LOX)-LNG will be very valuable. The latest available information on these phenomena have been provided by Blackstone et al, with details of tests and analytical procedures. As a guide to Committee F-7, the current Air Force specifications for cryogenic propellants and pressurizing gases with details of the current assay procedures have been provided. These specifications described by Forbes have been used for procurement but with help and "massaging" by Committee F-7 can be modified to become ASTM standards. Also, in support of Committee F-7, a complete bibliography of the thermodynamic and transport properties of cryogenic fluids by V. J. Johnson has been included. It is a survey article that shows where information on these properties can be found for helium, hydrogen, argon, nitrogen, oxygen, fluorine, and methane.

Thus, this book will become a reference or source document for all ASTM members since many ASTM committees will be required to interface with the cryogenic industry as the energy and pollution control problems are resolved. It should also be of benefit to industry, to many government agencies, and to academé since these problems affect our way of life and possibly our survival.

For example, unless man can prevent deterioration of the ozone layer in the stratosphere, we are in trouble from ultraviolet (UV) radiation. With a 50 percent reduction in ozone, a tenfold increase in UV will result and what this can do to our ecology—to plants and animals, including man, may be catastrophic. Therefore it is hoped this volume will provide the impetus for the immediate preparation of ASTM standards and that through the membership of the Cryogenic Society of America, including its Helium Division and other supporting agencies, the cryogenic problems requiring standards will soon be resolved.

In conclusion, this STP clearly shows that ASTM is on the move in cryogenics. We have launched a long-term growth pattern for the support of the cryogenic's industry.

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Cryogenic Society of America,
Los Angeles, Calif.;
symposium general chairman.

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Microbiological Standards for Frozen Foods

REFERENCE: Appleman, M. D., Appleman, M. D., and Appleman, M. D., Jr., **"Microbiological Standards for Frozen Foods,"** *Cryogens and Gases: Testing Methods and Standards Development, ASTM STP 537,* American Society for Testing and Materials, 1973, pp. 3–11.

ABSTRACT: Factors predetermining quality and safety of frozen food products along with different types of standards are discussed. Attention is drawn to the fact that microbiological standards for frozen foods must be studied thoroughly prior to establishment. Certain standards of communities have been enacted with haste and regulations involving Standard Plate Counts (SPC) impossible to meet have been promulgated. In order to avoid fiascoes of this nature the Food and Drug Administration (FDA) working with the Advisory Council on Microbiology (ACM) of the Association of Food and Drug Officials of the United States (AFDOUS) has been making intensive studies of foods. To date, microbiological standards have been released for frozen pot pies only. The advisory council, which is composed of persons from industry, educational institutions, and public health agencies, has been evaluating microbiological risks associated with most foods and beverages prior to decisions as to whether or not standards should be established. At present the relative risk involved in each foodstuff or beverage as a possible source of coliforms, faecal coli, faecal streptococci, *Salmonella, Shigella, Staphylococcus, Pseudomonas, Clostridium,* molds (both as mycotoxin producers and as pathogens,) viruses and other agents involved in toxigenicity or pathogenicity are under study. The sources and methods of transmission of diseases through the agency of frozen foods and methods of evaluating and minimizing risk are clarified. The inherent inconvenience and danger of establishing microbiological standards for foods without careful evaluative techniques are explained. The impact of microbiological standards for foods upon incipient or frank spoilage is discussed.

KEY WORDS: cryogenics, frozen foods, standards, microbiology, bacteria, toxicology, pathology

The single greatest point of controversy related to frozen foods is whether or not microbiological standards should be established for all frozen foods.

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The second point that follows closely is, if standards of this nature are established, what shall they be.

The authors have published rather extensively [*1–9*][4] in the area of quantitations and significance of microorganisms in foods, particularly frozen foods. The method of approach to the problem of microbiological standards has been selected from the concepts most likely to be advantageous to both the bacteriologist and the nonbacteriologist working with frozen foods. There will be no discussion of methods of freezing foods as this has been discussed elsewhere and is not involved per se in the development of standards.

Background

Quality of Food Product

It should be noted that certain microbiological standards for a limited number of frozen foods are in existence and will be mentioned later. In order to develop the topic consistently it is necessary to discuss some background information relative to standards and also to quality and safety of foodstuffs. To be valid a microbiological standard must indicate or measure either or both the quality and the safety of the frozen food product to which it will be applied. Quality of a foodstuff consists of a number of closely interlocked characteristics which, ignoring safety for later consideration, might be listed as follows:

1. Organoleptic changes including those of taste, odor, and texture.
2. Effects upon the keeping quality of the product.
3. Changes in color or blemishes due to microorganisms and their enzymes in addition to the enzymatic activity of the product.
4. Changes in nutritive value due to dissimilation of sugars and other substrates.

It should be realized that the foregoing can include changes in pH of the products which most frequently will be reflected in two or more of the above.

Safety of Food Product

It is more important that microbiological standards, if used, reflect the safety, that is, the health hazards and hygiene of the frozen food products for which they are formulated. In general the microbiological standard cou-

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[4] The italic numbers in brackets refer to the list of references appended to this paper.

pled with other methods of measurement, if need be, should be able to measure one or possibly all of the following:

1. Were the raw materials, from which the frozen food product was manufactured, spoiled, infected, or so vitiated they should never have been processed into a frozen foodstuff.
2. Has the product in processing been so treated or held that it has become contaminated with human or other pathogens, or, if small numbers were present on the original food substance, have these pathogens increased in number.
3. Is the product free of pathogenic microorganisms and of indicators of pollution or at least as free of these as can be obtained with good modern technological practice.

Microbiological standards have accomplished near miracles in certain areas of public health microbiology. One example was that at the turn of the century milk was often a rather filthy fluid frequently teeming with millions of microorganisms per milliliter responsible for the mass transfer of many outbreaks of diphtheria, scarlet fever, and tuberculosis. At present in California there is little difficulty in meeting the state standards of 75 000 bacteria/ml in the raw milk and 15 000 bacteria/ml on delivery to the consumer. Pasteurization and enforcement of microbiological standards for milk and chlorination, and enforcement of microbiological standards for water have almost eliminated two of the three great agencies for mass transfer of disease in the United States.

Determining Standards

In addition to microbiological standards there are guidelines which are actually in-house standards of agencies such as the FDA. Unlike standards the guidelines are usually not known to the food processor.

Obviously it takes only a moment to realize that determinations of numbers, whether by microscopical methods or by SPC techniques, should not be used for all foods whether frozen or unfrozen. An unfortunate example of lack of forethought occurred in one large city in the East which recently established a maximum SPC of 100 000 bacteria/g or ml of food. If this standard were enforced all fermented foods and a good portion of others such as ground meat and a significant amount of poultry and fish would disappear from the market. There definitely would be no buttermilk, cottage cheese, yoghurt, cheese, butter, fresh sauerkraut, or pickles which in itself would be catastrophic for certain industries.

The AFDOUS has believed that microbiological standards and the effect of these standards should be studied prior to enactment of legislation. The present AFDOUS ACM first studied and selected methodologies that might be used for sampling, sample treatment, SPC, coliforms, *Escherichia coli, Salmonella, Staphylococcus,* and other microorganisms. Subsequent to this a study was made by the members of the council which involved representitives of government agencies, industry, and universities relative to frozen pot pies.

At the end of the study the microbiological standards established were of the type known as prohibitory standards in that there were definite limits established relative to numbers per gram and to coliforms.

Microbiological standards may be established by the purchaser to ensure that a uniformly high quality product is obtained by the processor for in-plant control or by a regulatory agency as in the case of frozen pot pies.

Frequently a standard is established as a target which gives to industries willing to cooperate a certain period of time in which the monitoring of the production by in-plant studies can be done. If portions of the operations are conducive to high counts or if certain machinery is particularly at fault changes can be made. If during this period the governmental agency finds that the standards proposed are too stringent, there is time for modification. Since presumptive standards are normally preceded by intensive studies of the products of companies known to operate under good control procedures, usually little or no alteration in standards is necessary. Eventually this will become a legal or statuary standard. Other standards such as voluntary standards do exist but are not enforceable in law.

Temperature Conditions

Frozen

If a food is maintained hard frozen no microbiological increases in number will occur although gradual biochemical changes primarily of an oxidative nature in rancidity and color may be evident. However, it must be remembered that gross changes may take place near the freezing point of water since the concentration of salts, starches, and sugar in most frozen foodstuffs render the products liquid or nonfrozen at 0°C (32°F). Psychrophilic yeasts and bacteria can grow in orange concentrate maintained at this temperature or below producing off flavors and even gasses to such pressures that rupture of the can may occur.

Defrost

It is well known [*10–13*] that defrost damage in many foods such as meat pot pies, TV dinners, single-dish units, and other foodstuffs occurs, and a hundred or more articles have been written in this area of research. With many foodstuffs that have defrost temperatures of 15 to 28°F about −7 to −2°C not only can preformed enzymes of the food substrate and surviving microorganisms damage the product so as to render it unacceptable but, in addition, psychrophilic organisms can increase in numbers. *Pseudomonas, Achromobacter, Flavobacterium,* and other organisms can degrade the product producing obnoxious flavors and odors. If the temperatures range too high above the freezing point, that is 38°F (3.3°C) for appreciable periods of time *Clostridium botulinum* Type E, if present, can grow and produce toxin.

It is equally obvious that if a frozen food defrosts and is maintained at ambient temperature, particularly that of a warm room for 5 to 12 h, the food probably will be spoiled and may be dangerous.

Observations

It is impossible for any commercial company or government agency with respect for the funds of the taxpayer to examine even representative samples of all frozen foodstuffs for all indicators of pollution and pathogens that might be present, particularly if the product history including sanitation and handling is not known for each sample. The question becomes whether or not the many groups of organisms that might be used can be viewed objectively and integrated into an established standard.

There is a story going back into antiquity of seven men of Persia, blind since birth, who had heard about elephants but never had the opportunity to examine one. One day a crowd in the street shouted that the Shah mounted on an elephant with his mahout and accompanied by his guards was coming down the street. "Of your mercy, sire," they cried, "may we examine the strange beast?" The Shah was kindhearted, the elephant stopped and the blind men were led forward—one to the side, one to a leg, one to the trunk, another to the tail, one to an ear, one to the mouth, and the last to a tusk. After the elephant was examined they moved back and the Shah passed on his way.

"Truly it is a strange beast," said the first, "it is like a great wall." "You're crazy," cried the next, "it is like the trunk of a tree." "You're wrong, it's like an anaconda." No, it's like a rope." "Its more like a great fan." "It's almost like a cave filled with rocks." "You are all mad," cried the last, "it's like a sharp spear."

Probably many persons in industry view microbiological standards as hopeless walls, an impenetrable forest, a snake they must fear, a rope with which they can be bound, a fan that may blow their business away, a rocky cavern in which they may be lost, or a spear on which they may be impaled.

Guidelines

There is a certain amount of truth in the complaints and confusion of the processor as he is often working blind against a series of unpublished guidelines that function in almost the same way as microbiological standards. Although specifications are published by the military for purchase of frozen eggs and many other foodstuffs and standards for dairy products and certain fisheries products are published by other agencies, there are few microbiological standards published by the various food and drug agencies. Mold fragments for tomato products were established early; standards regarding these were published and similar standards were extended to other foods including frozen foods. Although it has been known that certain tolerances existed for filth in foods, these have not been published, but it is of interest that a news release of this past week by Dr. Virgil B. Wodica announced that these guidelines would be released for the benefit of both producers and consumers.

It is to be hoped that the microbiological guidelines will be released in the near future. These should be sufficiently strict with both the processor and consumer being aware of the guidelines and their reason for existence. The guidelines should also be attainable by the processor operating under modern sanitary methodology using wholesome materials.

Standardization

In 1963 in the Report of the International Committee on Microbiological Standards certain sampling schemes were recommended based on the experience of the international agencies of the United States, Canada, the United Kingdom, the Benelux Countries and of military organizations participating in the studies. The standards for frozen cooked sea foods, for example, shrimp, prawns, crab meat, and lobster meat, and also frozen precooked meats and closely related products were the same. The basis is that the SPC at 35°C does not exceed 100 000 bacteria/g, the coli aerogenes do not exceed 20/g (or the nearest most probable number (MPN), and coagulase positive staphylococci do not exceed 100/g. If foods were suspected to be harboring *Salmonella* sp. an examination should be made for these organisms.

An excellent review in 1961 [*14*] discussed various suggested standards for chilled and frozen foods. Although eleven years later we know more in a sense that the FDA has been encouraging the standardization of methodologies of examination for pathogens and for indicators of pollution by the various public health agencies, it is also known that the same standards expressed as SPC could not apply universally to all frozen foodstuffs. The same numbers per gram cannot be used for enchiladas with cheese for the blanched vegetables and for a rice or bean component with chopped pickles or relish present in a TV dinner. The same numbers should not apply to a component containing fermented materials as to nonfermented. In raw foods, for example, ground meats, an initial count of 100 000 to 1 000 000 bacteria/g might be excellent to acceptable products, whereas the latter count would be unacceptable in a cooked meat component of a TV dinner.

Contamination

Certain interesting problems relate to the presence of pathogens in frozen foods. *Clostridium botulinum,* which is essentially a soil organism, may contaminate many foodstuffs including vegetables of all kinds, meats, and processing equipment. The spore of the organism is extremely heat resistant, and few of the spores of strains A and B are destroyed in blanching. If the frozen food product contains a few spores of *Cl. botulinum* and the product is not grossly mishandled there is no danger from these frozen foods. If selection and sanitation in the processing plant are supervised within reason, the routine examination for *Cl. botulinum* would be a needless expense. This does not mean there has never been a case of botulism from frozen foods, but it does mean mishandling has been associated with these cases. There are certain similarities but more differences with *Clostridium perfringens.* This latter produces a much less severe but extremely common food infection. The spores of this organism are present not only in the human gut but also in the intestinal tract of poultry, cattle, sheep, swine, and other food animals. In the slaughter of food animals, the carcass usually becomes contaminated, and these organisms will be present on meats and ground meats. The organisms contaminate many vegetables grown on manured lands, in seafood products, particularly from inshore waters, in dried fruits, and sometimes in spices. The spores are not as resistant as those of *Cl. botulinum* but will withstand blanching and frequently normal cooking temperatures. These spores can be widely disseminated in a food processing plant growing in protected, insanitary, and anaerobic conditions of flumes, pipelines, and other equipment. Relatively high numbers of *Cl. perfringens* can contaminate a foodstuff in this manner. However, if a frozen food processing plant uses good processing and sanitation techniques, there is still the likelihood that low numbers of *Cl. perfringens* will be present in certain foodstuffs.

It is in part due to the great variability of foodstuffs that the present ACM of AFDOUS is attempting to evaluate the probability of food infection or food intoxication from almost all types of foods and beverages now marketed in the United States. The relative risks of the various pathogens in each food of beverage and also the possible presence of each indicator of pollution is included. Foodstuffs may contain *Salmonella, Shigella, Staphy-*

lococcus, Pseudomonas, Clostridium, molds, and viruses that might be pathogens. In addition certain of the fungi may produce mycotoxins which can produce many different symptoms in man and animals. The common indicators of pollution are the coliforms, faecal coli, and faecal streptocci. It should be remembered that these are not completely indicative of pollution since they are measures of faecal pollution and do not measure all pathogens that can be transmitted via foodstuffs as these eliminate consideration of the respiratory pathogens. It is hoped that after this intensive survey is completed, a certain degree of sanity can be attained relative to the various foodstuffs.

Summary

It has been pointed out by the FDA [*15, 16*] that probably ten million cases of food-borne disease occur annually in the United States. The source of mishandling of approximately one half of these cases were identifiable. Of these outbreaks 85 percent were due to food abuse in the home or in food service establishments, restaurants, institutions, etc., and only 15 percent to abuse in the processing plants. Food service establishments were involved in more than twice as many outbreaks in the above as there were from foods prepared in the home.

The FDA recognizes that microbiological standards for frozen and other foods must be technologically attainable using good methodology but not too permissive as to be associated with high consumer risk. To a certain extent these are sought through the use of guidelines based upon experience in the examination of the products of many processors.

It is somewhat difficult to present the philosophy of the FDA, particularly when this has not been clearly spelled out relative to microbiological standards. The following might be somewhere close to the thoughts of many officials. If a product contains microbial counts that indicate the product might be potentially dangerous but not dangerous per se, the product should be regarded as substandard in this regard and should be so labelled. The presence of certain pathogens in low numbers might place the product in this category. However, if the product contains organisms at such a level, whether this has occurred by using material that was originally filthy, putrid, or decomposed, or if the product has been so held or stored under conditions where microorganisms have multiplied so that the product is regarded as filthy, putrid or decomposed or dangerous to health, it must be deemed to be adulterated or adulterated and misbranded and, thus, liable to seizure.

References

[*1*] Martinez, J. and Appleman, M. D. *Food Technology* Vol. 3, No. 12, 1949, pp. 392–394.

[*2*] Hahn, S. and Appleman, M. D., *Food Technology,* Vol. 6, No. 4, 1952, pp. 156–157.

[*3*] Hahn, S. and Appleman, M. D., *Food Technology,* Vol. 6, No. 5, 1952, pp. 165–167.

[*4*] Kaplan, M. T. and Appleman, M. D., *Food Technology,* Vol. 6, No. 5, 1952, pp. 167–170.

[*5*] Appleman, M. D., *Journal of Applied Bacteriology,* Vol. 18, No. 3, 1955, pp. 503–509.

[*6*] Ferraro, F. M. and Appleman, M. D., *Applied Microbiology,* Vol. 5, 1957, pp. 300–303.

[*7*] Litsky, W. L. and Appleman, M. D., *Food Scientist,* Vol. 5, No. 1, 1961, pp. 17–21.

[*8*] Appleman, M. D. and Appleman, M. D., Jr., *Hospital Management,* Vol. 108, No. 4, 1969, pp. 34–39.

[*9*] Appleman, M. D., *Journal of Applied Nutrition,* Vol. 21, Nos. 3 and 4, 1969, pp. 61–69.

[*10*] Gunderson, M. F. in *Low Temperature Microbiology Symposium,* Campbell Soup Co., Camden, N. J., 1961, pp. 299–312.

[*11*] Peterson, A. C. in *Low Temperature Microbiology Symposium,* Campbell Soup Co., Camden, N. J., 1961, pp. 157–195.

[*12*] Fanelli, M. J. and Gunderson, M. F., *Food Technology,* Vol. 15, No. 10, 1961, pp. 419–422.

[*13*] Peterson, A. C., Fanelli, M. J. and Gunderson, M. F., *American Journal of Public Health,* Vol. 54, No. 4, 1964, pp. 649–659.

[*14*] Elliott, R. P. and Michener, H. D., *Applied Microbiology* Vol. 9, No. 5, 1961, pp. 452–468.

[*15*] Olson, J. C., Jr., "Microbiological Standards for Foods—Present Standards Development in the Food and Drug Administration," Food Research Institute, Madison, Wis., 9 April 1969.

