DOCUMENT RESUME

ED 059 866 SE 012 306

AUTHOR	Lawrence, Richard M.
TITLE	Space Resources for Teachers: Chemistry; Including Suggestions for Classroom Activities and Laboratory Experiments.
INSTITUTION	National Aeronautics and Space Administration, Washington, D.C.
REPORT NO	EP-87
PUB DATE	Feb 71
NOTE	221p.
AVAILABLE FROM	Superintendent of Documents, U.S. Government Printing Office , Washington, D.C. 20402 ($2.50)
EDRS PRICE	MF-$0.65 HC-$9.87
DESCRIPTORS	*Aerospace Education; *Aerospace Technology; *Chemistry; Resource Materials; *Science Activities; *Secondary School Science; Space Sciences; Teaching Guides
IDENTIFIERS	NASA

ABSTRACT

This publication is composed of 10 units, each based on an area of space science and technology in which chemistry plays an important role. Each resource unit can be used independently of the others and materials can be selected from within a unit. The materials range in difficulty from the junior high level of understanding to those that will appeal to the advanced student seeking challenging research activities. The 10 resource units are arranged in a sequence of topics similar to many general chemistry textbooks. Unit topics include: cabin atmospheres in space vehicles, life-support systems, chemical rocket propellants, electrochemical cells for space power, rates of high-temperature reactions associated with space vehicles, space vehicle lubrication, optical coatings for temperature control of space vehicles, ablative materials for high-temperature thermal protection, chemical evolution, and detection of extraterrestrial life. Each unit consists of three parts: a brief monograph providing background information; several activities for demonstrations, experiments, or projects; and a list of literature sources. For some units, a list of related films is also included. (Author/PR)

SPACE RESOURCES FOR TEACHERS

CHEMISTRY

including suggestions for classroom activities and laboratory experiments

A curriculum project prepared at Ball State University
Muncie, Indiana
Richard M. Lawrence, Director

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546, February 1971

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C. 20402 - Price $2.50

PROJECT STAFF

Director and Author	*Richard M. Lawrence* Department of Chemistry Ball State University Muncie, Ind.
Coauthor	*William H. Bowman* Department of Chemistry Ball State University Muncie, Ind.
	Earl J. Montague[1] Science Education Center The University of Texas Austin, Tex.
	Jack A. Bateman[2] Miami-Dade Junior College South Miami, Fla.
Cooperating Chemistry Teachers	*Douglas North* Kokomo High School Kokomo, Ind.
	Stanley O. Hall Chrysler Memorial High School New Castle, Ind.
	Also assisting on early chapters were *L. L. Coleman*, Burris Laboratory School, Ball State University; *R. L. Watson* and *W. J. Phares*, North Central High School, Indianapolis; and *D. W. Alley*, Southside High School, Muncie, Ind.
NASA Technical Monitor	*Walter T. Olson* Assistant Director NASA Lewis Research Center Cleveland, Ohio

---

[1] *Dr. Montague initiated and directed this project until leaving Ball State for the University of Texas in 1967. Thereafter he served as its editorial consultant and science education adviser.*

[2] *Mr. Bateman served on the project staff as staff assistant until 1967, prior to accepting a position at Miami-Dade Junior College.*

preface

INTRODUCTION

During the past few years, manned and unmanned space probes have been launched to investigate the nature of the Earth, the Moon, the Sun, and nearby planets of the solar system America's space program has stirred the imaginations of many science-oriented students in secondary schools and colleges.

In 1958, Congress established the National Aeronautics and Space Administration. The Space Act required that NASA make available, "for the benefit of all mankind," the results of its activities. As a part of this mission, the Educational Programs Division of NASA's Office of Public Affairs has sponsored the writing of teacher resource units in several disciplines.

Space Resources for Teachers: Chemistry is the fourth of a series of curriculum supplements developed for NASA. Those previously published include *Space Resources for the High School: Industrial Arts Resource Units; Space Resources for Teachers: Biology;* and *Space Resources for Teachers: Space Science.* In preparation are *Space Resources for Teachers: Physics* and *Space Resources for Teachers: Mathematics.*

HOW TO USE THIS BOOK

This publication is composed of 10 units, each based on an area of space science and technology in which chemistry plays an important role. Each resource unit can be used independently of the others and materials can be selected from within a unit. The materials range in difficulty from the junior high level of understanding to those that will appeal to the advanced student seeking challenging research activities. Thus, a chemistry instructor can choose materials of appropriate depth and breadth for his particular teaching situation.

The 10 resource units are arranged in a sequence of topics similar to many general chemistry textbooks. For instance, the gas laws and stoichiometry are treated in early units, whereas topics in organic chemistry and biochemistry appear in later units. Traditional topics that can be enriched through use of a resource unit are listed at the beginning of the unit. Following this introduction are tables of contents by unit and by topic; the latter is a graphic display of relationships among units in this supplement and topics in general chemistry.

Space Resources for Teachers: Chemistry will enrich general chemistry instruction materials with recent developments in the Nation's space program. This publication will provide a source from which teachers, supervisors, curriculum specialists, and textbook writers may draw space-oriented material.

This publication is neither a textbook, a laboratory manual, nor a course of study. It is a compilation of resource units designed as an educational tool for the chemistry teacher. The contents are based on the staff's search of the literature and on visits and discussions with numerous space scientists at NASA research centers.

The Ball State University faculty members who developed this project have taught chemistry at both secondary and college levels and are intimately concerned with science education. The materials developed were field tested by chemistry teachers in neighboring high schools and by project staff members in their Ball State classes. They were also evaluated by an ad hoc committee of the Council of State Science Supervisors.

Each of the resource units has three parts: (*a*) a brief monograph to provide background information; (*b*) several activities that can be used as demonstrations, laboratory experiments, or projects; and (*c*) a list of literature sources and, for some units, related films. The literature sources include technical references and supplemental sources of information.

The monograph at the beginning of each unit can be used to provide background information for the activities included in the unit, or it can be used directly in class discussion for citing space-related applications of chemical principles.

The part of a unit labeled "Activities" comprises teacher-tested activities, each including sufficient detail to make it directly usable as an experiment or demonstration. (NOTE: Where experiments involve an element of danger, the authors have indicated such by inserting the word CARE.) In some units, "Topic(s) for the Development of Additional Activities" are suggested. These topics are not described or developed in detail; rather, they provide subjects that may be developed by teachers for individual student projects or group activities.

In the reference section at the end of each unit, the items marked with an asterisk are resources giving broader coverage. Some of the bibliographic entries from Government sources are available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 (identified by initials GPO). The rest may be obtained from the National Technical Information Service (NTIS),[1] U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va. 22151. For publications with a NASA center listed as a source, write to the Educational Programs Office at the center. (See Appendix D.) For publications with AIAA identified as the source, write to the Technical Information Service, American Institute of Aeronautics and Astronautics, 750 Third Avenue, New York, N.Y. 10017.

In the film lists that follow some of the reference sections, those films listed as available from NASA may be obtained by writing NASA Headquarters, Code FAD, Washington, D.C. 20546. If the source for the film is listed as a specific NASA center, it may be obtained by writing the Educational Programs Office at the center. (See Appendix D.) Most of the films listed give broad, general coverage of topics and therefore can be used to provide background information and inspirational material. It is suggested that a film be previewed in order to determine its appropriateness.

ACKNOWLEDGMENTS

The project staff is grateful to the many NASA scientists who discussed their research work with us and made helpful suggestions. In particular, we would like to mention Dr. Walter T. Olson of the NASA Lewis Research Center, the NASA technical monitor for this project.

We also appreciate the assistance of staff members of the Educational Programs Division, Office of Public Affairs, NASA: Dr. Frederick B. Tuttle, Director, who served as NASA Headquarters project coordinator, and James V. Bernardo, former Director; and of George Gardner and Howard S. Golden in the Planning and Media Development Division of NASA's Office of Public Affairs for helping us develop and refine this project. We thank

---

[1] *Documents are available from NTIS at a standard price of $3 for hardcopy (printed facsimile, or reproduced from microcopy) of less than 550 pages for NASA and NASA-supported documents and $10 for NASA and NASA-supported documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70-12345#).*

Dr. Alfred B. Garrett, NASA Consultant and Vice President for Research, The Ohio State University, for his constructive suggestions and Joseph C. Chizanskos for diagrams and technical illustrations.

To the members of the ad hoc committee of the Council of State Science Supervisors: Charles R. Davis, Jr., Virginia, coordinator of the committee; John V. Favitta, New York; Frances Jones, Alabama; Richard S. Peterson, Utah; Calvin S. Story, Texas; and Ivan Taylor, West Virginia, we express appreciation for their helpful and constructive evaluation of this manuscript. To Franklin D. Kizer, Virginia, director of the Council's appraisal efforts, we also express appreciation.

Finally, to those of the administration and faculty at Ball State University who bore with us and supported us on this project, we are grateful.

RICHARD M. LAWRENCE
Ball State University

WILLIAM H. BOWMAN
Ball State University

February 1971

table of contents

TOPICAL TABLE OF CONTENTS

unit 1

15

unit 1

CABIN ATMOSPHERES IN SPACE VEHICLES

Topics that may be enriched by use of this unit:

- Gas laws
- Diffusion of gases
- Partial pressure
- Respiration

Manned explorations always have been hampered by man's physiological limitations. In choosing to explore space, man is placing even greater demands on his knowledge of his own physiological needs and on his technological capability of meeting them. Man is adapted only to the environmental conditions prevalent near the surface of the Earth. These conditions include an atmosphere composed principally of nitrogen and oxygen gases (Table 1–1) at a total pressure of about 760 mm Hg (or 1 atm). This atmosphere (troposphere) extends to an altitude of about 10 miles with little change in composition (1). Yet, with only a few exceptions, human communities are all located at altitudes of less than 1 mile (2). If man is exposed to altitudes in excess of 2 miles for extended periods of time, he begins to develop symptoms of oxygen deficiency (3).

Man has an absolute need for oxygen; an insufficient supply quickly results in unconsciousness and eventually in death. The partial pressure of oxygen in the atmosphere at sea level is 159 mm Hg (Table 1–1). Although this is sufficient to supply man's oxygen requirements, the total pressure and hence the partial pressure of oxygen decreases with increasing altitude (Figure 1–1). At an altitude of about 12,000 ft, for example, the ambient pressure drops to 480 mm Hg and the partial pressure of oxygen is only 100 mm Hg. At this oxygen partial pressure, borderline hypoxia (oxygen deficiency) occurs in man (3). From 12,000 to 40,000 ft, man can use a supplementary oxygen supply at ambient pressure to increase the percent of oxygen in inhaled air; but beyond this altitude, compression of the ambient atmosphere or a sealed cabin is required (3).