[*16*] Olson, J. C., Jr., "Role and Development of Microbiological Criteria for Foods," Pennsylvania Manufacturing Confectioner's Association, 27–29 April 1971.

R. K. Johnson[1]

Installation of Liquefied Natural Gas Fuel Containers and Systems on Motor Vehicles

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REFERENCE: Johnson, R. K., **"Installation of Liquefied Natural Gas Fuel Containers and Systems on Motor Vehicles,"** *Cyrogens and Gases: Testing Methods and Standards Development, ASTM STP 537,* American Society for Testing and Materials, 1973, pp. 12–16.

ABSTRACT: This article outlines the procedures for installation of a liquefied natural gas (LNG) system on a motor vehicle. Emphasis is placed on safety devices required in the system to minimize the hazards of LNG when used as a motor fuel.

KEY WORDS: cryogenics, liquefied natural gas, motor vehicles, fuel oil, containers, safety devices

The use of gaseous fuel has increased considerably in the past three years. In 1970 the California Legislature recognized the need for regulations and standards regarding fuel containers and fuel systems on motor vehicles using compressed or liquefied natural gas (CNG) (LNG) and liquefied petroleum gas (LPG). Vehicle Code Section 2402.6 enacted into law November 1970 assigned the responsibility to the California Highway Patrol. Prior to this time, only LPG systems were regulated by the Department of Industrial Safety.

In response to the new Vehicle Code requirement and with the assistance of industry, the California Highway Patrol adopted Article 2 Sub Chapter 4, Title 13, California Administrative Code (CAC) regulations for compressed and liquefied gas fuel systems. This paper contains excerpts from Title 13, regulations applicable primarily to LNG systems.

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These regulations apply only to vehicles which are equipped with gaseous fuel carburetor systems certified by the Air Resources Board. Certified carburetors are required on motor vehicles with a gross vehicle weight rating of 6000 lb or less manufactured after 1966, and all motor vehicles manufactured after 1969, except for vehicles with diesel engines that were converted to gaseous fuel prior to January 1973.

Container Construction

The fuel supply container shall be constructed in accordance with Department of Transportation (DOT) regulations for cryogenic gases, except that the service temperature need be no lower than −260°F. The working pressure shall be adequate to withhold gases from exhausting to the atmosphere under normal conditions for a period of 72 h. Maximum working pressure shall be no greater than 100 psi.

The tank shall be designed with a dip tube to prevent filling beyond 90 percent of volume at atmosperic pressure. The tank shall be equipped with a gage that will indicate the liquid level at all times.

Container Marking Requirements

1. DOT 4L with the maximum working pressure.
2. Serial number.
3. Manufacturer's name, initials, or trademark as registered with DOT.
4. Inspector's mark.
5. Date tested.
6. The words FOR LNG ONLY, 1 in. in height (decals or stencils are acceptable.)
7. All inlets and outlets, except relief valves and gaging devices, shall be marked to designate whether they communicate with vapor or liquid space.
8. All markings shall be visible directly or by mirror when installed, except that the words FOR LNG ONLY shall be visible directly.
9. Tanks that are designed for low temperatures of liquid nitrogen may be tested with liquid nitrogen.

Valves and Gages

All valves used shall be certified for LNG use or certified for cryogenic service at temperatures down to and including −320°F.

Relief valves shall be directly connected to the vapor space of the container and one shall be installed between two shutoff valves in a line to prevent buildup of pressure when the valves are in the off position. Relief valves shall contain the required markings and be approved by the Bureau of Explosives as to type, size, quality, and location.

Manual operated shutoff valves shall be installed in each vapor and liquid tank outlet with no intervening fitting, except for a relief valve on the vapor outlet, and marked with the appropriate words VAPOR SHUTOFF VALVE or LIQUID SHUTOFF VALVE.

A positive shutoff control valve shall be installed in the supply line as close to the manual shutoff valve as possible, automatically closing off and preventing the flow of fuel when the ignition switch is in the off or accessory position.

Gages shall be designed to operate under the most severe pressure and temperature conditions with a safety factor of not less than 4. Valves and gages shall be securely mounted and shielded or installed in a protective location to prevent damage from excessive vibration and unsecured objects.

Venting

All devices which require bleeding of the product shall be bled to the outside of the vehicle compartment.

Every compartment in which LNG containers are installed shall be vented to the atmosphere unless all piping and connectors are exterior to the compartment. The vent or vents shall be installed at the highest point of the compartment as is practicable and shall have an open area totaling not less than 3 in.^{2}.

Installation

A container shall not be installed in or about the passenger or driver's compartment of a bus (ten persons including the driver.) A cargo container, mounted on a motor vehicle, which complies with the Unfired Pressure Vessel Safety Orders, Division of Industrial Safety, Title 8, California Administrative Code, may be used for a fuel container. Fuel to a motor vehicle shall not be supplied from a container mounted on a trailer or semitrailer.

Each container and container cradle shall be secured to the vehicle body, bed, or frame by either:

1. Attaching bolts not less than $\frac{7}{16}$ in. in diameter to at least 4 securement points, and where bolts pierce body metal but not the frame, by reinforcing both sides of each securement point with metal plates at least $\frac{1}{8}$ in. thick and 7 in.^{2} in area; or

2. By using other means capable of withstanding static loading in any direction with a force equivalent to that determined by the weight of the fully loaded container with a safety factor of not less than 8, based on the ultimate strength of the material used.

3. Cradles are the same as No. 2.

Two or more containers connected by piping, tubing, or hose, are referred to as a manifold. A manual shutoff valve is required on the manifold outlet. An automatic shutoff valve which is held open by an electrical solenoid and automatically closes upon opening of the electrical circuit may be used in lieu of the manual valve. The valves are required to be marked either "manual" or "automatic." The automatic valve shall be wired so that it shuts off when the ignition switch is off or in the accessory position or when engine vacuum is not present.

Automatic gaseous fuel cutoff is required in the system to prevent the flow of fuel to the carburetor when the ignition switch is off or from the carburetor when engine vacuum is not present. On dual fuel units a bypass relief device shall be installed in the fuel pump or between the fuel pump and automatic solenoid.

The pressure reducing regulator shall be installed so that its weight is not placed on or supported only by the attached tubing or flexible lines.

The engine exhaust system shall extend to the outer edge of the vehicle body or bed on passenger cars, station wagons, housecars, pickup trucks with campers, buses, and delivery type vans.

Electrical Equipment

Radio transmitters and receivers, electric motors, or other electrical equipment (except vehicle lamps) shall not be mounted in a compartment with fuel supply containers unless one of the following conditions are met:

1. All piping, connectors, and valves on the fuel supply containers are exterior to and sealed from the vehicle compartment to prevent seepage of gas;
2. All piping, connectors, and valves within the compartment are contained in a vapor-tight enclosure and vented to the atmosphere exterior of the vehicle; or
3. The electrical equipment is contained in a vapor-tight enclosure that is vented to the atmosphere exterior of the vehicle; or
4. The electrical equipment is approved for use in Class I, Division II, Hazardous Locations, in accordance with Article E501, Title 24, California Administrative Code.

Road Clearance

The fuel system, including the fuel supply container, shall be installed with as much road clearance as practicable. The lowermost part of any component in the system, including protective guards, shall not be lower than the lowest edge of the vehicle differential housing under maximum spring deflection; but, on cargo carrying vehicles with a gross vehicle weight rating of 6000 lb or more, the lowermost part of the container may be at the lowest part of the vehicle body.

F. S. Forbes[1]

Specifications for Cryogenic Propellants and Pressurizing Gases

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REFERENCE: Forbes, F. S.,"**Specifications for Cryogenic Propellants and Pressurizing Gases,**" *Cryogens and Gases: Testing Methods and Standards Development, ASTM STP 537*, American Society for Testing and Materials, 1973, pp. 17–39.

ABSTRACT: Cryogenic propellants and pressurizing gases have been and will continue to be used for missile and space propulsion systems. To maintain the high degree of reliability that these propulsion systems have exhibited, close control of propellant quality is necessary. Specifications are the basic documents that establish the technical requirements for procurement purposes. These requirements are dictated by the needs of the user, with due consideration given to the manufacturing ability of the suppliers, and possible deterioration of the product during handling and storage. Specifications also contain quality assurrance provisions that detail the sampling plans and analytical procedures to be used to ensure that the propellant conforms to the specified requirements. Gas chromatography has been widely accepted as the principal method of analysis for cryogenic and gaseous materials.

Specifications are continually revised and updated as required by the rocket community. The rationale for the establishment of the specific requirements for oxygen, nitrogen, helium, fluorine, and hydrogen is presented. Current sampling techniques and analytical methods for these products are also reviewed. Other cryogens, such as OF_2 and methane, have received limited attention and are briefly discussed.

KEY WORDS: cryogenics, cryogenic rocket propellants, pressurizing, specifications, impurities, tests, oxygen, nitrogen, helium, hydrogen, fluorine, argon

The quality control of cryogenic propellants and pressurizing gases plays a very important role in missile and space vehicle reliability as higher performance propulsion systems are developed. As the reusability concept

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TABLE 1—*Cryogenic propellants and pressurizing gases.*

Commodity	Specification	Amendment or Revision	Date	Status
Oxygen	MIL-P-25508	E	4 Jan. 71	
		(1)	30 Apr. 71	
Hydrogen	MIL-P-27201	B	30 June 71	
Nitrogen	MIL-P-27401	B	19 Sept. 62	in Revision
Fluorine	MIL-P-27405		28 June 68	
Helium	MIL-P-27407		4 Feb. 64	in Revision[a]
	(USAF)	(1)	8 Jan. 65	
Argon	Not issued			in Preparation

[a] Will be issued as a revision to the Federal Specification BB-H-1168.

becomes a reality, quality control will become even more important. The military specification controls the quality of these materials at the point of manufacture. Propellant quality can be affected throughout the entire logistics cycle of manufacturing, transportation, storage, servicing operation, and ultimate use. To this end, use limits for propellants are designed to allow for some deterioration in propellant quality during normal handling between procurement and ultimate consumption in a missile or space vehicle. The current military specifications for cryogenic propellants and pressurizing gases are presented in Table 1.

The Air Force is the Department of Defense's single manager for the 9135 Federal Supply commodity class which consists of all rocket propellants and related pressurants. This task consists of specification preparation, procurement, and all related logistics activities such as storage, transportation, and disposal.

Specification Format and Preparation Procedures

Specifications are identified by number and title, for example, MIL-P-27201B, Propellant Hydrogen. All military specification numbers begin with MIL, followed by the first letter of the specification title, which for rocket propellants is the letter P. The number assignment is prescribed by a system that precludes duplication of numbers whether prepared by the Army, Navy, Air Force, or the Defense Supply Agency. A suffix letter indicates a revision. A numerical indicator is used to identify an amendment. An amendment is a short-form revision and, when approved, becomes a part of the basic specification as an attachment. The latest amendment will contain all previous amendment data [*1*].[2]

A specification that has not been fully coordinated among the Army, Navy and Air Force is a limited coordinated specification. It is identified by the symbol designation of the preparing agency. For example, MIL-P-27406 (USAF) has received coordination only within the United States Air Force.

A specification consists of six sections. In the Scope, Section 1, a listing of the different types or grades is presented as applicable. The term type implies chemical or physical differences in like terms which are for different, specifically but equally important uses and is designated by a Roman numeral. The oxygen classification, for example, covers two types: Type I, Gaseous and Type II, Liquid. The term grade is used to imply differences in quality and is designated by capital letters, thus, Grade A, Grade B, etc. This term has been gaining wider use in cryogenic specifications. However, the use of different grades produces a problem since users have a tendency to order the higher purity grade whether or not the better quality is needed.

Only those documents identified and cited in the specification are listed in Section 2, Applicable Documents. References are confined to currently available documents such as military standards for marking for shipment and storage, federal test methods or American Society for Testing and Materials (ASTM) standards, specifications for shipping containers and samplers, and Department of Transportation (DOT) regulations.

Section 3, Requirements, is the heart of the specification. It must state only the actual minimum needs of the government and describe the required propellant in a manner which encourages maximum number of acceptable suppliers. The essential requirements and description applying to the chemical and physical characteristics are stated in this section. The minimum standards of quality and workmanship which the commodity must meet to be acceptable are also stated as definitively as practicable. The requirements are so worded as to provide a definite basis for rejection in those cases where the quality and workmanship are such that the item is unsuitable for the purpose intended.

The Quality Assurance Provisions, Section 4, include all of the examinations and tests to be performed in order to determine that the propellant offered for acceptance conforms to the Requirements section of the specification. Detailed descriptions of the tests, equipment, reagents, analytical methods, and criteria for determining requirement conformance are presented in this section. Standard test methods such as those of ASTM are usually in-

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[2] The italic numbers in brackets refer to the list of references appended to this paper.

cluded only by reference. The sampling plan is described, identifying the lot, the number and size of each sample, and the mode of obtaining a sample.

Applicable requirements for packaging, marking for shipping, and hazardous-substance labeling are covered in Section 5 of the specification. Containers such as cylinders and tank cars, and materials thereof, which are suitable for the specified propellant, are also identified.

The last section of the specification, Notes, contains information of a general or explanatory nature only such as the intended use of the propellant, detailed ordering data, definitions, National Aeronautics and Space Administration (NASA) coordination, etc. The information in Section 6 is contractually nonmandatory upon the contractor.

Amendments are issued when a significant change, addition, or correction to the specification is necessary, but a complete revision of the specification is not warranted. Amendments are prepared and coordinated in the same manner as specifications.

The first specification on a new propellant is often based on the product as produced by the chemical manufacturer. The users' requirements are certainly considered, but may not be well defined at this point in time. A limiting factor in establishing firm requirements is often a lack of good analytical procedures. Although considerable help is received from industry in this

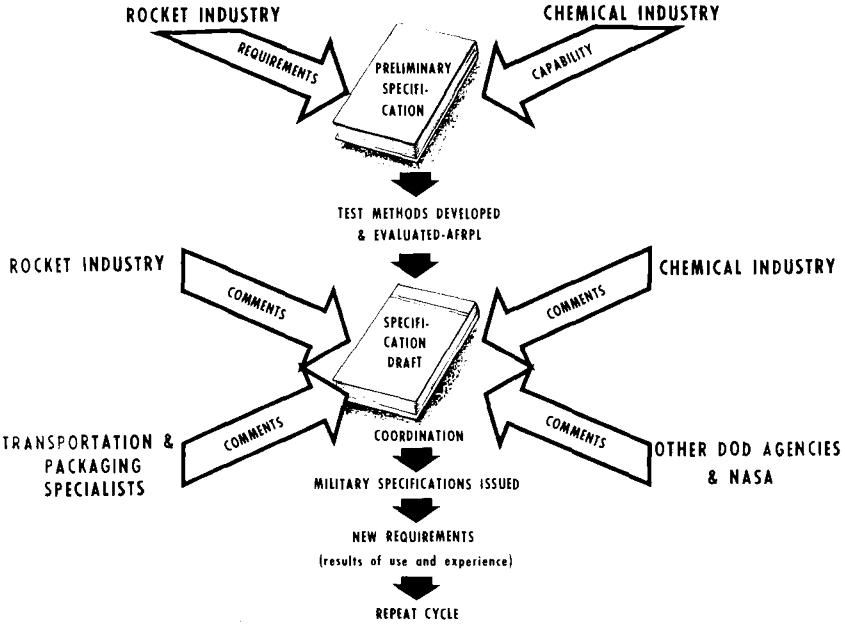

FIG. 1—*Specification preparation cycle.*

area, it is preferable that the test procedures be finalized in the laboratories of the preparing service. This enables them to be in a better position to give technical support to government quality control inspectors, and to better serve as a referee should conflicts arise. When reasonable requirements and adequate analytical procedures have been identified, we have the makings of a military specification, and a draft is prepared. It is circulated to all interested organizations for comments. Upon resolving differences, the specification is formally coordinated and issued. As new requirements are identified, or better analytical procedures are developed, the cycle starts over and a revised specification or an amendment is issued (Fig. 1).

Establishing Specification Requirements

The establishment of detailed requirements for Section 3 of the specification is an important and difficult task carrying considerable responsibility. The propellant quality established must meet the needs of the specific system; for example, the Atlas, Centaur, Saturn, Space Shuttle, etc. Several criteria are used to specify propellant quality. Performance is usually paramount; thus nonenergetic materials or diluents should be kept to a minimum. Impurities that may present a hazardous condition, such as hydrocarbons in liquid oxygen, must be controlled. Impurities that cause decomposition or corrosion cannot be tolerated; for example, moisture in fluorine. However, the requirements cannot be too stringent if adequate quantities of propellant at a reasonable cost are to be made available.

When a new propellant is made available to the rocket community, the first specification, usually an informal one, is based on the product as it comes from the manufacturer. As experience is gained during rocket engine development, refinements in propellant quality are made. An impurity that affects the ignition or combustion process may be found or suspected. The propellant manufacturer also strives to improve his products, and, as his production and facilities increase, higher purity often results. Thus, from these considerations, a formal specification emerges and is published as a limited coordinated military specification. Other factors often enter into the considerations. For example, there must be analytical procedures capable of measuring the propellant assay and controlled impurities or constituents with the desired precision. It is not reasonable to set a limit for some impurities of 0.1 percent by weight when the analytical method will detect only 0.5 percent. A value is occasionally established on the grounds that it appears reasonable or is believed to be significant. The ASTM rounding off method for expressing significant figures is used in all current propellant specifications. (ASTM Recommended Practices for Indicating Which Places of Figures are to be Considered Significant in Specified Limiting Values (E 29-67).)

Some propellants are subject to inherent evaporation or contamination during the time they are in transit between the manufacturer and user. When this occurs, the specification must be made more stringent than required by the user to allow for such changes.

Changes to specifications can originate from many sources:

1. The preparing activity may find new requirements as a result of continued surveillance, additional experience, or long-term storage studies.
2. A manufacturer may change his process, resulting in new levels of purity or introduction of different impurities.
3. New applications resulting in additional or more stringent requirements may develop.
4. Advances in analytical chemistry can result in quality control improvement.

The following discussion describes how some of these requirements evolved for cryogenic propellants and pressurants.

Liquid Oxygen

The prime requirement for oxygen purity is based on safety. Hydrocarbons in oxygen produce a very hazardous condition [*2*]. Impurities that have low solubilities are especially undesirable since they can act as ignition sources. Acetylene is limited to 0.25 ppm by weight maximum for this reason. During transfer and storage considerable oxygen boils off [*3*]; a 60

TABLE 2—*Requirements, MIL-P-25508E, propellant, oxygen.*

Composition	LIMITS		
		Type II	
	Type I	Grade A	Grade B
Oxygen (O_2) assay, percent by volume, min	99.6	99.6	99.5
Total hydrocarbons as methane, ppm by volume, max	50.0	50.0	66.7
Alkynes as acetylene, ppm by weight, max	...	0.25	0.5
Moisture, ppm by volume, max	8.0	3.0	26.3
Particulates, mg/liter, max	...	1.0	1.0

percent loss between procurement and launch is not uncommon. This causes the impurities to concentrate and to precipitate if their solubilities are reached. In addition to the specific control of acetylene and total hydrocarbons, the requirement for 99.6 percent purity (Table 2) forces greater care in the air separation plants and provides greater margins on the impurities. While industry complained that the government was restricting availability of product, or may be increasing costs with this increased purity, subsequent events proved this was not the case. Industry has improved their production methods and equipment considerably during the past ten years. The problems that plagued the early flights of the Atlas, Thor, Jupiter, and Titan I did not occur during the Saturn development programs. While much of the credit for this success must be given to improved components, perfected cleaning procedures, and extensive testing of systems, higher quality propellants undoubtedly played an important part.