In the near vacuum of outer space, a sealed cabin is the only feasible means of survival. As the name implies, a sealed cabin is

TABLE 1-1 COMPOSITION OF INSPIRED AIR (DRY BASIS)

Gas	Percent Composition by Volume	Partial Pressure, mm Hg at sea level
O_2	20.95	159
CO_2	.04	.3
N_2	79.0	600

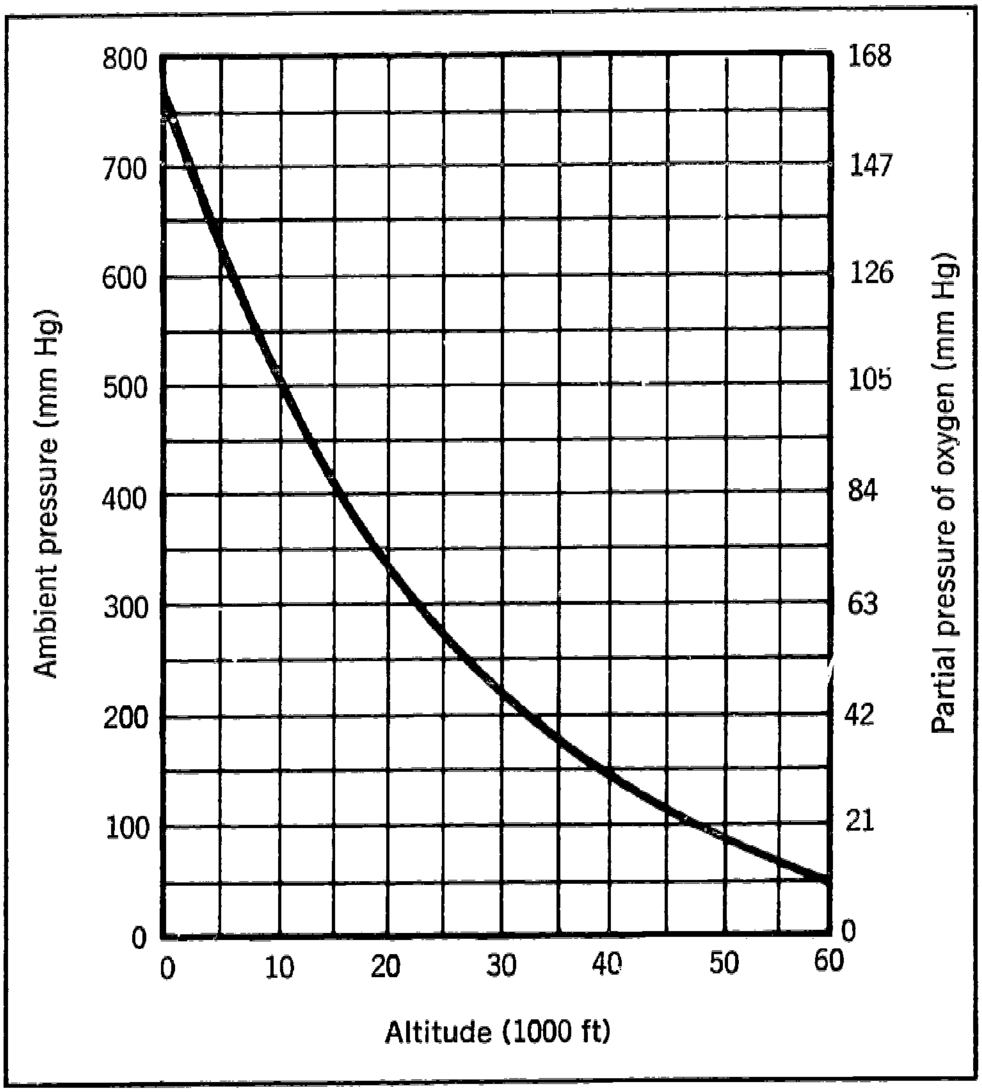


FIGURE 1-1. *Change of atmospheric pressure and oxygen partial pressure with altitude.*

completely isolated from its surroundings. Within the cabin, the total pressure, the partial pressures of oxygen and carbon dioxide, the temperature, the relative humidity, and the levels of microcontaminants are controlled to meet man's requirements. Ideally, this atmosphere should duplicate that found near sea level on Earth. Nevertheless, constructing a spacecraft capable of maintaining a duplicate of man's "normal" atmosphere and placing it into the near vacuum of outer space present many formidable technological problems, some of which are discussed later. In resolving the dilemma of man's physiological needs versus his technological capability to fulfill them, NASA scientists arrived at a compromise solution; and a cabin atmosphere of pure oxygen gas at a pressure of 1/3 atm was selected for America's early manned missions in space. Let us examine further some of the relevant physiological and technological aspects of this problem.

OXYGEN PARTIAL PRESSURE

Man requires a constant supply of energy to live. This energy is released through oxidation of the food he eats. The ultimate oxidizing agent for this process is molecular oxygen that is obtained from inhaled air and transported to his body tissues by the blood. A brief description of the process of breathing may be helpful in understanding the importance of controlling the partial pressure of this gas in the atmospheres of manned spacecraft.

When a man breathes, air flows alternately into and out of his lungs because the volume of the lungs is alternately increased and decreased by the respective downward and upward movement of the diaphragm and the expansion and contraction of the rib cage. The process of breathing is represented schematically in Figure 1–2. Following exhalation, the volume of gas contained in the lungs is at the normal minimum, and the pressure in the lungs is equal to that of the atmosphere. During inhalation, the volume of the lungs increases, and the pressure in the lungs decreases slightly below that of the atmosphere causing air to be inhaled.

The total pressure in the lungs, however, is not entirely caused by the inhaled air. Carbon dioxide and water vapor in sufficient quantities to maintain relatively constant partial pressures of 40 and 47 mm Hg, respectively, also are found in the lungs. The carbon dioxide is an end product of the oxidation of foodstuffs in the body and is eliminated through the lungs. The water vapor arises from the evaporation of the water serving as the dispersion medium of the body cells. Considering the relatively constant vapor pressures of carbon dioxide and water vapor and assuming that the atmospheric pressure is 760 mm Hg, the inhaled air exerts a partial pressure of $760 - 40 - 47 = 673$ mm Hg.

Because air is 21 percent oxygen (by volume), the partial pressure of oxygen in the lungs should be 141 mm Hg. Oxygen, however, dissolves in the blood; and its partial pressure is less than this calculated value. The relatively constant partial pressure produced by oxygen in the lungs is about 108 mm Hg.