It will be necessary to reactivate the government-owned, contractor-operated (GOCO) air separation plants to provide sufficient oxygen for the initial phases of the Space Shuttle program. Since the GOCO plants were designed to produce a product in accordance with MIL-P-25508D which will not meet the current standards for flightworthy systems, the product will be used only for development programs. As the quality of the plant output still must be controlled, the E revision was amended to include a Grade B equivalent to the specification under which the plants were designed.

Nitrogen

Nitrogen is a pressurizing agent used for purging and pressurization of rocket engine propellant systems. Other requirements for high quality nitrogen include environmental control for analysis of moon rocks obtained from the Apollo program, wind tunnels, and nuclear programs. The Federal Specification for Nitrogen, BB-N-411, does not control hydrocarbons. The resulting product is thereby unsuitable for use with cryogenic and earth-storable oxidizers, as well as the other specialized applications which require controlled levels of hydrocarbon impurity.

Because of the multitude of diverse applications, and the different agencies involved, a large number of specifications for nitrogen were issued. San Antonio Air Material Area (SAAMA) was procuring liquid nitrogen to seven specifications or Air Force Purchase Identification Descriptions (AFPIDs) at one time. This number was subsequently reduced to four. A C revision to the military specification for nitrogen, which will consolidate user requirements, is in preparation. Four grades of liquid nitrogen are proposed as listed in Table 3.

Grade V nitrogen is the purest and is normally used for liquid propulsion

TABLE 3—*Proposed requirements*[a], *MIL-P-27401C, pressurizing agent, nitrogen.*

Composition	Type I	Type II			
		Grade V	Grade W	Grade X	Grade Z[b]
Nitrogen (N_2) assay, percent by volume, min	99.5	99.995	99.9929	99.99	99.5
Dew point, °F	−63.5	−90.0	...	−84.0	−63.5
Moisture, ppm by volume, max	26.3	3.5	10.0	5.7	26.3
Total hydrocarbons as methane, ppm by volume, max	58.3	3.0	1.0	5.0	58.3
Oxygen (O_2),					
ppm by volume, max	...	20.0	10.0	50.0	...
percent by volume, max	0.5	...	...	...	0.5
Hydrogen (H_2), ppm by volume, max	...	...	10.0	...	...
Carbon dioxide (CO_2), ppm by volume, max	...	...	10.0	...	...
Carbon monoxide (CO), ppm by volume, max	...	...	10.0	...	...
Argon (Ar), ppm by volume, max	...	...	20.0	...	...
Particulate, mg/liter, max	...	1.0	1.0	1.0	1.0
Total allowable impurities, ppm by volume, max	...	...	71.0	100.0	...

[a] Uncoordinated values presented for information only. Not to be used for procurement.

[b] Grades identified to avoid confusion with existing specifications, nomenclature may be changed at a later date.

systems. Since nitrogen can transfer moisture and hydrocarbons to cryogenic and storable oxidizers, impurity limits are set on both of these contaminants. Tight control of oxygen as an impurity is required for nitrogen use as a pressurizing agent in systems using storable fuels such as hydrazine and pentaborane; wind tunnel studies at NASA's Langley Research Center also require close control of oxygen. Nuclear research activities conducted by the Atomic Energy Commission (AEC) require control of argon to a maximum level of 150 ppm by volume. A special grade for this specialized use has not been identified because at least two of the grades listed, V and W, will meet the argon limit.

As previously discussed, the GOCO plants will be returned to service. The proposed specification revision contains Grade Z, which is equivalent to the current B revision and is the standard which the GOCO plants were designed to meet.

Hydrogen

The development of liquid hydrogen technology for rocket propulsion presented a major challenge to scientists and engineers. This effort culminated with the first successful launch of a liquid hydrogen-oxygen propelled Centaur in November 1963.

The unique chemical and physical characteristics of hydrogen make it rather easy to produce a high purity product. Much of the hydrogen in the United States is produced by the catalytic steam-reforming process. The natural gas source used in this process contains moderate amounts of helium; thus, helium is a major impurity. The helium content in liquid hydrogen is normally below 30 ppm.

Many of the other contaminants are almost totally insoluble in liquid hydrogen. To avoid particulate buildup, the quality of this product is controlled to a high purity level as noted in Table 4. Frozen particles of oxygen are impact sensitive in hydrogen; thus, they present a particularly hazardous situation. Because the analytical method used does not adequately separate oxygen and argon, a composite value is specified for these two impurities. Carbon monoxide and carbon dioxide are limited to provide a product suit-

TABLE 4—*Requirements, MIL-P-27201B, propellant, hydrogen.*

Composition	Limits Type I	 Type II
Hydrogen (H_2) assay, percent by volume, min	99.995	99.995
Parahydrogen, percent by volume, min (balance orthohydrogen)	...	95.0[a]
Moisture, volatile hydrocarbons, nitrogen (N_2) combined, ppm by volume, max	9.0	9.0
Oxygen (O_2) plus argon (Ar), ppm by volume, max	1.0	1.0
Helium (He), ppm by volume, max	39.0	39.0
Carbon monoxide (CO) plus Carbon dioxide (CO_2), ppm by volume, max	1.0	1.0
Total allowable impurities, ppm by volume, max	50.0	50.0

[a] Parahydrogen shall be determined by thermal conductivity type in-stream analyzers installed in the manufacturer's plant, which shall be calibrated integrally by the appropriate use of temperature controlled catalyst beds.

able for spacecraft fuel cells. This eliminates the need for a special grade or separate specification, and does not affect the price or availability of hydrogen. Control of other impurities, namely, fluorine, chlorine, and nitrogen oxides has been requested by some users; however, due to the nature of the production process the contaminant level is so low that these impurities are not likely to be a problem.

Since gaseous hydrogen is normally used for liquid hydrogen system purging and pressurization, this material must also meet the same purity standards established for the liquid. It is recognized that such levels are more difficult to achieve in cylinder packaging of gaseous hydrogen; however, the requirements for a high purity product are well documented.

Liquid hydrogen exists in two forms, ortho and para. Orthohydrogen will slowly convert to parahydrogen with evolution of heat. This heat release will increase the evaporation rate and thus the loss of liquid hydrogen. Spacecraft operations could be adversely affected by premature hydrogen loss. Catalytic conversion of ortho- to parahydrogen is accomplished by the manufacturer. Conversion of greater than 95 percent of the orthohydrogen would unduly increase plant operating costs and decrease product capacity. For this reason, the specification calls for a minimum of only 95 percent by volume of parahydrogen.

Fluorine

Fluorine, the most reactive chemical oxidizer, has been of interest to the rocket engineer since 1946. The degree of interest has oscillated considerably over the years. Currently, fluorine is under consideration as a reactant for the chemical laser.

A specification is of limited usefulness unless the requirements can be verified by test. The fluorine specification presented a major problem to analytical chemists. This is reflected in the fact that the military specification was ten years in the making and still has a serious deficiency.

The principal impurities in fluorine are: *(a)* nitrogen and helium, which are used to purge equipment and containers, and *(b)* oxygen, tetrafluoromethane (CF_4), hydrofluoric acid (HF), carbon dioxide (CO_2), and perhaps ozone and peroxides, which enter into the product during manufacture.

Noncondensables, nitrogen (N_2), helium (He), and to a lesser extent oxygen (O_2), dilute the product; these are controlled to provide a high fluorine assay which results in maximum end use performance. The condensables, specifically, CO_2 and HF, have limited solubility in liquid fluorine and can freeze out in lines, resulting in a blockage. The condensable impurities are controlled near the solubility level. Concentration of impurities will not occur because liquid fluorine is never allowed to self-refrigerate. Ozone and

TABLE 5—*Requirements, MIL-P-27405, propellant, fluorine.*

Composition	Limits
	Types I and II
Fluorine (F_2) assay, percent by volume, min	99.0
Sum of hydrofluoric acid (HF) and carbon dioxide (CO_2) percent by volume, max	0.1
Noncondensables[a] percent by volume, max	0.9

[a] As defined in the appropriate specification test method, for example, O_2, N_2, He, CF_4.

peroxides are believed to be the culprits that caused several explosions in fluorine manufacturing and liquification systems. These impurities are not controlled in the specification as they present a greater hazard to the manufacturer than the user and can be assumed to be absent from the final product.

There has been controversy over the control of other possible impurities such as sulfur hexafluoride (SF_6). The processes used to remove specified impurities will also remove others, and no documented problems have been reported. The major source of difficulty has been the presence of particulate matter. Unfortunately, there is no test procedure suitable for specification purposes. Normally this specification would have included requirements for a filter to be installed in the loading lines to control particulates within the propellant while filling shipping containers. However, no adequate filter was available. Subsequently, NASA developed a sintered nickel filter, 40 μm nominal, 60 μm absolute, which will be included during the next revision of the specification. Table 5 presents the current specification limits.

Helium

Helium, in both the liquid and gaseous state, is used in a variety of ways: from the filling of toy balloons to research at temperatures approaching absolute zero. A 1967 survey by the Bureau of Mines showed that 370 million cubic feet of helium were used for purging and pressurizing; this number represents nearly 41 percent of the total helium used. Helium, the lightest inert gas, is used to pressurize cryogenic and storable propellants such as liquid oxygen and liquid hydrogen. It is used as the pressurant in the propulsion systems of the Atlas, Centaur, and Saturn boosters, and also the Apollo program's Lunar Lander and space module. Because helium does not become radioactive, it can be used as a heat transfer medium in gas cooled nuclear reactors. Other uses of helium include welding operations, synthetic breathing mixtures, controlled atmospheres, and leak detection.

With such a variety of applications it is not surprising that a total of six different specifications related to gaseous helium exist today. Table 6 represents an effort to consolidate these requirements in a realistic fashion. Grade A helium is used primarily for lighter than air use, such as weather balloons. No severe limits on impurities exist for such application and this fact is reflected in the specification. Both moisture and hydrocarbons are closely controlled in Grade B helium, used in missiles and space vehicles, as

TABLE 6—*Proposed requirements*[a], *BB-H-1168b helium.*

Composition	Limits[b]			
	Type I			
	Grade A[c]	Grade B	Grade C	Grade D
Helium (He) assay, percent by volume, min	99.8	99.995	99.995	99.998
Dew point, °F	...	−78.0	−87.0	−90.0
Moisture, ppm by volume, max	none condensed	9.0	4.0	3.0
Hydrocarbons (condensed), ppm by volume, max	none	...	0	0
Total hydrocarbons as methane, ppm by volume, max	...	5.0	1.0	0
Oxygen (O_2), ppm by volume, max	...	3.0	1.5	1.0
Nitrogen (N_2), ppm by volume, max	...	14.0	8.0	5.0
Neon (Ne), ppm by volume, max	...	23.0	20.0	5.0
Hydrogen (H_2) ppm by volume, max	...	1.0	0.5	0.5
Argon (Ar), ppm by volume, max	...	1.0	1.0	1.0
Carbon dioxide (CO_2), ppm by volume, max	...	1.0	0.5	0.5
Carbon monoxide (CO), ppm by volume, max	...	1.0	0.5	0.5
Other gases, ppm by volume, max	...	1.0 each	1.0 each	0.5 each
Total allowable impurities, ppm by volume, max	...	50.0	50.0	20.0

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[a] Proposed requirements presented for information only, and are subject to change. Not to be used for procurement.

[b] Type II liquid helium shall be filtered through a 10 μm absolute filter and shall be certified as helium by an acceptable test.

[c] Not to be interpreted as Bureau of Mines' previous Grade A now known as "high purity."

well as in welding and other shielding gas operations. The reason for this control, from a rocket engineering standpoint, is the requirement for high purity propellants and safety. It would be ironic to tightly control impurities in a propellant only to introduce them through impure pressurant. The Grade C and Grade D helium both represent requirements of the AEC (Lawrence Radiation Laboratory). A tighter and more detailed control of impurities is imposed due to uses in high intensity radiation fields. While helium itself does not become radioactive, the impurities can, and a buildup of radioactive gases is highly undesirable.

Since there is presently no developed and reliable inspection or test procedure for testing liquid helium, the only requirements that can be made for filtration and to ensure that the product received is helium. The means by which the product can be certified as liquid helium are by analysis of the vent gas through a mass spectrometer, or by demonstrating that the temperature of the loaded fluid is below the hydrogen triple point 13.8 K.

By a recent agreement with the Federal Supply Service, General Services Administration, the Air Force has accepted engineering and preparing responsibilities for the helium specification. Table 6 represents the suggested requirements for Proposed Revision b to Federal Specification BB-H-1168, Helium, which is to be the singular specification for all government buys.

Argon

Argon is used in a variety of ways and has only recently come under consideration as a pressurizing agent for missile and space vehicle propellant utilization systems. Major uses of argon include: the filling of electric light bulbs, shielded arc welding operations, and blanketing of metallurgical operations where contact of surface metal and the atmosphere is undesirable. Argon is not recommended for use in nuclear activities because of the ease with which it will form radioactive species; therefore, argon is tightly con-

TABLE 7—*Requirements*[a], *AFPID 9135-19, pressurizing agent, argon.*

Composition	Limits[b]
Argon (Ar) assay, percent by volume, min	99.85
Dew point, °F	−80.0
Moisture, ppm by volume, max	7.8
Hydrogen (H_2), ppm by volume, max	350.0
Oxygen (O_2), ppm by volume, max	30.0
Nitrogen (N_2), ppm by volume, max	1000.0

[a] The AFPID requirements are listed due to the lack of a specification. Limits may change when the specification is issued.

[b] Type II, liquid only.

trolled as an impurity in helium when used by the AEC. The earth's atmosphere is the commercial source for argon (argon comprises approximately one percent, by volume, of the earth's atmosphere).

Table 7 lists the current requirements for liquid argon used as a pressurizing and purging gas. Moisture, as in other specifications for pressurants, is controlled below 10 ppm by volume. Both hydrogen and oxygen are controlled because of possible hazards and to prevent contamination of propellants. Nitrogen, another inert gas used as a pressurizing agent, is not controlled very tightly because it poses no special problems. The basic test methods for argon are mass spectrometry and gas chromatography.

Argon is currently procured under AFPID 9135-19 until an Air Force specification is written. The Federal Specification for argon does not take into account those properties required for use as a pressurizing agent and cannot be used.

Other Cryogens

Throughout the years other cyrogenic materials have been investigated as possible rocket propellants. The status of these cryogens as propellants follows:

Oxygen Difluoride (OF_2)—This oxidizer was a contender as a "space storable" propellant, but because of engine development problems, interest has now focused on fluorine-oxygen (FLOX). No work on an OF_2 specification is contemplated.

FLOX—Several mixtures of fluorine and oxygen have been studied. NASA is currently evaluating a mixture composed of 88 percent fluorine and 12 percent oxygen. With continued success in the current program a specification will be prepared. The liquid fluorine specification, MIL-P-27405, will most likely be used as the starting point.

Ozone (O_3)—This oxidizer is no longer given serious consideration because of the ease with which violent decomposition occurs. Highly pure oxygen is required for the preparation of stable ozone. The ozone studies accomplished in the 1950's contributed greatly to advancements in liquid oxygen quality and analytical procedures.

Liquid petroleum gases—Methane, ethane, butane, propane, and various mixtures thereof are periodically evaluated for various propulsion systems, the latest being the Space Shuttle. Should a propellant specification be required, it will probably be developed around Federal Specification BB-G-110, "Butane, Propane, and Butane-Propane Mixtures".

Analytical Procedures

The requirements delineated in a specification have little meaning unless they can be measured with accuracy and preciseness. The development and evaluation of suitable test methods is usually the most difficult and time consuming part of specification preparation. The specification must present the procedures in sufficient detail so they can be performed by any reasonably skilled analytical chemist in an average control laboratory. Analytical methods that involve considerable specialized experience or are unduly subject to personnel error are avoided. Methods that require highly specialized or costly equipment are not desirable since the government must, either directly under cost reimbursable contracts or through higher propellant price, pay for such items. Government quality control laboratories must also acquire whatever equipment is specified. In specification preparation there is a trend toward using standard methods such as those of ASTM and Federal Test Method Standard No. 791. There are no acceptable standard methods for cryogenic or gaseous propellants.

The specification preparing activity collects all available methods and evaluates them for simplicity and accuracy. The methods may be modified, or new ones developed if necessary. Most of the evaluation is performed by government personnel in the preparing agency's laboratories for two major reasons:

1. Conflicts that arise between the propellant manufacturers and the rocket engine developer can be resolved more equitably.
2. The preparing activity is the organization that receives the technical questions on the procedures, and has chemists with personal experience in performing the various procedures for better technical support.

The preparing activity works closely with industry to obtain quality assurance provisions that are satisfactory. Many difficulties and differences that arise are settled by concentrated efforts. Everyone realizes that such provisions must be adopted, and if not satisfactory, they will be a continual irritation to all concerned. Personnel often visit other laboratories to resolve differences by working with those who are perhaps more experienced, or who have developed better techniques. Round robin samples are another means of checking the results of different laboratories, but one must assure that the propellant does not change during such a laboratory interchange. The resulting procedures are written to provide stepwise instructions for the analyses, spelling out volumes and weights of materials to be used as well as phenomena to be observed, such as color changes. All required reagents and equipment are identified. If calibration charts or calculation formulas are needed, they are also included.

The following discussion describes some of the analytical methods used for cryogens and the rationale for their selection. It will be noted that the test methods used in current specifications are chemical in nature. Physical property measurements have not proven adequate for quality control purposes. Some specifications covering storable propellants contain physical measurements, but the trend is to delete such tests upon revision. Fluorine is discussed separately because of its unique characteristics.

Impurities—Gas chromatography (GC) is the principal technique used for measuring the level of most impurities in cryogenic propellants and pressurants. Assay is then determined by difference. GC is precise and easy to perform. The equipment is modestly priced and is now a standard item in many laboratories. As specifications are revised, the GC technique will be incorporated wherever it is suitable.

At the present time hydrocarbons in nitrogen and helium are determined colorimetrically with a hydrocarbon analyzer. This method will be replaced by GC in future specification revisions. The colorimetric technique for measuring oxygen in nitrogen will also be superceded by gas chromatography. GC, infrared, and the classical Ilosvay colorimetric methods are acceptable for alkyne (acetylene) determinations. The test for oxygen in helium utilizes a galvanic cell. This test will be retained in the revision as the referee method, with a GC technique included as an alternate. Producers of cryogens normally use on-stream analyzers for their process control. Approval to use on-stream analyzers for quality control may be given by the procuring activity providing that data are furnished to show that such equipment produces results with sensitivities and accuracies equivalent to or better than the specified methods. Unfortunately, most requests for such approval present comparison data for a product that is well within specification limits. To properly assess the validity of on-stream analysis, the data submitted also must show that on-stream equipment will discriminate between acceptable and nonacceptable products, as determined by the specification methods. On-stream analyzers are acceptable for measuring ortho to para conversion of liquid hydrogen.