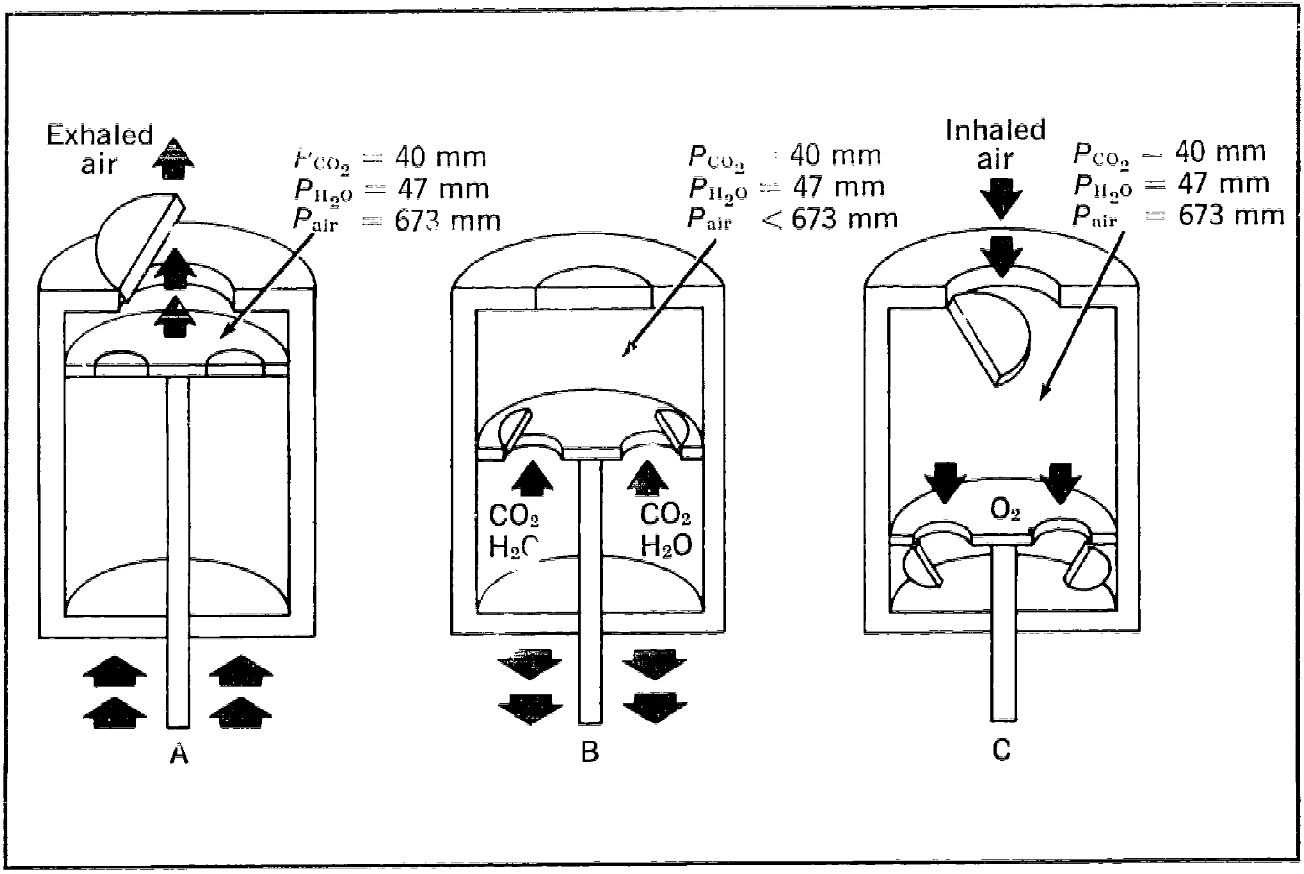


FIGURE 1–2. *Schematic representation of breathing. In each case, the piston represents the combined effects of the diaphragm and the rib cage, and the enclosed space above the piston represents the volume of the lungs. The atmospheric pressure is taken to be 760 mm Hg.* A *Exhalation: Lungs are compressed to their minimum volume:* $P_{lungs} = P_{atmospheric}$. B *Diaphragm is lowered allowing volume of lungs to increase; therefore,* $P_{lungs} < P_{atmospheric}$. *$CO_2$ and H_2O vapor enter at a rate sufficient to maintain a constant partial pressure for each. For simplicity, air is assumed not to enter in this step.* C *Inhalation: Sufficient air enters the lungs to make* $P_{lungs} = P_{atmospheric}$. *Oxygen is removed.*

From the lungs, oxygen is physically dissolved in the blood in accordance with Henry's law, which states that the amount of dissolved gas is directly proportional to the vapor pressure of the gas. As applied to this situation, Henry's law may be expressed as

$$P_{O_2} = K_{O_2,\,\text{blood}} X_{O_2}$$

where

P_{O_2} = the partial pressure of O_2 in equilibrium with the blood
K_{O_2} = the Henry's law constant for O_2 in blood
X_{O_2} = the mole fraction of O_2 dissolved in the blood

Almost as rapidly as it dissolves, however, oxygen combines with the hemoglobin present in the red blood cells. This reaction effectively removes the oxygen from solution, allowing additional oxygen to be dissolved. The overall process may be represented as follows (Hb represents hemoglobin):

$$O_2\,(g) \leftrightarrows O_2\,(\text{soln}) \qquad (1\text{-}1)$$

$$O_2\,(\text{soln}) + \text{Hb}\,(\text{soln}) \leftrightarrows \text{HbO}_2\,(\text{soln}) \qquad (1\text{-}2)$$

Both of these reactions are readily reversible, and the position of each at equilibrium is determined by the partial pressure of oxygen in contact with the blood. As the blood leaves the lungs, it has an oxygen tension of approximately 100 mm Hg, which is sufficient to produce 97 to 98 percent saturation of the hemoglobin (Figure 1-3, from Anderson (4)). ("Oxygen tension" refers to the amount of oxygen dissolved in a solution, in this case the blood. Because the amount of oxygen is determined by its partial pressure in accordance with Henry's law, it is customary to express the concentration in terms of the partial pressure of oxygen with which the solution would be in equilibrium.)

The transfer of oxygen from blood into body tissues occurs by diffusion. Arterial blood, having an oxygen tension of about 100 mm Hg, flows into capillaries permeating the body tissues. The fluid bathing these tissues has an oxygen tension of only

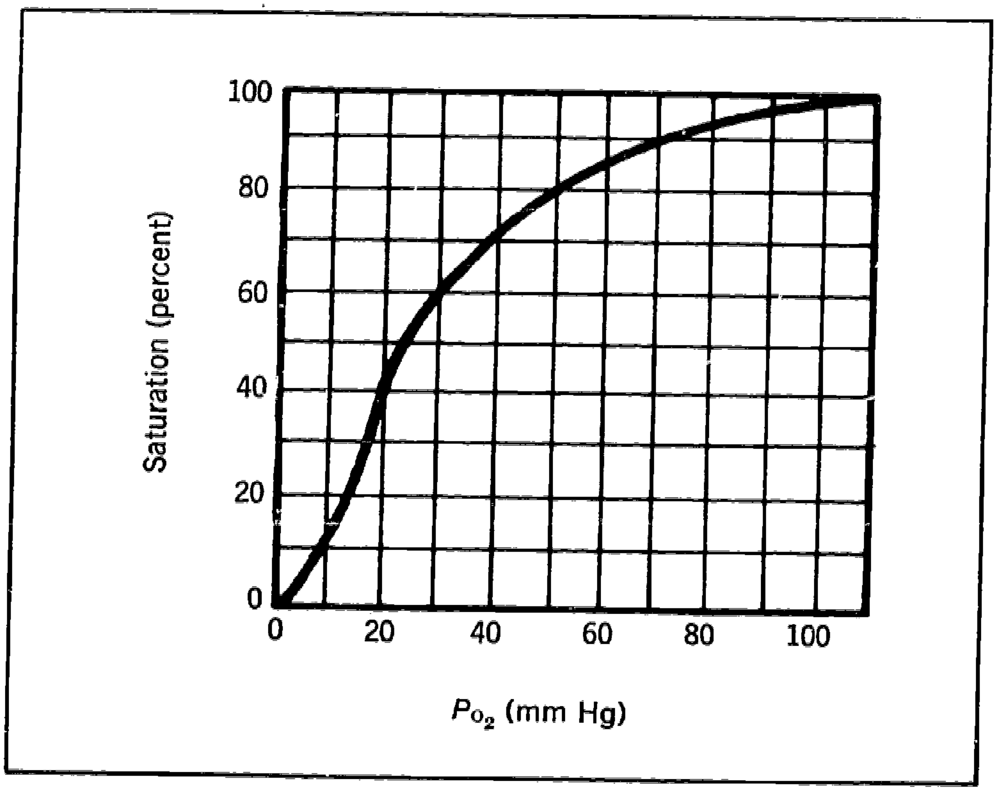


FIGURE 1-3. *Percent saturation of hemoglobin with oxygen when exposed to different oxygen partial pressures at a constant CO_2 partial pressure of 40 mm Hg (4).*

20 to 50 mm Hg. Consequently, oxygen dissolved in the blood diffuses into this tissue fluid. Loss of dissolved oxygen from the blood causes a reversal of reaction (1–2), thus maintaining a supply of dissolved oxygen in the blood. By the time the blood has passed through the capillaries, 25 to 30 percent of its initial oxygen content has been lost, and the oxygen tension is reduced to about 40 to 50 mm Hg. Returning to the lungs, the blood is resupplied with oxygen and the cycle is repeated.

Even though it is not necessary to our present discussion, it might be noted that the transport of carbon dioxide from body tissues to the lungs is also effected by a pressure gradient. The values in Table 1–2 illustrate this point. Just as the major portion of oxygen in the blood is transported in combination with hemoglobin, so is the major portion of carbon dioxide in the blood transported in a chemically combined form as the bicarbonate HCO_3^- ion.

Man requires a supply of oxygen at sufficient pressure to maintain a partial pressure in the lungs at the "normal" value of about 108 mm Hg. In a pure oxygen atmosphere, the minimum pressure that will provide the necessary amount of oxygen, taking into account the constant pressures of carbon dioxide and water vapor in the lungs, is about $40+47+108=195$ mm Hg.

The partial pressure of oxygen in the lungs can vary within limits with little adverse effect. The extent of hemoglobin saturation can be reduced to about 90 percent before the symptoms associated with oxygen deficiency appear (2). As shown in Figure 1–3, this means that the partial pressure of oxygen in the lungs can drop as low as 65 mm Hg with little apparent danger to the individual. The upper limit, however, is less well defined. It is known that breathing pure oxygen at pressures of 150 to 250 mm Hg for periods up to 14 days does not appear to produce any serious effects; but at a pressure of 450 mm Hg, man can survive for only about 1 day (6). Current evidence suggests that the upper limit of oxygen partial pressure is in the range of 400 to 425 mm Hg (3), and studies to determine the mechanism of toxic effects of oxygen are currently in progress at NASA's Ames

TABLE 1–2

PRESSURE RELATIONS OF CO_2 IN A PHYSIOLOGICAL SYSTEM

System Component	P_{CO_2}, mm Hg
Tissues	50–70
Venous blood	46
Arterial blood	40
Lungs	40
Expired air	20–30

From Kleiner and Orten (5).

Research Center.[1] Until more definitive information is available, however, it appears best to maintain the partial pressure of oxygen in the lungs as near the normal value of 108 mm Hg as possible. In the atmosphere of pure oxygen at a total pressure of 254 mm Hg (1/3 atm) chosen for early manned missions in space, the oxygen partial pressure in the lungs is approximately 165 mm Hg.

COMPOSITION AND TOTAL PRESSURE OF THE CABIN ATMOSPHERE

Man is accustomed to breathing an atmosphere of oxygen mixed with nitrogen, and his body cavities are acclimated to an ambient pressure of about 1 atm. Why then is an "abnormal" atmosphere selected for our manned space flights? Several technological factors influenced this decision. One of these is the knowledge that although a cabin should be hermetically sealed, some leakage is inevitable. This leakage is essentially unidirectional—from the spacecraft into the vacuum of outer space. Thus, a continual loss of gas occurs for the duration of a mission. Nitrogen (M.W. = 28) effuses more rapidly than oxygen (M.W. = 32) (Graham's law). This, combined with the fact that the mole ratio of nitrogen to oxygen in a normal atmosphere is about 4 to 1, means that a greater weight penalty of nitrogen than of oxygen would be required to compensate for this loss. (To place any object into space requires an amount of thrust proportional to the mass of the object. Each launch vehicle is capable of generating only a limited amount of thrust. On this basis the total mass of the payload that can be launched is calculated. The mass of each item in the payload is then assessed against this total allowable mass. This assessment is referred to as the "weight penalty" for that item.) Another consequence of this fact is that relatively complex instrumentation would be required to maintain a constant ratio of the two gases in the cabin atmosphere.

A factor that is relevant in the selection of the total pressure of the cabin atmosphere is the strength of the spacecraft; the greater the internal pressure, the greater is the strength required to keep it from exploding in the vacuum of space. The prevention of such an occurrence at higher cabin pressures would require additional structural support and concomitantly an additional weight penalty.

Apart from explosion, slow decompression of the cabin, whether accidental or intentional, is also a consideration in choosing the total pressure. The rate at which decompression occurs is determined by the volume of the cabin, the area of the orifice, and the

---

[1] *T. Wyderen, personal communication.*

pressure gradient. A high cabin pressure allows more time for the astronauts to react during a decompression emergency. For example, if a 150-ft^3 cabin were punctured in space, forming an orifice of 0.5-in. diameter, the time for decompression from 14.7 to 4.36 psi (the pressure at which an individual breathing a normal atmosphere tends to lose consciousness) would be 187 sec. For the same cabin at an initial pressure of only 7.0 psi, only 68.4 sec would be required for decompression (2). The higher the cabin pressure, therefore, the greater the reaction time available to the astronauts in such an emergency.