Assay—Assay is normally determined by difference after the total impurities have been measured. Oxygen assay may be determined by the nitrometer method, Orsat analysis, paramagnetic or thermal conductivity type analyzer, or by GC; the nitrometer method is the referee test in case of dispute.

Moisture—Recent specifications permit the use of several standard methods for determining moisture. The electrolytic method (based on the current required to electrolyze the water) is preferred, and is the reference method for oxygen and hydrogen. The current helium and nitrogen specifications list the accelerated gravimetric technique (absorption of water by phosphorus pentoxide) as the referee method. Forthcoming revisions will permit use of alternate procedures, with the referee being the electrolytic method. This change from the accelerated gravimetric method has come about because of the inherent inaccuracy of determining a small change in weight.

Fluorine (F_2)

Fluorine presents unusual problems to the analytical chemist. Condensables, hydrogen fluoride and carbon dioxide, are determined by near-infrared and infrared spectroscopy, respectively. These methods require the preparation of calibration curves and are not ideal. However, for present state of the art they are the most practical from the standpoint of accuracy, ease of operation, and economy. A gas chromatographic method would be more de-

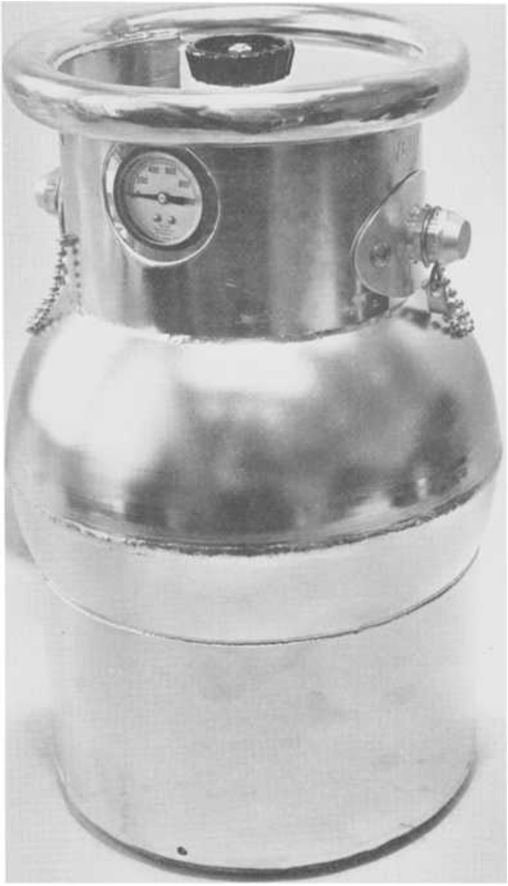

FIG. 2—*Cosmodyne cryogenic sampler.*

sirable; however, no chromatographic columns are yet available which will provide adequate separation of all volatile impurities.

To determine noncondensables, the fluorine sample is reacted with sodium chloride to release chlorine which is then absorbed by potassium hydroxide (KOH). The remaining gases are then measured to give the total value for the noncondensables, normally considered to be oxygen (O_2), nitrogen (N_2), helium (He), and tetrafluoromethane (CF_4). Individual species are not identified by this procedure.

The reduced chlorine from the preceding analysis is treated with nitric acid, then titrated with silver nitrate using a potentiometric apparatus. A simple calculation gives the fluorine (F_2) assay.

Samplers

Sampling is required to obtain a small quantity of product for analysis. This sample must be representative of the lot or batch submitted by the producer. The sampling of cryogens presents an unusual problem. It is difficult to obtain a top, middle, and bottom sample, and impractical to agitate the vessel. A vapor sample of the product would not contain nonvolatile impurities.

Liquid samples are obtained by a sampler specified in MIL-S-27626C (USAF), or one that is functionally equivalent (Fig. 2). The unique feature of this sampler is that it will extract a liquid sample and then allow the operator to vaporize the total sample without loss, thus maintaining the original composition and purity of the sample. The composition of this gas is identi-

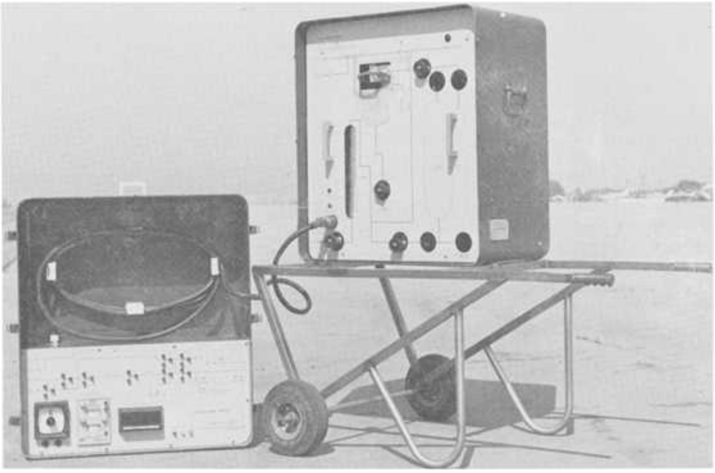

FIG. 3—*Liquid fluorine sampler.*

cal to that of the original liquid. The sampler with the gasified sample may then be carried or shipped safely to a quality control laboratory [*4*].

Figures 3 and 4 illustrate a liquid fluorine sampler that utilizes this same principle developed under an Air Force contract [*5*]. To provide for personal safety, the sampler is operated remotely and incorporates a scrubber to neutralize the excess fluorine. This unit contains an integral filter enabling a particulate analysis to be made. Successful operation of this sampler has been demonstrated. The low usage rate of fluorine precludes the manufacturing of additional units.

Particulate

All of the propellant and pressurant specifications now require, or will require upon revision, a 10-μm nominal, 40-μm absolute filter to be installed between the manufacturer's plant system and the manifold used to fill gas or liquid containers for delivery. It has been argued that this requirement is unnecessary because the product can and should be filtered at the point of use. Such practice places a heavy burden on the user's filter. Experience has

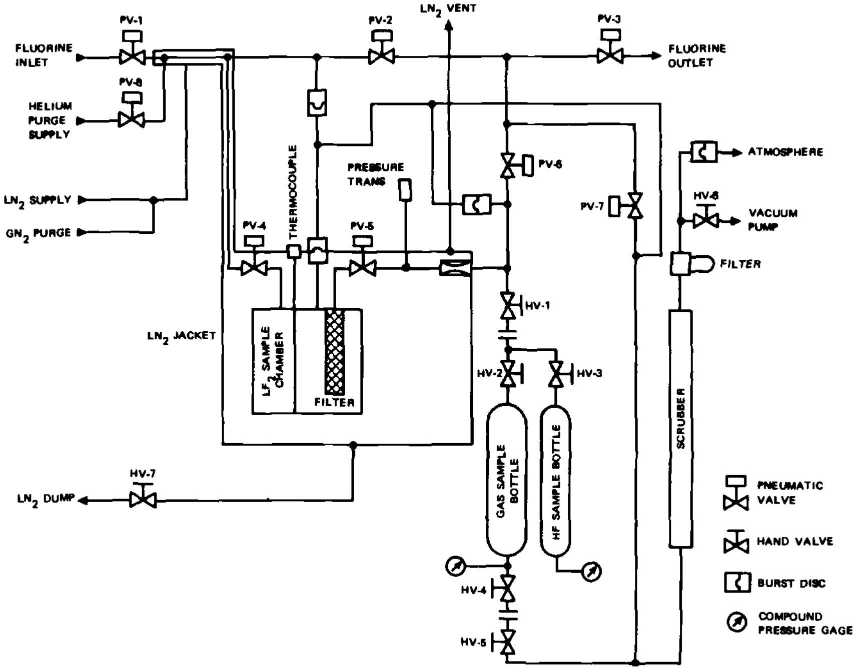

FIG. 4—*Liquid fluorine sampler schematic.*

proven that satisfactory propellant quality can best be maintained by filtration at all transfer points.

Most of these specifications also set a maximum limit of 1 mg/liter particulate matter for the liquids. This requirement is not applied to the gases because of the difficulty in complying when cylinders are used for packaging. This requirement is also not placed on liquid hydrogen because there has been no problem with such foreign matter reported. There have been considerable problems with particulates in fluorine, but a satisfactory test suitable for use with such a reactive oxidizer is not available.

The quality assurance procedure for particulates is based on filtration of the sample using Gelman, Millipore, or an equivalent filter. Particles or fibers are examined visually and shall not exceed 1000 μm in any dimension or 6000 μm in length, respectively. Particle count is not used because no suitable method is available. Manual counting through a microscope is too time consuming and dependent on operator experience for routine analysis of a large number of samples. Instrumental methods involve some cost, but, more important, they require the definition of a particle to be established. Some of the available instruments measure the particle by surface area, volume, or one dimension (length or width). The specifications call for weighing of the filter to the nearest one tenth of a milligram; the particulate content must be below 1 mg/liter.

Propellant Quality Control and Field Surveillance

The Department of Defense, through Defense Contract Administration Services' (DCAS) quality control representatives (QAR), and individual manufacturers, must work to ensure that product quality control is achieved. This is accomplished through periodic inspections of the manufacturers' plant, process, instrumentation, calibration, and internal quality control programs. The enforcement of specification requirements through periodic surveillance of suppliers is the heart of quality control.

The specification is a procurement document and should not be used for field quality control or surveillance (Fig. 5). After the propellant is accepted at the vendor's plant, it can be exposed to many sources of contamination beyond the control of the vendor. Most cryogenic propellants are subject to boil-off, thus concentrating the impurities. The specification requirements are selected to allow for some propellant change, to assure that the delivered propellant is usable. Otherwise, a propellant that just meets the procurement requirements at acceptance may not do so at the point of delivery.

The quality of the propellant required at the destination will depend on the application. Each user should specify a use limit that is meaningful for his specific application and represents the minimum quality the propellant must have for satisfactory performance. For missiles stored in a ready condition, a loading limit may be established that identifies the propellant quality to be met when the missile is serviced and selected so that the use limit will not be reached through degradation during storage period. Thus, a propellant may be permitted to degrade from the procurement specification quality to the loading limit with further degradation to the use limit. The loading and use limits germane to a given system are included in the applicable operating manuals or technical orders. The use limit may identify other impurities not included in the procurement specification and may delete those that are peculiar to the manufacturing process and not acquired during handling or storage.

Although the procurement specification requirements cannot be properly used for field use, the quality assurance provisions often are. The analytical methods and sampling procedures are very valuable for all surveillance activities, since these techniques are usually selected for their simplicity and readily available equipment.

Engine model specifications should not always stipulate that the rocket engine use propellants conforming to the requirements of the procurement specification. If the propellant is subject to degradation during shipping and storage, use or loading limits should be established during the engine development program. This will preclude the problem of trying to supply specification-grade propellants in the field, when the propellant will begin to deviate from the specification as soon as it leaves the manufacturing plant.

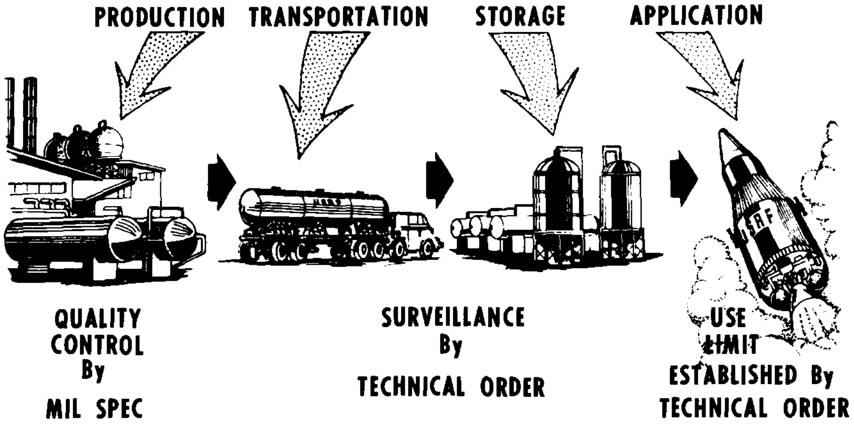

FIG. 5—*Propellant quality controlled by different documents during logistics cycle.*

Summary

Military and federal specifications are important documents that define the required quality of rocket propellants and pressurizing gases procured by the government. They are used by quality control inspectors as the criteria for the acceptance of products from suppliers.

The two most important parts of a specification are the Requirements and Quality Assurance Provisions sections. The Requirements section contains the specific properties, composition, and impurity limits that the propellant or pressurant must meet. The requirements are established to assure that the product will accomplish the purposes intended. Data from research and development programs, field use, and engine manufacturers are used in the preparation and revision of specifications. The application requirements must be balanced by the ability of the chemical industry to produce large quantities of the propellant at an acceptable price. The factors of safety, storability, and analytical difficulty are as important as performance in setting specification values. Criteria for the selection of impurity limits in various cryogenic propellants and pressurants are presented on an individual basis to acquaint the reader with the workings of specification preparation.

The Quality Assurance Provisions section consists of the test methods or analytical procedures used to determine conformity of the propellant or pressurant with the specified requirements. The methods selected must provide the necessary accuracy and should be simple and easy to perform. The use of specialized and expensive instruments is to be avoided when possible. Most analytical methods for cryogenic materials are currently based on gas chromatographic procedures. The most difficult and time-consuming function of specification preparation is the development of suitable analytical methods. Current and proposed techniques for cryogenic materials of interest to the rocket propulsion community are reviewed.

Military and federal specifications, being procurement documents, are not adequate for field quality control. Cryogenic propellants are subject to evaporation loss and contamination, causing deviation from the specification requirements during shipping or storage. Loading limits and use limits should be established by the using organization to assure control of propellant quality between procurement and ultimate consumption. The specification analytical procedures are satisfactory for field use and are widely utilized.

The specification is a dynamic instrument. It is the product of extensive cooperation and coordination among the rocket and chemical industries and government agencies. Specifications are continually reviewed, and are revised frequently as rocket propulsion technology advances. They form an important part of the interface between government and industry which has achieved the many successes in space that all of us can look at with pride.

References

[*1*] Defense Standardization Manual, 4120.3-M, "Standardization Policies, Procedures and Instructions," Office of the Assistant Secretary of Defense Installations and Logistics, Department of Defense (DOD).

[*2*] Foster, R. H., "Study of Liquid Oxygen Contaminants," final Report SSD-TRD-62–8, Air Products, Inc., Allentown, Pa., May 1961.

[*3*] Lieberman, P., "Transient and Steady-State Heat Transfer Problems Associated with Rocket Utilizing Liquid Oxygen," Air Force Rocket Engine Test Laboratory, Edwards, Calif., Aug. 1967.

[*4*] "Cryogenic Sampler Design and Development," final Report Contract AF 04(611)-5677, The Cosmodyne Corp., Hawthorne, Calif., Jan. 1961, AD292764.

[*5*] Randle, W. N., "Liquid Fluorine Sampler Development Program," Technical Report AFRPL-TR-70-83, Air Force Rocket Propulsion Laboratory, Edwards, Calif., July 1970, AF Contract FO4611-69-C-0101.

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Sensitivity and Reaction Intensity Studies of LOX-LNG Mixtures

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REFERENCE: Blackstone, W. R., Wenzel, A. B., and Every, R. L., "**Sensitivity and Reaction Intensity Studies of LOX-LNG Mixtures,**" *Cryogens and Gases: Testing and Methods and Standards Development, ASTM STP 537*, American Society for Testing and Materials, 1973, pp. 40–58.

ABSTRACT: Mixtures of liquid oxygen (LOX) and liquid natural gas (LNG) are very attractive as commercial explosives because they exhibit very high brisance, or shattering power, and because the basic materials are readily available and inexpensive. However, the mixtures can be quite dangerous if mishandled, and there is little or no information available concerning the handling hazards. The objective of this program was to obtain such information by conducting a series of drop tests to characterize the impact ignition and reaction intensity behavior of various LOX-LNG mixtures and to determine whether the addition of an inert inhibitor would change the reaction intensity or the impact sensitivity. Impact tests were conducted using pentaerythritol tetranitrate (PETN), and the results were compared with those for the various LOX-LNG mixtures.

KEY WORDS: cryogenics, liquid oxygen, liquid natural gas, explosives, impact sensitivity, intensity, desensitizing

During the early 1960's, a number of laboratories were trying to develop an inexpensive and readily available rocket propellant system which would not cause health or safety hazards at blast-off. Also involved was a search for a propellant with sufficient specific impulse to allow the space crafts to exit and reenter the atmosphere without the necessity of jettisoning the fuel tanks. The only propellant which came close to meeting these requirements was liquid oxygen (LOX) and kerosine (RP-1 grade); however, the specific impulse of this combination was not sufficient.

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Calculations showed the specific impulse of mixtures of LOX and liquid methane (LCH_4) would meet the specifications put on a monopropellant and would be significantly better than LOX-RP1. The results of these studies have been published [*1, 2*][3] and indicate the validity of the specific impulse calculations. However, an unexpected and accidental explosion did occur while testing these mixtures and indicated that further test work would be required to fully describe the safety measures necessary. This, coupled with the cancellation of the Dynasoar Program (recoverable vehicles) caused abandonment of this work.

More recently, other uses for the highly explosive LOX-LCH_4 mixture, or LOX-liquid natural gas (LNG) have suggested themselves and have prompted renewed interest in the safety aspects of handling. As a result of this renewed interest. Southwest Research Institute (SwRI) began to evaluate LOX-LNG mixtures in relation to standard explosives and to study the safety problems involved.

TABLE 1—*Program test plan.*

Test No.	Material	O/F Ratio by Volume	Test Type	No. of Test Drops	Drop Height, in.	Plummet Weight, lb
1.1	PETN	...	S[a]	19	variable	20
1.2	PETN	...	RI[b]	10	42	20
1.3	LOX-LNG	1.50	RI	10	42	20
1.4	"	1.34	RI	10	42	20
1.5	"	1.50	S	10	variable	20
1.6	"	1.34	S	19	variable	20
1.7	"	1.96	RI	11	42	20
1.8	"	3.00	S	10	variable	20
1.9	"	1.96	S	10	variable	20
1.10	"	1.96	RI	11	42	20
1.11	"	3.21	RI	10	24[c]	20
1.12	"	1.07	RI	10	42	20
2.1	LOX-LNG	1.50	RI	20	42	20
2.2	CBS	1.96	S	7	variable	20
2.3	"	1.96	RI	13	42	20
2.4	"	1.21	RI	6	42	20
2.5	"	3.21	RI	10	42	20
2.6	"	1.96	RI	10	42	20
2.7	"	1.07	RI	10	42	20
2.8	"	1.07	RI	5	42	20

[a] Sensitivity.

[b] Reaction Intensity.

[c] After fifth test of Test No. 1.11, drop height was increased to 42 in.

[3] The italic numbers in brackets refer to the list of references appended to this paper.

The experimental approach chosen was comprised of impact tests to characterize the impact sensitivity and reaction intensity of various mixtures of LOX-LNG and to determine whether the addition of an inert inhibitor would change the sensitivity or reaction intensity. For a base comparison with other energetic explosives, tests also were conducted using pentaerythritol tetranitrate (PETN) explosives.

The program was conveniently divided into two test series. Tests 1.1 through 1.12 determined the sensitivity and reaction intensity of PETN and various mixtures of LOX-LNG without an inert component. Tests 2.1 through 2.8 determined the sensitivity and reaction intensity of various mixtures of LOX-LNG with a fumed silica (CAB-O-SIL, Grade EH) component. A total of 221 drop tests was conducted.

In this paper, the approach and setup of the experiments are given. Results and analyses are presented in the form of graphs, tables, and illustrations, and conclusions are made from them.

Test Equipment and Procedures

Test Plan

The test plan is given in Table 1. Tests 1.1 and 1.2 determined the ignition sensitivity levels and reaction intensity for a primary explosive PETN. These tests generated values which were used as a baseline for the subsequent LOX-LNG tests. Tests 1.3 through 1.12 were designed for the purpose of characterizing both the ignition levels and the reaction intensity of LOX/LNG mixtures without the addition of the inert component. Tests

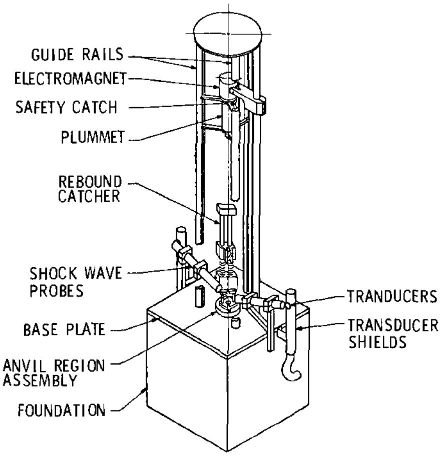


FIG. 1—*AFAPL impact tester.*

2.1 through 2.8 were designed to characterize the effects of CAB-O-SIL, Grade EH. The results are reported in Section III.

Test Apparatus

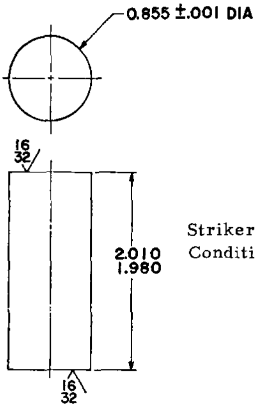
The data reported herein were obtained in the impact sensitivity laboratory located in the Department of Fluids and Lubrication Technology of SwRI. The basic test apparatus used is known as the Air Force Aero Propulsion Laboratory (AFAPL) impact tester (a modification of the well-known Army Ballistic Missile Agency (ABMA) machine.) The original version of this apparatus was installed in 1958, and the facility has since been used to test hundreds of different types of materials in contact with LOX.

A complete description of the AFAPL impact tester, as shown in Fig. 1, would be inappropriate in this paper; for such details, the reader may consult Refs *1* and *2*. Here, the basic design parameters pertinent to an evaluation of the test results are discussed briefly.

The basic parameters include a 20-lb plummet which can be released from any height up to 48 in. The impact force is transmitted through a striker pin (Fig. 2) to the specimen resting in the specimen cup (Fig. 3). An anvil region assembly serves to hold the striker pin and specimen cup in proper alignment.

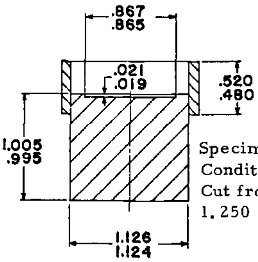
The rebound catcher (Fig. 1) arrests the plummet after its initial impact since the allowance of secondary impacts would reduce the control of ignition stimuli.

The reaction intensity measuring system (Fig. 1) consists of two identical but independent subsystems. In visualizing how this measuring system



Striker Pin: 17-4PH Stainless;
Condition H-900 Heat Treat

FIG. 2—*Striker pin.*



Specimen Cup: 17-4PH Stainless Steel Condition H-900 Heat Treat. Sleeve: Cut from 6061-T6 Aluminum Tubing, 1.250 in. O.D., 0.065 in. Wall Thickness.

FIG. 3—*Specimen cup and sleeve.*

works, it should first be noted that each impact on a drop-weight tester creates shock waves in the air, ranging from very low order sound waves when a reaction does not occur, to the blast waves emanating from a detonation. These shock waves are picked up at the nearby inlet ends of the two stainless steel tubes (the shock wave probes.) While in a tube, a shock wave cannot expand; therefore, its peak pressure will remain essentially undiminished. This means that a piezoelectric transducer located near the outlet end of the tube can read practically the same peak pressure as that occurring at the inlet end very near the wave source. At the same time, the transducer can be protected from the deleterious effects of violent explosions. The transducer signal then goes through a charge amplifier to a peak pressure meter, where a voltage reading corresponding to the peak pressure of the shock wave is obtained. The two identical measuring subsystems are used in order to increase the probability of measuring the highest part of directional reactions.

Figure 4 shows the tester, test cell, and remote instrument and control console.

Impact Sensitivity

In this paper, impact sensitivity is expressed in terms of the drop height at which the test material has a 50 percent probability of reaction. This drop height is called, for brevity, the 50 percent point. The test method by which the 50 percent point is obtained is known as the "up-and-down," or Bruceton method [*3*, *4*]. Briefly, it involves a predetermined number of test drops made from varying heights, in equal log increments, in such a manner as to bracket the 50 percent point of the test material. Recently, Dixon [*5*] has described the application of this method with small samples (for example, sample size $N < 6$), and this method was utilized in this program.

It should be noted that in conducting an impact sensitivity test, one must assign a value of positive to a test result if any evidence of reaction is found, regardless of the severity. This means that a test drop yielding a slight pop is

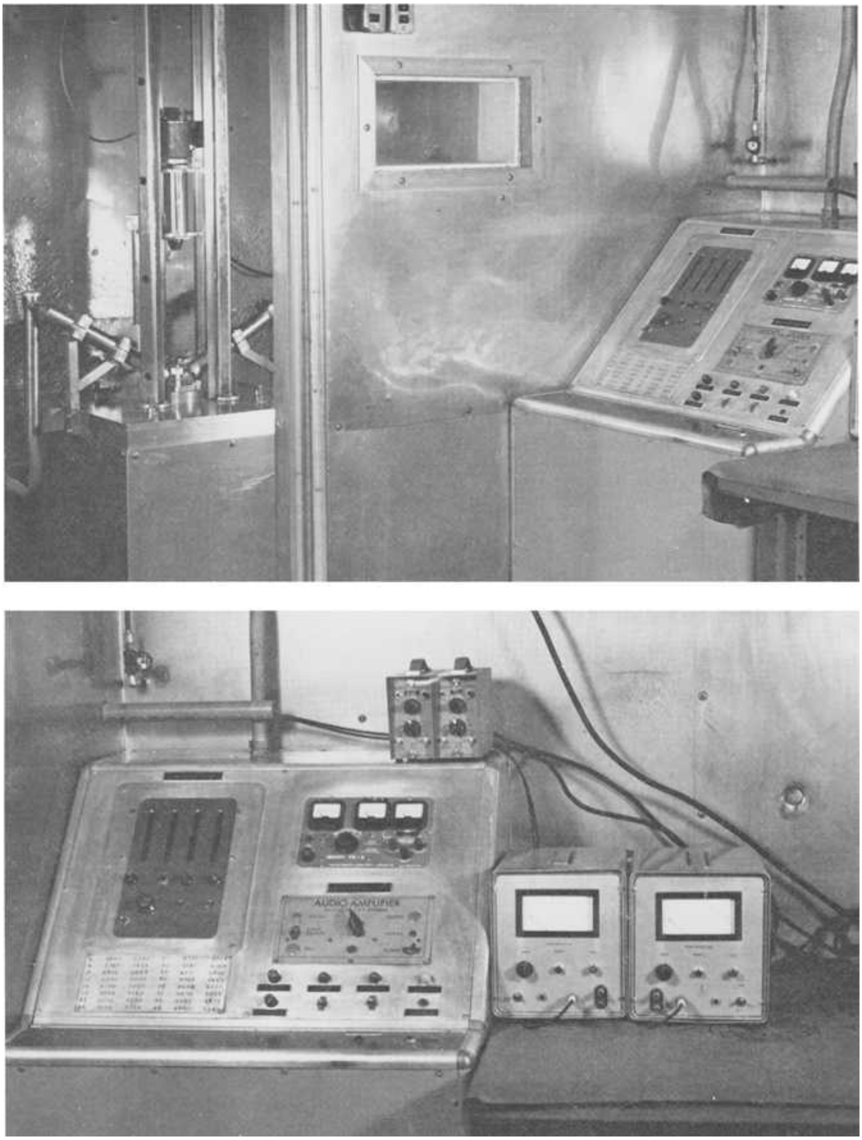


FIG. 4—*The LOX impact test facility at SwRI.*

assigned the same value as one yielding a violent detonation. Clearly, a material which yields only mild reaction under a given energy input is less hazardous than one yielding detonations under the same conditions. By definition, however, an impact sensitivity test cannot evaluate this difference quantitatively. Thus, the reaction intensity test is necessary for an adequate hazard evaluation.

Reaction Intensity

The reaction intensity test consists simply of conducting a predetermined number of test drops from a single, predetermined drop height. The intensities are measured in the manner described previously. For this program, the sample size ranged from 5 to 20, and the drop height used was 42 in.

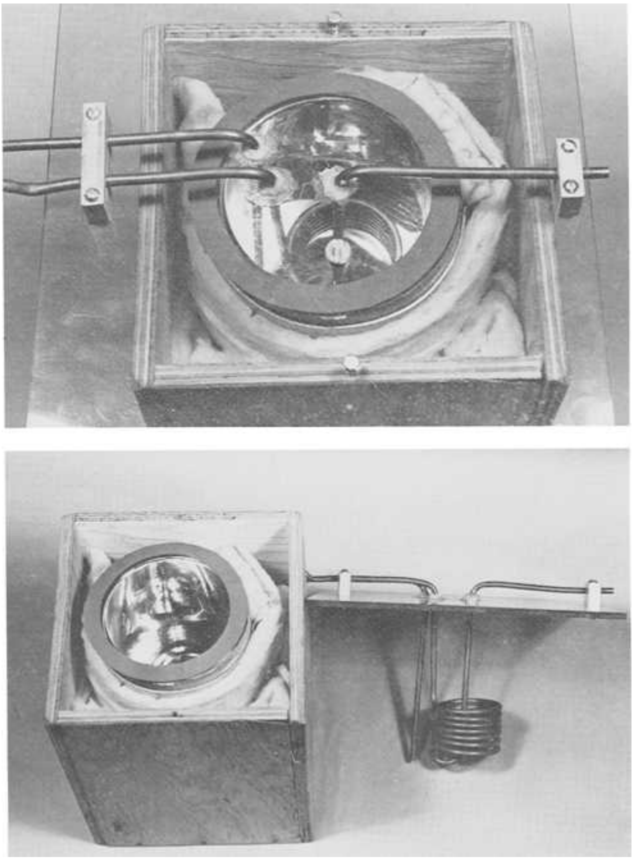


FIG. 5—*Details of LNG condenser.*

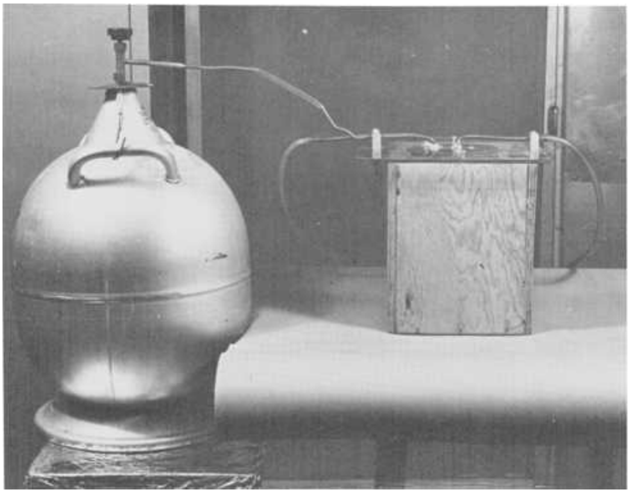


FIG. 6—*Assembled LNG condenser.*

Test Materials

The basic materials used for these tests were PETN, LOX, LNG, and CAB-O-SIL, Grade EH.

The PETN was commercially obtained and tested in a dry condition. The LOX was procured commercially. The procurement specification was MIL 0-25508.

The LNG used in the program was condensed from ordinary natural gas. Figures 5 and 6 show the still constructed for this purpose. Liquid nitrogen was circulated through the copper coil resting in the insulated dewar. A separate copper tube introduced the natural gas into the dewar, wherein it condensed on the coils and fell to the bottom. As much as 1 liter of LNG could be made in about 2 h by this technique.

Of course, the composition of the LNG was not known exactly. However, most impurities in natural gas will solidify at LCH_4 temperatures and sink to the bottom. Thus, when the LNG is taken from the dewar by dipping only from the top portion of the liquid, the resultant mixture consists mostly of LCH_4 with some liquid ethane.

The inhibitor used for some of the tests reported herein was CAB-O-SIL, Grade EH.

The various mixtures of LOX and LNG tested were prepared with small dippers. For example, to prepare a sample with 1.21 oxidizer/ fuel (O/F) ratio by volume, nine dippers (0.75 ml/dipper) of LOX were mixed with eight dippers (0.70 ml/dipper) of LNG.

The various mixtures were made in glass beakers, prechilled to LOX temperature. Figure 7 shows the mixing station in one corner of the test cell. The polycarbonate shield shown served as a fragment shield in case of accidental ignition of the mixtures, but no such accident occurred.

For the tests involving the inhibitor, the LOX and LNG were first mixed as described previously. Then the required volume of inhibitor was added, producing a paste-like substance of a consistency that could be easily poured.

As will be seen later, the test results showed that one aspect of the sample preparation procedure was of more significance than anticipated. Initially, the sample material was distributed among the specimen cups immediately after mixing, and LOX was maintained around the bottom of the cups during the test series. Later, it was concluded that the LOX, with its lower boiling point, was boiling off the individual specimens rapidly enough to cause a significant change in O/F ratio between the first and last specimens of a group of, say, 10. Thereafter, the sample material was left in the beaker after mixing, and each specimen cup was filled only as its test drop occurred. Thus, the exposed surface area of the mixture was reduced, lowering the LOX boil-off rate, and retarding the change of O/F ratio. The significance of this will be pointed out in the discussion of test results.

Results and Discussion

General

As mentioned previously, the primary objective of the test program was to characterize the impact ignition and reaction intensity behavior of LOX/LNG mixtures and to determine whether the addition of an inert inhibitor would change this behavior favorably. In other words, it was desired to establish the relative handling hazard of such mixtures and whether the inhibitor would lessen the hazard. In view of the difficulties involved in attempting an absolute definition of hazard, it was agreed that the tests should include PETN for reference measurements, since the relative degree of handling hazard associated with PETN is well known.

Table 2 presents a summary of all test results obtained in the program, and the following paragraphs discuss the analysis of the sensitivity and reaction intensity data.

Sensitivity Tests

To establish a quantitative reference level for this particular tester, the first sensitivity test was performed on PETN (Test 1. 1). Figure 8 shows a view of test drops 12 through 16 of Test 1. 1. Test drops 12 and 16 reacted

FIG. 7—*Sample mixing station.*

while test drops 13, 14, and 15 did not. Note that one aluminum sleeve was expanded sufficiently by the reaction to separate from the specimen cup. The scatter of the test data was quite low, and the measurement is therefore considered a reliable one. The measured value of 11.3 in. obtained with a 20-lb plummet may be compared with values of approximately 13 cm (5.12 in.) obtained with 2-kg (4.4 lb) plummets as reported in the literature. Such results illustrate the significant role of sample configuration and restraint in impact testing and emphasize the fact that sensitivity test results are meaningful only when used as relative points of comparison. It is clearly fallacious to draw conclusions from such tests regarding the ability of a material to withstand specific loads of impact energy without ignition.

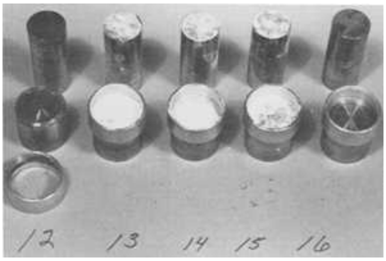


FIG. 8—*Post-test view of specimen cups and striker pins for Test 1.1.*

TABLE 2—*Summary of test results.*

Date	Test No.	Material	O/F by Volume	Test Type	No. of Test Drops	Peak Pressures, psi $\bar{X}$	Peak Pressures, psi S	Peak Pressures, psi $\bar{X}'$	Reaction Frequency, %	Sensitivity, in.
2/22	1.1	PETN	. . .	S	19					11.3
2/22	1.2	PETN	. . .	RI	10	32.7[a]	5.3		100	
2/12	1.3	LOX-LNG	1.50	RI	10	33.5	11.5	1.3671	80	
2/24	1.4	"	1.34	RI	10	37.0	18.8	1.3817	70	
2/12	1.5	"	1.50	S	10	42.5	7.9	1.5295		12.8
2/24	1.6	"	1.34	S	19	50.0	1.4	. . .		6.2
2/24	1.7	"	1.96	RI	11	61.6	32.6	1.6433	82	
2/12	1.8	"	3.00	S	10	48.7	24.8	1.5181		11.6
2/25	1.9	"	1.96	S	10	46.7	21.9	1.5408		5.9
2/25	1.10	"	1.96	RI	11	40.0	14.3	1.4710	55	
2/25	1.11	"	3.21	RI	10	. . .	. . .	. . .	10	
2/25	1.12	"	1.07	RI	10	43.7	14.9	1.4981	70	
2/12	2.1	LOX-LNG CBS	1.50	RI	20	30.6	8.4	1.3262	100	
2/24	2.2	"	1.96	S	7	67.7	35.2	1.7131		2.7
2/24	2.3	"	1.96	RI	13	67.0	19.8	1.7390	85	
2/24	2.4	"	1.21	RI	6	25.0	6.4	1.2015	100	
2/25	2.5	"	3.21	RI	10	30.0	11.3	1.3115	20	
2/25	2.6	"	1.96	RI	10	39.7	19.1	1.4298	70	
2/25	2.7	"	1.07	RI	10	65.4	21.0	1.7299	100	
2/25	2.8	"	1.07	RI	5	178.0[a]	2.8	. . .	100	

[a] Excluded from analysis.