On the other hand, the danger of decompression sickness is a disadvantage of having a high cabin pressure. Decompression sickness results from the rapid release of dissolved gases from the blood in response to a rapid reduction in partial pressures of gases (Henry's law). This rapid evolution of gas in blood produces bubbles within the bloodstream with accompanying painful distentions of the tissues (bends). The seriousness of this bubble formation depends on the amount of the gas present in physical solution as well as the rate at which evolution occurs. The smaller the pressure gradient, the slower the rate of release of gas from the blood. Also, nitrogen, being present only in physical solution, presents a greater problem than oxygen, the release of which is buffered by its combination with hemoglobin.

A final consideration to be mentioned is the absolute need of oxygen versus the apparent "luxury" of nitrogen. Although our knowledge of this matter is extremely limited, nitrogen appears to serve no essential function except as a filler gas. Man can apparently survive well breathing pure oxygen at controlled pressures. Nevertheless, concern over the long-term effects of breathing pure oxygen does exist, and an effort is being made to find another gas such as helium that will serve the function of nitrogen but is more suitable for use in space.

The advantages of helium over nitrogen may be summarized as follows (7):

1. Helium has a lower solubility in blood, thus the danger of decompression sickness is decreased.

2. Although the rate of diffusion of helium is about 2.5 times that of nitrogen (Graham's law), its mass is only about one-seventh that of nitrogen. Thus, the weight penalty of helium would be less.

3. Helium has a higher thermal conductivity than nitrogen so that astronauts can tolerate higher ambient temperatures. For example, the comfort range for air is 18° to 24° C, whereas for a He/O_2 mixture it is 25° to 29° C.

ACTIVITIES

PARTIAL PRESSURE CALCULATIONS

For missions in space and at high altitudes, man must be provided with artificial atmospheres. The partial pressures of oxygen and filler gases, if any, along with the total pressure of the atmosphere must be selected. As explained before, the minimum oxygen partial pressure in the lungs required to prevent hypoxia is about 65 mm Hg. Assuming no absorption of oxygen by the blood, calculate the minimum volume percent of oxygen that must be present in atmospheres of various values of total pressure. For instance, make the calculation for a pressure of 254 mm Hg, the pressure chosen for manned missions in space. Also perform this calculation at total pressures that are equivalent to those found at altitudes in the range of 10,000 to 40,000 ft. (See Figure 1-1.) Remember to include the partial pressures of CO_2 and H_2O vapor in your calculations. For instance, at a total pressure of 250 mm Hg the pressure of air in the lungs is $250-87=163$ mm Hg. The minimum percent oxygen is then 100 (65/163) or 40 percent.

IDEAL GAS LAW CALCULATIONS

The volume of air normally inhaled in a single breath is about 0.5 liter. Assuming ideal gas behavior, calculate the number of moles of oxygen in a breath of normal air (see Table 1-1) at 20° C and 1-atm pressure. Calculate the volume of this air in the lungs at 37° C, assuming no absorption of oxygen by the blood. What volume of pure oxygen at 254 mm Hg, the pressure chosen for manned spacecraft, must be inhaled to obtain the same number of moles of oxygen contained in 0.5 liter of normal air?

TOTAL PRESSURE AND FORCE CALCULATIONS

The total pressure of the atmosphere of a manned spacecraft is selected on the basis of several factors, including the required strength of the spacecraft. The greater the total pressure, the greater is the tendency of the spacecraft to explode in the vacuum of space. To illustrate the magnitude of this problem, calculate the force tending to explode an Apollo spacecraft having an internal volume of 300 ft^3 and a cabin pressure of 5 psi. To simplify the calculation and to obtain the minimum value, assume the Apollo spacecraft is spherical in shape (a sphere has the smallest surface area in relation to the volume contained). (The surface area of a sphere is equal to $4\pi r^2$ and its volume is $4/3\pi r^3$.)

HENRY'S LAW

Several gases including N_2, O_2, and CO_2 are dissolved in blood. Their concentrations are dependent on their partial pressures in equilibrium with blood as related by Henry's law, which states that the amount (mole fraction) of a gas dissolved in a liquid is proportional to the partial pressure of the gas in equilibrium with the solution. This activity is an experiment that applies Henry's law to a system of carbon dioxide and water.

The apparatus is assembled as shown in Figure 1-4. A eudiometer is filled about one-third full of water and fitted with a one-hole stopper containing a glass tube. A gas bottle is filled par-