As shown in Table 2, Test 1.5 (LOX/LNG–1.5 by volume) yielded a 50 percent point of 12.8 in., which one might take at first as an indication of slightly less sensitivity relative to PETN. However, the data scatter was considerable. Therefore, the measurement cannot be considered as significantly different than that of PETN.

Tests 1. 6, 1. 8, and 1. 9 also exhibited considerable scatter, and it would be unwarranted to conclude that any of these show a sensitivity significantly different than that of PETN. One can safely say that the impact ignition hazard of this material, when mixed, is of the same order of magnitude as that of PETN.

An additional consideration for these tests is that at the very low drop heights (<6 in.) guiderail friction on the plummet causes the plummet drop time to deviate considerably from that of theoretical free fall. Hence, it becomes difficult to obtain an accurate measurement of sensitivity at these levels, and this concept is thought to account for a portion of the data scatter obtained.

Test 2.2 on LOX/LNG = 1.96 + CBS yielded a 50 percent point of 2.7 in. This is far enough below the previous measurements so that possibly, in spite of the scatter, etc., the addition of the inhibitor actually increases the mixture sensitivity somewhat. To conclude more than this would require more data. On the other hand, the mere fact that the specimens were mixed and tested without incident shows that it is possible to handle the material safely with adequate precautions.

Reaction Intensity Tests

As indicated previously, the testing emphasis in this program was on reaction intensity, as it was believed that this parameter would be more useful

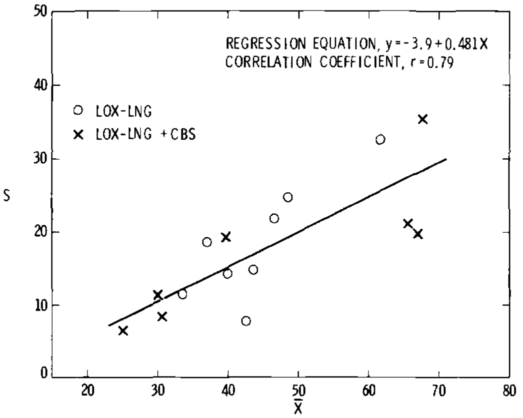


FIG. 9—*Regression of standard deviation mean for reaction intensity measurements.*

TABLE 3—*Transformed data for the standard deviation and mean for reaction intensity measurements.*

Test No.	1.3	1.4	1.5	1.7	1.8	1.9	1.10	1.12	2.1	2.2	2.3	2.4	2.5	2.6	2.7
X'_i	1.681	1.792	1.644	1.778	1.764	1.475	1.505	1.764	1.146	1.415	1.826	1.279	1.146	1.580	1.602
	1.000	1.041	1.580	1.415	1.869	1.415	1.415	0.903	1.415	1.431	1.756	1.415	1.477	1.000	1.662
	1.301	1.380	1.447	2.064	1.716	1.342	1.301	1.580	1.301	1.716	1.756	1.114		1.146	1.623
	1.255	1.041	1.447	1.079	1.000	1.447	1.255	1.531	1.079	2.100	1.580	1.322		1.531	1.792
	1.505	1.644		1.857	1.505	1.663	1.602	1.602	1.146	1.643	1.851	0.903		1.832	1.778
	1.301	1.255		1.415	1.255	1.903	1.748	1.505	1.580	1.924	1.908	1.176		1.505	1.380
	1.447	1.519		1.820				1.602	1.505	1.763	1.845				1.748
	1.447			1.505					1.447		1.279				1.954
				1.857					1.342		1.591				1.806
									1.301		1.917				1.954
											1.820				
Test No.	1.3	1.4	1.5	1.7	1.8	1.9	1.10	1.12	2.1	2.2	2.3	2.4	2.5	2.6	2.7
$\overline{X}'$	1.3671	1.3817	1.5295	1.6433	1.5181	1.5408	1.4710	1.4981	1.3262	1.7131	1.7390	1.2015	1.3115	1.4298	1.7299
S'	0.2022	0.2896	0.0984	0.3078	0.3346	0.2068	0.1862	0.2749	0.1632	0.2481	0.1889	0.1805	0.2340	0.2785	0.1723

in assessing hazard. Thus, the amount of data gathered was sufficient for the use of standard analysis of variance techniques which, in turn, permitted the extraction of the maximum amount of information.

The first step in the analysis was to calculate means and variances for the reaction intensity data as summarized in Table 2. Here, $\bar{X}$ indicates the mean and S the standard deviation, assuming that this type of data would be reasonably normally distributed in the region $+\sigma$ to $-\sigma$. It should be noted that many of the tests produced data similar to those for Test 2. 6, in which 3 out of 10 tests produced either partial or negative reactions. For purposes of calculating $\bar{X}$ and S, the negative or partial or both results were excluded, as it was judged that their inclusion would produce unacceptable abnormality of the distribution. (Such results were not discarded, however, since they were used to calculate reaction frequencies.)

The next step was to plot $\bar{X}$ versus S for all tests, as shown in Fig. 9 (excluding, of course, the PETN tests.) Here, it is apparent that the data scatter increases with $\bar{X}$. Since the analysis of variance technique requires homogeneous variances, it was clearly necessary to rectify the situation by a transformation. For a dependency of the form $S = A\,(\bar{X} + B)$, the transformation $X' = \log(X + B)$ is appropriate. For Fig. 9, the transformation was calculated to be $X' = \log(X - 8)$. Table 3 shows the transformed data.

As a check on the transformation, $\bar{X}'$ was plotted versus S', and the regression was found to be nearly parallel to the abscissa. This leads to the conclusion that the transformed data adequately fulfill the homogeneity of variance criterion.

Table 4 shows the results of the analysis of variance and also the one statistic for which all the previous mathematical calculations were performed, namely, the pooled estimate of sample variance, S_p^2. The usefulness of this statistic is felt to be worthy of emphasis through an example. Assume it is desired to calculate a 90 percent confidence interval for the mean of the transformed data of Test 1.7, for which $\bar{X}' = 1.6433$, $S' = 0.3078$, and $n = 9$. The confidence limits would be defined by

TABLE 4—*Analysis of variance for transformed reaction intensity data.*

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square
Between Treatments	14	2.8337	0.2024
Within Treatments	91	4.9052	0.0539
Total	105	7.7389	

$$\bar{X}' \pm \frac{S'}{\sqrt{n}}\, t$$

wherein t would be obtained from a table of the Student's "t" distribution for $\alpha = 0.05$ and $n - 1$ degrees of freedom. The numbers would be

$$1.6433 \pm \frac{0.3078}{\sqrt{9}}\ 1.860$$

or

$$1.6433 \pm 0.1908$$

But, S_p^2 is an overall average sample variance, which takes into account much more than just the nine specimens of this particular test. It is, in fact, a better estimate of the population variance for this particular group of specimens than is S'. If $S_p = \sqrt{S_p^2}$ is used in place of S', a t value for 91 degrees of freedom can also be used. Now, the confidence interval is

$$1.6433 \pm \frac{0.2322}{3}\ 1.662$$

or

$$1.6433 \pm 0.1286$$

which illustrates the value of the pooled estimate of variance.

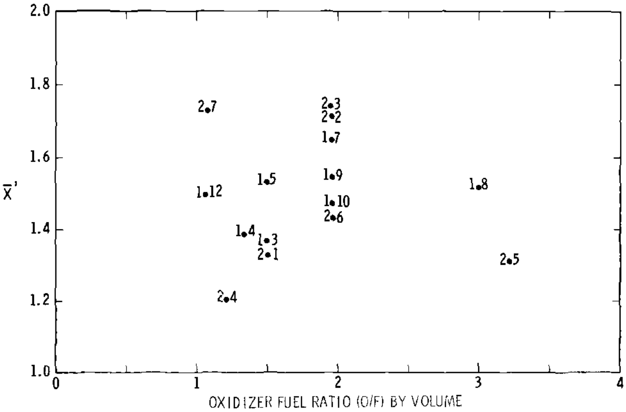


FIG. 10—*Reaction intensity versus O/F Ratio.*

TABLE 5—*Comparison of means by Duncan's multiple range test.*

Test No.	2.4	2.5	2.1	1.3	1.4	2.6	1.10	1.12	1.8	1.5	1.9	1.7	2.2	2.7	2.3
$\bar{X}'$	1.2015	1.3115	1.3262	1.3671	1.3817	1.4298	1.4710	1.4981	1.5181	1.5295	1.5408	1.6433	1.7131	1.7299	1.7390
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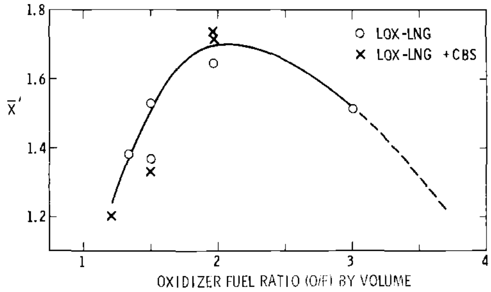

FIG. 11—*Reaction intensity results for tests conducted on 12, 15, and 24 Feb. 1971.*

Getting back to the problem, the next step is to determine which of the various $\bar{X}$'s are significantly different. Currently, the best method for this is Duncan's multiple range test [6] for unequal sample sizes. Without going through the mathematics of this procedure, it can be stated briefly that the differences between the various means, S_p, and a table of least significant ranges are used to yield the results in Table 5. Here, the means are arranged in ascending order of magnitude. Those means which are underscored by the same solid line are not significantly different at the 0.05 level of significance. Note that $\bar{X}'_{2.3}$ is significantly different from $\bar{X}'_{2.6}$, but not from $\bar{X}'_{1.10}$.

Thus, the data scatter is considerable, and it would be difficult to substantiate many conclusions concerning the effects of the various sample material treatments. On the other hand, it is clear that the presence of CAB-O-SIL has little effect, if any, on the reaction intensity.

However, if we plot reaction intensity data obtained on 12, 15, and 24 Feb. 1971 on one graph and those obtained on 25 Feb. 1971 on another, we get the results shown in Figs. 11 and 12. As discussed earlier, sample preparations on 12, 15, and 24 Feb. 1971 consisted of mixing a batch and pouring a mixture in all the individual test cups prior to testing. On 25 Feb.

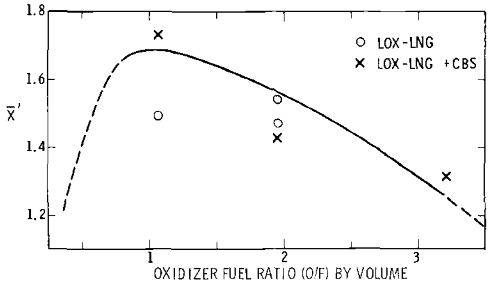

FIG. 12—*Reaction intensity results for tests conducted on 25 Feb. 1971.*

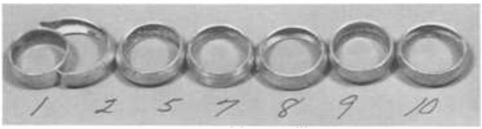

FIG. 13—*Post-test view of specimen cup sleeves for Test 1.10.*

1971, the procedure was changed to pouring the mixture into a test cup and testing the sample before pouring the next one. In Figs. 11 and 12 we have drawn in trend lines roughly through the middle of the various groups. It can be seen that the entire trend seemed to shift to the left in Fig. 12. It is believed that this behavior reflects the differences in sample preparation procedure (and thus the rate of change of O/F ratio) discussed in the previous section. It is also believed that this same factor caused the previously discussed difficulties in the sensitivity measurements.

Finally, it is interesting to note that the LOX-LNG mixtures as a group were more energetic than equivalent amounts of PETN impacted under similar conditions. This is exemplified in the reaction intensity data discussed previously. Also, Fig. 13 shows that when the reactions occurred the damage to the specimen cup sleeves was greater than that of equivalent amounts of PETN (see Fig. 8).

Conclusions

It appears that the addition of CAB-O-SIL has little or no effect on either sensitivity or reaction intensity of mixtures of LOX and LNG.

The sensitivities of O/F ratios between 1 and 3 (by volume) are of approximately the same order of magnitude as PETN. Above O/F = 3, the sensitivity is less.

The reaction intensities of O/F ratios between 1 and 3 are higher than that of PETN, but diminish rapidly for O/F ratios greater than 3.

Test results were apparently affected by boil off of LOX during the test. Such boil off would cause the O/F ratio originally mixed to change rapidly during the course of a test, and this would affect both sensitivity and reaction intensity. Considering the sensitivity and reaction intensity behavior of O/F mixtures greater than 3, this suggests that starting a job with overly lean mixtures would be a good safety practice.

In general, LOX/LNG mixtures appear to have about the same degree of handling hazard as PETN, but are potentially more energetic. Further, the mixture need not be made until the last minute, thus avoiding most handling hazards.

References

[*1*] Blackstone, W. R., Baber, B. B., and Ku, P. M., *Transactions,* American Society of Lubrication Engineers, Vol. 11, No. 3, July 1968.

[*2*] "Proposed Method of Test for Compatibility of Materials with Liquid Oxygen (Reaction Intensity Method)," published for information only in 1970 edition of Part 18, *Book of Annual ASTM Standards.*

[*3*] Dixon, W. J. and Massey, F. J., Jr., *An Introduction to Statistical Analysis,* McGraw-Hill, New York, 1957.

[*4*] Rothman, D., Alexander, M. J., and Zimmerman, J. M., "The Design and Analysis of Sensitivity Experiments," NASA CR-62026, Vols. I and II, National Aeronautics and Space Administration, May 1965.

[*5*] Dixon, W. J., *American Statistical Association Journal,* Vol. 60, 1965, pp. 967–978.

[*6*] Duncan, D. B., *Biometrics,* Vol. 13, 1957, pp. 164–176.

R. D. Leonard[1] *and J. McCarty*[2]

Considerations for Design Specifications and Testing of Low Temperature Cryogenic Equipment

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REFERENCE: Leonard, R. D. and McCarthy, J., "**Considerations for Design Specifications and Testing of Low Temperature Cryogenic Equipment,**" *Cryogens and Gases: Testing Methods and Standards Development, ASTM STP 537,* American Society for Testing and Materials, 1973, pp. 59–63.

ABSTRACT: The growth of the cryogenic industry has allowed low temperature experimenters the option to purchase (commerically) low temperature cryogenic equipment for sophisticated and exacting needs. Suggestions and considerations are presented for the specifications, design, testing, and use of such equipment.

KEY WORDS: cryogenics, low temperature research, temperature measurement, design, equipment specifications, testing equipment

Recent advances in technology have managed to significantly reduce the steady state low temperature available to those interested in the field. This, together with the increase in the use of cryogenic fluids in both industry and research laboratories, has led to a situation where innovation and initiative are essential to the maintenance of competitive products. One must be able to construct systems that maintain stable temperatures under extreme and adverse conditions. It is not unreasonable to expect request for systems that will contain large volumes of liquid ^{3}He at a temperature of 0.2°K that will sustain heat loads from 2 W to less than 1 erg/s. The modifications necessary to compensate for this variable input are unfortunately not just a matter of scaling. There are many experiences, techniques, and hopeful extrapola-

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tions necessary to accomplish this. However, we can outline some of the problems. Just as the experience gained with standard ^{3}He refrigerators at temperatures of 0.3°K are useful when building a ^{3}He/^{4}He Dilution Refrigerator it is by no means the only requirement. Although the temperature of those devices is reduced by an order of magnitude (0.03°K), the problems associated with temperature measurement, environment, and quality control have more than compensated by increasing several orders of magnitude.

The first consideration before attempting a design is to clarify the equipment specifications. Most customers initially desire a system with as many variables as money allows. These would include temperature range, heat extraction, modular components, and versatility for many experimental uses. One should first attempt to define what the major purpose is and then limit and assign priorities to the remaining items. Systems have been designed for excellent multipurpose uses. Frequently, because of unreasonable expectations, one can construct a dewar system that does many things, although none of them well!

Design Specifications

As the systems become more sophisticated, more care must be given to precise statements about the requirements and capabilities. For a standard dewar designed to hold 10 liters of liquid ^{4}He at 4.2°K for 100 h while in a typical laboratory environment, there are little uncertainties. As the required temperature of the system is lowered, those items that were given little consideration or taken for granted become extremely important.

In particular, consider the problems involved with the ^{3}He/^{4}He Dilution Refrigerator System where temperature of 0.020°K must be maintained as long as several weeks. The obvious aspects of the environment that can significantly affect the capabilities of the system include:

1. Isolation of systems from external vibration;
2. Physical limitation due to space of external pumps and gas lines; and
3. Isolation of system from AC and RF pickup.

It is always possible to reduce the above items so they do not seriously degrade systems performance. However, whether or not they are still large enough to limit how well we measure the operation is another question. Most techniques for measuring temperature in the milli-degree region require complex electronics at room temperature and sensors with low heat capacity at the cold region. These devices, such as carbon resistors or paramagnetic salts, are frequently more sensitive to an adverse environment than the Dilution Refrigerator itself.

In the region of temperature where gas thermometry is no longer feasible, careful consideration must be given to the exact type of thermometer that will be used to define the temperature. These questions should be discussed and agreed upon before design for the system is undertaken. If enough thought is devoted to these problems, one can expect to avoid situations where a system achieves design temperature only from midnight to six a.m. or when an offending FM radio station is on the air.

Design

In systems of moderate complexity a decision must be made whether to build an integral unit or one with modular components. The initial cost of the modular unit is higher. However, it allows access to all vacuum areas of the system and can be easily modified or repaired. This can be accomplished with rubber O-ring flanges at room temperature and the reliable metal seals in the cold area. Factors which govern the initial choice of design include:

1. Reliability and mechanical strength of vacuum joints;
2. Intended time period for dewar use;
3. Where and how dewar will be used;
4. Expected multipurpose functions; and
5. Cost.

Many materials are now commonly accepted for cryogenic use. In addition to the old standby stainless steel, structural members are being constructed of fiber glass epoxy laminates. These laminates are nearly as strong as aluminum (tensile strength 20 000 psi) and have thermal conductivities of the order 0.5×10^{-2}W – cm/cm^2 – K (approximately 20 times less than stainless steel.) By the use of suitable epoxies and other improved joining techniques almost any materials can be joined together.

Another consideration may be the elimination of the nitrogen shield for helium vessels. Such designs can and often do have lower boil-off rates than with a nitrogen shield. However, due to the extra mass to be cooled with the boil-off gas, cool down times are generally longer (6 to 10 h as compared to 2 to 3 h with the nitrogen shield.)

Testing

For dewars to accept cryogenic inserts, the primary consideration for testing purposes is the measured boil-off rate. If, however, the system is to function as a refrigerator by the forced evaporation of a cryogenic fluid or the circulation of ^{3}He/^{4}He, provisions must be made for measuring several other variables. The ^{3}He/^{4}He Dilution Refrigerator is the most demanding in regards to environment and system monitors. Besides measuring normal boil-off rates from atmospheric pressure N_2 and ^{4}He, it is necessary to monitor the temperature and heat extraction rates of the low pressure ^{4}He condensing bath and the Dilution Refrigerator.

The most exacting requirement is that of temperature measurement. This value together with the heat extraction capability is of primary importance to the user. Where the experimentor is only interested in the temperature dependence of some physical variable, for the designer this measurement is the end result. With this in mind every effort should be made to establish a testing facility where accurate temperature measurements can be made. If one surveys existing low temperature laboratories, it will become clear that this is not a trivial problem nor is there a common opinion on how it should be solved.

We can quickly catalog the areas of design and testing that become increasingly important as temperature reaches the milli-degree region:

1. Thermal heating due to external vibrations of pump, building, etc.

2. Fluxuating heat leak due to absorption of residual exchange gas (generally ^{4}He used to precool refrigerator.)

3. Thermal radiation from warm surfaces to cold region. The radiation from heat shields at 4.2°K is of the order 1.2 erg/min cm^2, and this level already can influence the refrigerator operation. The effect on the thermal sensors such as carbon resistors is even more drastic since they are typically maintained at heat loads of 10^{-15} W or smaller.

4. Temperature gradients created when small heat inputs are applied to the refrigerator. This is a result of the rapidly decreasing thermal conductivity of most metals at these temperatures and the increasing Kapitza resistance.

5. Transmission of radio frequency voltages through monitor leads to low temperature components. This can be a perplexing and time consuming problem. The attitude toward a solution depends frequently on past difficulties encountered. At times, it is possible to overcome this problem by just doing an adequate job of shielding external cables. Depending upon the location of the system, it may be necessary to construct a shielded room completely enclosed with copper conductor, power lines, filtered lines, and all other service lines insulated from the room. This facility aids accurate measurements, but due to its cost, it is probably worthwhile to make several tests initially before deciding that it is needed.

Use

If it were possible, we should license cryogenic users. However, the next best of all possible worlds would be to generate elaborate operating manuals and insist upon a strict obedience to the rules. In a sense certain companies already require the equivalent of a driver's test by means of mandatory commissioning. We do not think it is necessary, we hope!

Bibliography

[*1*] Sarvinski, R. E., "Thermal Contact and Isolation in *Proceedings,* 1970 Ultralow Temperature Symposium, Naval Research Laboratory, Washington, D.C. 20390.

[2] Scott, R. B., *Cryogenic Engineering,* Van Nostrand, New York, 1959.

[*3*] Vance, R. W. and Duke, W. M., *Applied Cryogenic Engineering,* Wiley, New York, 1962.

V. J. Johnson[1]

Thermodynamic and Transport Properties of Cryogenic Propellants and Related Fluids

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REFERENCE: Johnson, V. J., **"Thermodynamic and Transport Properties of Cryogenic Propellants and Related Fluids,"** *Cryogens and Gases: Testing Methods and Standards Development, ASTM STP 537,* American Society for Testing and Materials, 1973, pp. 64–77.

ABSTRACT: Significant advances have been made in recent years in the quality and range of thermophysical data for the cryogenic propellants, pressurants, and inertants. These advances have resulted from improved evaluation and compilation techniques coupled with better and more extensive experimental data and from a better theoretical understanding of the physical properties of gases. A review of recently completed and current data compilation projects for helium, hydrogen, argon, nitrogen, oxygen, fluorine, and methane will be given as well as recommended references for thermodynamic and transport property data tables for these fluids. Modern techniques in the plotting of thermodynamic charts from tabular data (or from functions such as the equation of state) have greatly improved their precision and value. A list of such charts is included.

KEY WORDS: argon, bibliographies, compiliers, evaluation, cryogenics, measurement, fluorine, helium, hydrogen, methane, nitrogen, oxygen, fluid properties, reviewing, charts, thermodynamic properties, transport properties

This discussion will center primarily around the program of the Cryogenics Division of the National Bureau of Standards (NBS) in the measurement and critical evaluation of thermodynamic and transport property data for the principal cryogenic fluids. This program was initiated in 1958 under sponsorship of the United States Air Force (USAF) and resulted in the establishment of the Cryogenic Data Center and a highly sophisticated fluid properties measurements laboratory. Major sponsorship of the program was

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later transferred to the National Aeronautics and Space Administration (NASA), but the USAF and other agencies maintain a close interest and provided some support.

Precise property measurements have been made and published only for parahydrogen, oxygen, fluorine, and methane. These are discussed under the specific fluid headings, the principal publications are listed in the references, and charts are listed in the Appendix.

The critical evaluation and compilation program, which is one of the principal functions of the Cryogenic Data Center, covers an extensive list of cryogenic fluids and fluid properties. Of primary concern, however, are those covered by the initial USAF survey that resulted in a report issued in four parts in 1960 and 1961 [*1*].[2] The compendium summarized the status of thermophysical property data at that time for the materials covered. It also formed a basis for future data compilation tasks and showed the areas most in need of better data.

In the intervening period of more than twelve years, an extensive data compilation program (in addition to the measurements program just mentioned) has been carried on for thermodynamic and transport properties for most of the cryogenic fluids in both the liquid and gaseous state, including the following that are pertinent to this discussion:

Helium-4
Hydrogen (para, normal, and equilibrium)
Argon
Nitrogen
Oxygen
Fluorine
Methane

In this paper I will describe briefly the data compilation tasks for each of the materials listed, indicate those in which the Cryogenics Division of the NBS has made significant contributions, and list the more important tables and charts that may be used as sources of cryogenic engineering data. A more complete discussion of these tasks is given in a recent report [2] to the principal sponsor[3] of many of the tasks.

Thermodynamic (Equilibrium) Properties

These properties are the pressure-volume-temperature (PVT) and derived properties such as enthalpy, entropy, internal energy, specific heats C_P and C_V, and velocity of sound.

[2] The italic numbers in brackets refer to the list of references appended to this paper.

[3] NASA, Office of Advanced Research and Technology, Contract R-06-006-046.

Perhaps the best way to describe the various thermodynamic properties programs is to highlight current or past activities or both for each of the cryogenic fluids in the order listed previously.

Helium-4

A task for the critical evaluation of the thermodynamic properties of helium-4 from 2 to 1500 K and for pressures up to 1000 has been carried on for a number of years by R. D. McCarty and is nearly finished. He has fitted all available data to a new 34 term polynomial Benedict-Webb-Rubin type equation of state. This fitting effort has not only improved the correlation of existing data but has more clearly defined the areas in which better experimental data are needed. Before a completely satisfactory thermodynamic correlation can be accomplished it is essential that additional PVT, specific heat, and velocity of sound measurements be made over the temperature range of 2 to 70 K for pressures from 0.01 to 350 atm. The preliminary results of this task have been distributed for review [*3*]. A National Standard Reference Data System—NBS (NSRDS-NBS) monograph [*4*] is now in final draft form and two NBS Technical Notes presenting the data in the International System of Units (SI) and in British units will be published soon [*5, 6*]. This work extends and improves upon previous work by Mann [*7, 8*] which has been widely used throughout the world.

Parahydrogen

NBS Monograph 94 by Roder et al [*9*] is the latest and most authoritative publication for the thermodynamic and related properties of parahydrogen from the triple point to 100 K and pressures to 340 atm. This monograph was prepared from an extensive experimental measurements program conducted in the Cryogenics Division of NBS. Subsequently, Hall et al prepared a computer program for the thermodynamic and transport properties of hydrogen to 5000 R and pressures to 5000 psi [*10*]. This program, prepared for NASA,[4] was widely used by the NASA-Atomic Energy Commission (AEC) Space Nuclear Propulsion Office and its contractors in the nuclear propulsion project (NERVA). Eight properties are covered: pressure, volume, temperature, enthalpy, entropy, internal energy, viscosity, and thermal conductivity. Entry into the tabular code can be made with either pressure and temperature or pressure and enthalpy, and corresponding values will be listed for the other six properties. A similar set of computer programs (Tabcode II) for equilibrium hydrogen properties is nearly finished [*11*]. The equilibrium hydrogen properties code is useful in situations where parahydrogen has been subjected to an environment of high neutron

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[4] NASA-AEC Space Nuclear Propulsion Office, Contract R-45.

flux such as in a nuclear propulsion engine. Under such conditions rapid conversion to equilibrium concentrations of the ortho-para mixture may be expected. Ortho-para equilibrium is also approached in many other situations, so this new program should also be of fairly wide interest.

Other related compilations for parahydrogen are listed in Refs *12* and *13*. Reference *12* was an advance publication to NBS Monograph 94 [*9*] and is particularly useful in that it lists values for the properties of parahydrogen to 300 K. Reference *13* summarizes work done at NBS correlating the properties in the solid-vapor and solid-liquid regions.

The most extensive and comprehensive compilation of the thermophysical properties of parahydrogen from the freezing-liquid line to 5000 R for pressures to 10 000 psia was prepared by McCarty and Weber [*14*]. It is a recorrelation, interpolation, and extrapolation of all available data for the following properties and parameters: pressure-volume/density-temperature, entropy, enthalpy, internal energy, speed of sound, specific heats, thermal conductivity, viscosity, thermal diffusivity, Prandtl number, and dielectric constant for the saturated fluid and for 65 isobars. Also included in the isobaric tables are the following quantities of special utility in heat transfer and thermodynamic calculations: $(\partial P/\partial V)_T$, $(\partial P/\partial T)_V$, $V(\partial H/\partial V)_P$, $V(\partial P/\partial U)_V$, $-V(\partial P/\partial V)_T$, and $1/V(\partial V/\partial T)_P$. Surface tension of the liquid, pressure temperature (PT) values for the melting line, index of refraction, and derived JouleThomson inversion curve are also presented.

Normal Hydrogen

The most extensive compilation of the thermal properties of hydrogen was prepared by Woolley et al [*15*] in 1948. For normal hydrogen, Dean [*16*] in 1961, prepared a tabulation of the thermodynamic properties from low temperatures to 300 K and pressures from 1 to 100 atm (and a similar one in British units [*17*]) based on the circular by Woolley et al. These technical notes are much more convenient to use than the circular, and they have been quite popular.

A compilation of the property differences of orthohydrogen and parahydrogen or mixtures of orthohydrogen and parahydrogen was prepared by Hust and Stewart [*18*] in 1965 and has been useful where properties of various mixtures of orthohydrogen and parahydrogen are needed.

Argon

Thermodynamic properties of argon have been measured in many laboratories but usually for limited ranges of pressure and temperature. Collectively, however, the properties are well known over a wide range of pressure and temperature.

Gosman et al [*19*] have compiled the thermodynamic properties of argon from the triple point to 300 K for pressures to 1000 atm. It is interesting to note that this work is in very close agreement, in the areas of overlap, with a similar compilation by vasserman and Rabinovitch of the USSR [*20, 21*]. The Thermodynamic Tables Project of the International Union of Pure and Applied Chemistry (UIPAC) has compared these two compilations and have found the agreement sufficiently good to justify the preparation of an international table for argon over the full range of both sources. The international table is now published [*22*] and is available as indicated in the bibliography.

Nitrogen

Nitrogen is one of the most widely used of all cryogenic fluids, yet today we have relatively poorer knowledge of its wide range physical properties than the other common cryogenic fluids, namely, helium, hydrogen, argon, and oxygen. An extensive correlation of the thermodynamic properties of nitrogen from 64 to 300 K for pressures from 0.1 to 200 was completed in 1961 by Strobridge [*23, 24*]. This is still the most widely used source of data for values of volume, enthalpy, internal energy, and entropy for the liquid and gaseous phases within its range of pressure and temperature. These tables and the associated temperature-entropy chart [*D-23*] are based on a single equation of state which has become a model for many subsequent equations of state used to correlate properties of fluids.

More recently, Coleman and Stewart [*25*] have recorrelated the nitrogen data and extended it to 1000 K and 1000 atm pressure, using a somewhat similar single equation of the Benedict-Webb-Rubin polynominal type having 23 constants. In the area of common coverage their results are essentially equivalent to that of Strobridge and the user will find no significant difference in the numbers reported, except for the different datum values used for the derived properties.

The latest correlation and compilation of nitrogen data is reported by Jacobsen [*26*]. A thorough analysis of Coleman and Stewart's [*25*] equation and a recorrelation of the nitrogen data yielded a 32 coefficient equation that not only provided an improved fitting of the data (including calculation of the derived properties), but allowed an extension of the temperature and pressure ranges to 2000 K and 10 000 atm with an estimated inaccuracy of 0.3 percent or less. A saturation table ranging from the triple point to the critical point and 21 isobaric tables give values for pressure-volume/density-temperature, internal energy, enthalpy, entropy, specific heats (C_P and C_V), and velocity of sound. An extension of this work by Stewart et al is nearing completion, and a final report will soon be issued [*27*].

The ultimate accuracy of the property values compiled in these correlations is severely limited by the fact that there have been practically no new significant wide-range measurements performed on nitrogen in recent years. The quality of existing thermodynamic property measurements at low temperatures ranges from poor to nonexistent. Furthermore, there are no accurate calculations of the specific heats or sound velocities of liquid or compressed gaseous nitrogen at low temperatures. This is because there are very few accurate PVT measurements at low temperatures and in a wide pressure range, no C_v specific heat measurements, and practically no C_p specific heat measurements in the liquid range. Before any real improvement in property values for nitrogen can be achieved new experimental measurements must be made.

Oxygen

The initial correlation of the thermodynamic properties of oxygen done at NBS in the Cryogenic Data Center was completed by Stewart [*28*]. It was based on all of the thermodynamic property measurements then available in the literature, as well as new PVT measurements being made within the NBS Cryogenics Division by Weber [*29*]. Using a single equation of state, Stewart compiled values of density, enthalpy, internal energy, and entropy, for temperatures from 65 to 300 K and pressures from 0.02 to 340 atm.

In 1968 a most precise and extensive program for measurement of the PVT and specific heat at constant volume (C_v) for oxygen was completed for the range of temperatures and pressures from the triple point to 300 K and 350 atm. The results were first distributed in NBS Report form [*29*] and then published in the NBS *Journal of Research* [*30, 31*]. They represent over 80 percent of all published experimental measurements for the range covered. Tabulations of property values are given for volume, isotherm derivative $(\partial P/\partial \rho)_T$, isochore derivative $(\partial P/\partial T)_\rho$, internal energy, enthalpy, entropy, constant volume heat capacity (C_V), constant pressure heat capacity (C_p), and velocity of sound, for liquid and gaseous phases, including saturated liquid and vapor.

More recently McCarty and Weber prepared an extensive compilation of the properties of oxygen in British units for NASA [*32*] based on the data referred to in the above paragraph. It gives precise, closely spaced data for oxygen in the supercritical region in which the oxygen tanks on the Apollo command and service module operated. These data were used in determining the chain of events occurring in the Apollo 13 incident where the oxygen tank exploded.

Another contribution of the oxygen properties program is "an improved vapor pressure representation" developed by Prydz [*33*]. His vapor pressure equation represents the best available oxygen data to within their precision over the whole temperature range from the triple point to the critical point.

A program for measurement of the dielectric constant of compressed gaseous and liquid oxygen has been completed by Younglove [*34*], and the results are published in the NBS *Journal of Research.* These are very precise measurements which will, when combined with the accurate density data, provide a better Clausius-Mossotti function. This can be very useful in determining the density of oxygen in large storage tanks where a capacitance gage is used or making density extrapolations where it is difficult to determine density directly.

The measurement program for the velocity of sound in saturated and compressed fluid oxygen has also been completed. The results have been prepared for publication by Straty and Younglove [*35*]. These new data will be quite useful in checking other property values as well as for engineering purposes.

An extensive oxygen technology survey of the thermophysical properties of oxygen for NASA's Aerospace Safety Research and Data Institute (AS-RDI) was prepared by Roder and Weber [*36*]. It is a handbook covering all available property data. Extensive tables, charts, and a full description of the property values including source and uncertainties are included.

Fluorine

Fluorine is the third cryogenic fluid for which an extensive properties measurement program has been conducted in the NBS Cryogenics Division. Programs on hydrogen and oxygen have been completed, and a methane property measurements program is now in progress. There were practically no measured properties of fluorine that were reliable. Precise PVT and C_v measurements were made in 1969 and 1970 under sponsorship of the USAF[5] for temperature and pressure ranges from the triple point to 300 K and 200 atm. The resulting publication of the data by Prydz and Straty [*37*] provides a tabulation at closely spaced increments of temperature and pressure for density, the isotherm derivative $(\partial P/\partial \rho)_T$, isochore derivative $(\partial P/\partial T)_\rho$, internal energy, enthalpy, entropy, specific heats (C_v and C_p), and velocity of sound. Experimental measurement of the dielectric constant and molar polarizability of compressed gaseous and liquid fluorine has also been completed by Straty and Younglove, and the results have been submitted for publication [*38*]. The range covered is from near the triple point (53.48 K) to 300 K and for pressures to 200 atm.

[5] USAF Contract MIPR No. FO 4611-70-X-0001.

Calculated values for the viscosity and thermal conductivity coefficients of gaseous and liquid fluorine were assembled by Hanley and Prydz [*39*] and have also been submitted for publication. The range covered is from 70 to 300 K for pressures to 200 atm. These calculations were made from kinetic theory and the modified Enskog theory, given the new PVT data, since no reliable transport property data were available. Even so, the uncertainty of their values was believed to be less than 5 percent except near the critical point. Incidentally, new experimental measurements of viscosity have just been completed, and a preliminary analysis of the results indicate that they are in excellent agreement with Hanley's and Prydz's calculated values.

Methane

It is likely that many cryogenic processes will involve the liquefaction, storage, and pumping of methane either as a pure fluid or as the major component of liquefied natural gas (LNG) as the use of LNG continues to increase. Accordingly, there is a need for accurate thermodynamic property values for this fluid from room temperature down to the solid-liquid boundary with emphasis on the saturated and compressed liquid states. An extensive literature survey on the properties of methane was completed in 1968 and presented in the form of an annotated bibliography by Hall [*40*]. This search has since been updated and a critical review of the data made by Goodwin [*41, 42*]. The data were fitted to an equation of state and other thermodynamic functions and the results tabulated [*43*]. Values for internal energy, enthalpy, entropy, C_v, C_p, velocity of sound, and vapor pressure are given.

The Cryogenics Division is engaged in an extensive experimental measurements program for methane. PVT, specific heat (C_v), and dielectric constant measurements have been completed. Viscosity measurements are underway and velocity of sound and thermal diffusion measurements planned. A paper by Prydz and Goodwin on the experimental melting and vapor pressures of methane has been published [*44*], and one by Goodwin and Prydz on densities of compressed liquid methane and the equation of state has also been published [*45*]. A comprehensive report on the thermophysical properties of methane is now being prepared.[6]

Transport Properties

An extensive program to study the transport properties of the cryogenic fluids was undertaken about seven years ago. The object of the program was

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[6] This work is being sponsored by the American Gas Association (AGA).

to clarify the state of the art of the transport properties and to provide tables, correlations and predictive techniques for the transport coefficients. Very encouraging progress has been made on the program as can be noted from the list of publications that have evolved [*46–60*]. Viscosity and thermal conductivity coefficients for the dilute gas phase of the following fluids have been published: argon [*47*], nitrogen and oxygen [*48*], neon, krypton, and xenon [*49*], and hydrogen [*58*]. A preliminary compilation has also been completed for the viscosity and thermal conductivity coefficients of nine fluids from about two-thirds critical temperature to 300 K and for pressures to 200 atm [*59*].

The nine fluids are oxygen, krypton, xenon, hydrogen, helium, oxygen, nitrogen, methane, and fluorine.

The transport properties program might be summarized as follows:

1. Careful fundamental studies on transport phenomena have led to: *(a)* Re-evaluation of experimental work in NBS and elsewhere which has revealed some fundamental errors [*60*]. *(b)* A better testing procedure of transport property theories. *(c)* A prediction technique of the transport properties for fluids for which data are not available, for example, as has been done for fluorine.
2. The program is providing authoritative tables of viscosity, thermal conductivity, and thermal diffusion coefficients.

Documentation Activities

A major part of the Cryogenic Data Center is its documentation function which is essential to the Division's properties of materials programs as well as other Division programs. A complete review of these data and information service of the Cryogenic Data Center was recently published by Neil Olien [*61*], acting director of the center.

A thorough and continuous search of current published literature is conducted. Over 300 journals are reviewed cover to cover, as well as searches of abstracting services, patents, conference proceedings, and report literature made. Dissemination is made each week through the Current Awareness Service. In addition, two specialized bibliographies are published quarterly, the *Superconducting Devices and Materials Quarterly* and the *Liquefied Natural Gas Quarterly.* Documents from these lists are then selected for entry into the information retrieval system. Magnetic tapes containing title, author, author's affiliation, reference, abstract reference, and indexing terms are used for storage and search purposes. Some 7000 new documents are added each year, and the total file now contains more than 80 000 documents. The availability of these data on magnetic tape permits rapid access to a vast amount of information. With these resources the Cryogenic Division is undoubtedly the largest source of data on the properties of materials and other bibliographic information at cryotemperatures.

APPENDIX

Thermodynamic Charts for Properties of Cryogenic Fluids[7]

Helium-4

D-52 Temperature-entropy diagram for helium (15 to 300 K; 0.1 to 100 atm). National Bureau of Standards, Cryogenics Div., 1964. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-53 Temperature-entropy diagram for helium (3 to 25 K; 0.5 to 100 atm). National Bureau of Standards, Cryogenics Div., 1964. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-54 Enthalpy-entropy chart for helium (3 to 25 K; 1 to 100 atm). National Bureau of Standards, Cryogenics Div., 1964. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-13 Compressibility factor chart for helium, Z versus P (20 to 300 K; 1 to 100 atm), with tabular values. National Bureau of Standards, Cryogenics Div., 1961. Available 8½ by 11 in. and 17 by 22 in. sizes.

Parahydrogen

D-20 Temperature-entropy chart for parahydrogen (14 to 100 K; 0.1 to 340 atm). National Bureau of Standards, Cryogenics Div., 1965. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-21A Interim temperature-entropy chart for parahydrogen (in metric units; 80 to 300 K; 1 to 100 atm). National Bureau of Standards, Cryogenics Div., 1961. Available 8½ by 11 in.; 11 by 17 in. and 17 by 22 in. sizes.

D-22 Enthalpy-entropy chart for parahydrogen (16 to 64 K; 0.3 to 340 atm). National Bureau of Standards, Cryogenics Div., 1965. Available 8½ by 11 in. and 17 by 22 in. sizes.

Normal Hydrogen

D-4 Temperature-entropy diagram of normal hydrogen (0 to 150 K; 0.6 to 300 atm). National Bureau of Standards, 1948. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-5 Temperature-entropy diagram of normal hydrogen (130 to 300 K; 0.8 to 600 atm). National Bureau of Standards, 1948. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-14 Compressibility factor for normal hydrogen; Z versus P (16 to 300 K; 0.08 to 800 atm); with tabular values. National Bureau of Standards, Cryogenics Div., 1961. Available 8½ by 11 in. and 17 by 22 in. sizes.

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[7] Available from the Cryogenic Data Center, National Bureau of Standards, Boulder, Colo. 80302. (Use the D-number indicated).

Argon

D-61 Temperature-entropy chart for argon (85 to 300 K; 0.02 to 100 atm). National Bureau of Standards, Cryogenics Div., 1969. Available 11 by 17 in. size.

D-62 Compressibility factor chart for argon (90 to 300 K; 0.5 to 500 atm). National Bureau of Standards, Cryogenics Div., 1969. Available 11 by 17 in. and 8½ by 11 in. sizes.

Nitrogen

D-23 Temperature-entropy diagram for nitrogen (65 to 300 K; 0.1 to 200 atm). National Bureau of Standards, Cryogenics Div., 1963. Available 8-½ by 11 in. and 17 by 22 in. sizes.

D-16 Compressibility factor chart for nitrogen; Z versus P (90 to 300 K; 1 to 500 atm), with tabular values. National Bureau of Standards, Cryogenics Div., 1961. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-17 Compressibility factor chart for nitrogen; Z versus P (90 to 300 K; 300 to 3000 atm), with tabular values. National Bureau of Standards, Cryogenics Div., 1961. Available 8½ by 11 in and 17 by 22 in. sizes.

Oxygen

D-56 Temperature-entropy chart for oxygen (65 to 300 K; 0.002 to 340 atm). National Bureau of Standards, Cryogenics Div., 1966. Available 8½ by 11 in., 11 by 17 in. and 17 by 22 in. sizes.

D-57 Compressibility factor chart for oxygen (70 to 300 K; 1 to 340 atm). National Bureau of Standards, Cryogenics Div., 1966. Available 8½

D-63 Temperature-entropy chart for oxygen (100 to 600 R; 0.03 to 5000 psia). National Bureau of Standards, Cryogenics Div., 1971. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-65 Pressure-enthalpy chart for oxygen (120 to 580 R; 800 to 1050 psia). National Bureau of Standards, Cryogenics Div., 1971. Available 17 by 22 in. size.

D-66 Enthalpy-entropy chart for Oxygen (110 to 600 R; 0.03 to 5000 psia), by R. D. McCarty and L. A. Weber, National Bureau of Standards, Cryogenics Div., 1971. Available 8½ by 11 in. and 17 by 22 in. sizes.

D-67 Pressure-temperature diagram for oxygen (90 to 600 R; 0 to 5000 psia), by R. D. McCarty and L. A. Weber, 1971. Available 8½ by 11 in. and 17 by 22 in. sizes.

Fluorine

None

Methane

None

References

[1] "A Compendium of the Properties of Materials at Low Temperature," Phase I, V. J. Johnson, general Ed., July 1960 and Phase II, R. B. Stewart and V. J. Johnson, general Eds., Dec. 1961, WADD Technical Report 60–56.

[2] Johnson, V. J. and Diller, D. E., "Thermodynamic and Transport Properties of Fluids and Selected Solids for Cryogenic Applications," Summary Report of work performed on NASA Contracts R-06-006-046 and W-12, 745. National Bureau of Standards Report No. 9782, Oct. 1970, unpublished.

[3] McCarty, R. D., "Provisional Thermodynamic Functions for Helium-4 for Temperatures from 2 to 1500 K with Pressures to 100 MN/m^2 (1000 Atmospheres)," National Bureau of Standards Report, Aug. 1970, unpublished.

[4] McCarty, R. D., "Thermodynamic Properties of Helium-4 from 2 to 1500 K at Pressures to 100 MN/m^2," National Bureau of Standard, NSRDS-NBS Monograph, 1972, in preparation.

[5] McCarty, R. D., "Thermophysical Properties of Helium-4 from 2 to 1500 K with Pressures to 1000 Atmospheres," National Bureau of Standards Technical Note 631, Nov. 1972.

[6] McCarty, R. D., "Thermophysical Properties of Helium-4 from 4 to 3000 R with Pressures to 15,000 psia," National Bureau of Standards Technical Note 622, Sept. 1972.

[7] Mann, D. B., "The Thermodynamic Properties of Helium from 3 to 300 K Between 0.5 and 100 Atmospheres," National Bureau of Standards Technical Note 154, Jan. 1962.

[8] Mann, D. B., "The Thermodynamic Properties of Helium from 6 to 540 R Between 10 and 1500 PSIA," National Bureau of Standards Technical Note 154A Jan. 1962.

[9] Roder, H. M., Weber, L. A., and Goodwin, R. D., "Thermodynamic and Related Properties of Parahydrogen from the Triple Point to 100 K at Pressures to 340 Atmospheres," National Bureau of Standards Monograph 94, Aug. 1965.

[10] Hall, W. J., McCarty, R. D., and Roder, H. M., "Computer Programs for Thermodynamic and Transport Properties of Hydrogen," National Bureau of Standards Report, Aug. 1967, unpublished.

[11] Roder, H. M., McCarty, R. D., and Hall, W. J., "Computer Programs for Thermodynamic and Transport Properties of Hydrogen (Tabcode II)," National Bureau of Standards Technical Note 625, Oct. 1972.

[12] Roder, H. M. and Goodwin, R. D., "Provisional Thermodynamic Functions for Para-Hydrogen," National Bureau of Standards Technical Note 130, Dec. 1961.

[13] Sindt, C. F. and Mann, D. B., "Temperature-Entropy Diagram for Parahydrogen Triple-Point Region," National Bureau of Standards Technical Note 343, June 1966.

[14] McCarty, R. D. and Weber, L. A., "Thermophysical Properties of Para-Hydrogen from the Freezing Liquid line to 5000 R for Pressures to 10,000 PSIA," National Bureau of Standards Technical Note 617, April 1972.

[15] Wolley, H. W., Scott, R. B., and Brickwedde, F. G., "Compilation of Thermal Properties of Hydrogen in its Various Isotopic and Ortho-Para Modifications," *Journal of Research of the National Bureau of Standards,* Vol. 41, Research Report 1932, Nov. 1948.

[16] Dean, J. W., "A Tabulation of the Thermodynamic Properties of Normal Hydrogen from Low Temperatures to 300 K and from 1 to 100 Atmospheres," National Bureau of Standards Technical Note 120, Nov. 1961.

[17] Dean, J. W., "A Tabulation of the Thermodynamic Properties of Normal Hydrogen from Low Temperatures to 540 R and from 10 to 1500 PSIA," National Bureau of Standards Technical Note 120A, June 1962.

[*18*] Hust, J. G. and Stewart, R. B., "A Compilation of the Property Differences of Ortho and Para Hydrogen or Mixtures of Ortho and Para Hydrogen," National Bureau of Standards Report, May 1965, unpublished.

[*19*] Gosman, A. L., McCarty, R. D., and Hust, J. G., "Thermodynamic Properties of Argon from the Triple Point to 300 K at Pressures to 1000 Atmospheres," National Bureau of Standards, NSRDS-NBS 27, March 1969.

[*20*] Vasserman, A. A. and Rabinovich, V. A., "Thermophysical Properties of Liquid Air and Its Components," Publishing House for State Standards, Moscow, 1968; translation: Israel Program for Scientific Translations, Jerusalem, 1970; available from the National Technical Information Service, Springfield, Va.

[*21*] Vasserman, A. A., Kazavchinskii, Ya. Z., and Rabinovich, V. A., "The Thermophysical Properties of Air and its Components," Publishing House for State Standards, Moscow, 1966: translation: Israel Program for Scientific Translations, Jerusalem, 1971, available from the National Technical Information Service, Springfield, Va.

[*22*] Angus, S. and Armstron, B., Eds., *International Thermodynamic Tables of the Fluid State: Argon, 1971*, Butterworths, London, available from Butterworths Scientific Publication, Washington, D.C.

[*23*] Strobridge, T. R., "The Thermodynamic Properties of Nitrogen from 64 to 300 K Between 0.1 and 200 Atmospheres," National Bureau of Standards Technical Note 129, Jan. 1962.

[*24*] Strobridge, T. R., "The Thermodynamic Properties of Nitrogen from 114 to 540 R between 1.0 and 3000 PSIA," National Bureau of Standards Technical Note 129A, Feb. 1963.

[*25*] Coleman, T. C. and Stewart, R. B., "The Thermodynamic Properties of Nitrogen,"Research Report No. 11, University of Idaho; Second Progress Report to Office of Standard Reference Data, National Bureau of Standards Sept. 1970.

[*26*] Jacobsen, R. T., "The Thermodynamic Properties of Nitrogen from 65 to 2000 K with Presesures to 10,000 atm," Ph.D. thesis, Washington State University, 1972.

[*27*] Stewart, R. B., Jacobsen, R. T., and Myers, A. F., "The Thermodynamic Properties of Oxygen and Nitrogen, Part I—Thermodynamic Properties of Nitrogen from 115 R to 3500 R with Pressures to 150,000 psia," final Report to NASA-Manned Spacecraft Center, Houston, 31 Aug. 1972, prepared by the authors at the University of Idaho; Moscow, Idaho.

[*28*] Stewart, R. B., "Thermodynamic Properties of Oxygen," Ph.D. thesis, The University of Iowa, 1966.

[*29*] Weber, L. A., "Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 330 Atmospheres," National Bureau of Standards Report, June 1968, unpublished.

[*30*] Weber, L. A., "P-V-T, Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 33 MN/m^2," *Journal of Research of the National Bureau of Standards,* Vol. 74A, No. 1, Jan.–Feb. 1970.

[*31*] Goodwin, R. D. and Weber, L. A., "Specific Heats C_v of Fluid Oxygen from the Triple Point to 300 K at Pressures to 350 Atmospheres," *Journal of Research of the National Bureau of Standards,* Vol. 73A, No. 1, Jan. 1969.

[*32*] McCarty, R. D. and Weber, L. A., "Thermophysical Properties of Oxygen from the Freezing Liquid Line to 600 R for Pressures to 5000 PSIA," National Bureau of Standards Technical Note 384, July 1971.

[*33*] Prydz, R., *Metrologia,* Vol. 8, No. 1, Jan. 1972, pp. 1–4.

[*34*] Younglove, B. A., *Journal of Research of the National Bureau of Standards,* Vol. 76A, No. 1, Jan.–Feb. 1972, pp. 37–40.

[*35*] Straty, G. C. and Younglove, B. A., "Sound Velocity in Saturated and Compressed Fluid Oxygen," submitted to *Journal of Chemical Thermodynamics* for publication.

[*36*] Roder, H. M. and Weber, L. A., "ASRDI Oxygen Technology Survey, Volume I: Thermophysical Properties," submitted to NASA for publication as a Special Publication. (NASA SP-3071; 1972.)

[*37*] Prydz, R. and Straty, G. C., "The Thermodynamic Properties of Compressed Gaseous and Liquid Fluorine," National Bureau of Standards of Technical Note 392, Oct. 1970.

[*38*] Straty, G. C. and Younglove, B. A., *Journal of Chemical Physics*, Vol. 57, No. 6, Sept. 1972, pp. 2255–2259.

[*39*] Hanley, H. J. M. and Prydz, R., "Calculated Values for the Viscosity and Thermal Conductivity Coefficients of Gaseous and Liquid Fluorine," submitted to *Journal of Physical and Chemical Reference Data* for publication.

[*40*] Hall, L. A., "A Bibliography of Thermophysical Properties of Methane from 0 to 300 K," National Bureau of Standards Technical Note 367, May 1968.

[*41*] Goodwin, R. D., "Thermophysical Properties of Methane: Virial Coefficients, Vapor and Melting Pressures," Journal of Research of the National Bureau of Standards, Vol. 74A, Sept.–Oct. 1970.

[*42*] Goodwin, R. D., "Thermophysical Properties of Methane: Orthobaric Densities and Some Thermal Properties," Journal of Research of the National Bureau of Standards, Vol. 75A, No. 1, Jan.–Feb. 1971.

[*43*] Goodwin, R. D., "Methane Equation of State and Outline of Thermodynamic Functions," First Annual Progress Report to the American Gas Association, National Bureau of Standards Report, Feb. 1971, unpublished.

[*44*] Prydz, R. and Goodwin, R. D., *Journal of Chemical Thermodynamics*, Vol. 4, No. 1, Jan. 1972, pp. 127–133.

[*45*] Goodwin, R. D. and Prydz, R., *Journal of Research of the National Bureau of Standards*, Vol. 76A, No. 2, March–April 1972, pp. 81–101.

[*46*] Hanley, H. J. M., *Journal of Chemical Physics*, Vol. 44, No. 11, June 1966, pp. 4219–4222.

[*47*] Hanley, H. J. M., "The Viscosity and Thermal Conductivity Coefficients of Dilute Argon Between 100 and 2000 K," National Bureau of Standards Technical Note 333, March 1966.

[*48*] Childs, G. E. and Hanley, H. J. M., "The Viscosity and Thermal Conductivity Coefficients of Dilute Nitrogen and Oxygen," National Bureau of Standards Technical Note 350, Oct. 1966.

[*49*] Hanley, H. J. M. and Childs, G. E., "The Viscosity and Thermal Conductivity Coefficients of Dilute Neon, Drypton, and Xenon," National Bureau of Standards Technical Note 352, March 1967.

[*50*] Hanley, H. J. H. and Klein, M., "On the Selection of the Intermolecular Potential Function: Application of Statistical Mechanical Theory to Experiment," National Bureau of Standards Technical Note 360, Nov. 1967.

[*51*] Hanley, H. J. M., *Journal of Chemical Education*, Vol. 44, No. 12, Dec. 1967, pp. 717–723.

[*52*] Childs, G. E. and Hanley, H. J. M., *Cryogenics*, Vol. 8, April 1968, pp. 94–97.

[*53*] Klein, M. and Hanley, H. J. M., *Transactions*, Faraday Society, Vol. 64, No. 551, Part 11, Nov. 1968, pp. 2927–2938.

[*54*] Hanley, H. J. M and Childs, G. E., *Science*, Vol. 159, 1968, pp. 1114–1117.

[*55*] Hanley, H. J. M. and McCarty, R. D., *Journal of Chemical Physics*, Vol. 50, No. 2, Jan. 1969, pp. 857–870.

[*56*] Hanley, H. J. M. and Childs, G. E., *Journal of Chemical Physics*, Vol. 50, No. 10, May 1969, pp. 4600–4601.

[*57*] Hanley, H. J. M. and Klien, M., *Journal of Chemical Physics*, Vol. 50, No. 11, June 1969, pp. 4765–4770.

[*58*] Hanley, H. J. M., McCarty, R. D., and Intemann, H., *Journal of Research of the National Bureau of Standards*, Vol. 74A, No. 3, May–June 1970, pp. 331–353.

[*59*] Angerhofer, P. E. and Hanley, H. J. M., "The Viscosity and Thermal Conductiv-

ity Coefficients of Nine Fluids: Preliminary Values," National Burean of Standards Report, Aug. 1971, unpublished.

[*60*] Guevara, F. A., McInteer, B. B., Ottesen, D., and Hanley, H. J. M., "A Critique of the High Temperature Viscosity Measurement of Trautz and Zink," Los Alamos Scientific Laboratory Technical Note LA-4643-MS, June 1971.

[*61*] Olien, N. A., "The Cryogenic Data Center, an Information Service in the Field of Cryogenics," *Cryogenics*, Vol. 11, No. 11, 1971.