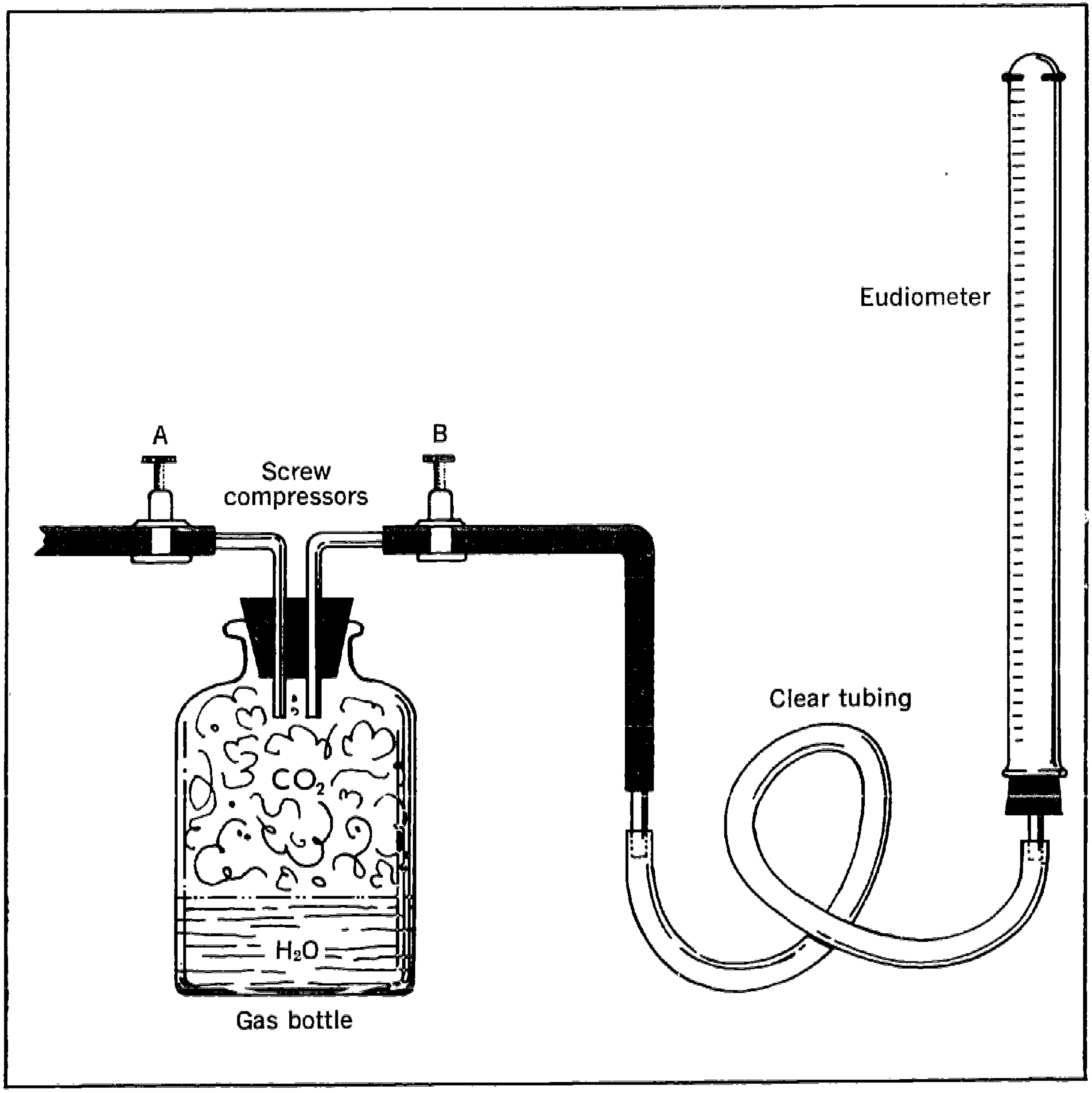


FIGURE 1-4. *Apparatus for demonstrating Henry's law. Dry Ice is placed in the gas bottle, and the equilibrium partial pressure of CO_2 is found by noting the volume of gas in the eudiometer.*

tially with water and fitted with a two-hole stopper with glass tubing; one of the glass tubes is connected to a short piece of rubber tubing that in turn is connected to several feet of *clear* plastic tubing. The bottle is tilted to fill the plastic tubing with water, and then the free end of the plastic tubing is connected to the eudiometer. Air bubbles remaining trapped in the tubing should be manipulated into the eudiometer or toward the gas bottle so that none remains between the free water surfaces in the eudiometer and tubing. The remainder of the water in the gas bottle is discarded, and then a measured quantity of water (ca. 100 ml) is added to the gas bottle. A short piece of tubing is placed on the second glass tube of the gas bottle and screw compressors are located on the tubing at positions *A* and *B* as indicated in Figure 1–4.

Having both screw compressors open, the height of the eudiometer or bottle is adjusted so that the water level is the same in the eudiometer and plastic tubing. The gas pressure in the eudiometer is now at atmospheric pressure. Once this is achieved, the screw compressor at *B* is closed tightly and the volume of gas in the eudiometer is recorded. The atmospheric pressure should be recorded during the course of the experiment. A small amount (ca. 10 g) of Dry Ice (CARE)[2] is placed in the gas bottle, and the bottle is again stoppered. One may wish to tape the stopper to the bottle with plastic electrical tape at this time because pressures sufficient to dislodge the stopper will occur in the bottle later in the experiment. When only a small amount of Dry Ice remains in the bottle, the screw compressor at *B* is opened and the screw compressor at *A* is closed slowly until the volume of gas in the eudiometer is compressed to about one-half its original volume. The screw compressor at *A* is closed completely when all the Dry Ice has sublimed. The bottle may be shaken to help dissolve as much CO_2 as possible. The free surfaces of water are adjusted to approximately the same level, and sufficient time is allowed for the bottle and CO_2 solution to come to room temperature. Then the height of the bottle or eudiometer is again adjusted until the free surfaces of the water in the plastic tubing and eudiometer are the same, the screw compressor at *B* is closed, and the volume of gas in the eudiometer is recorded.

The CO_2 solution is removed from the gas bottle and is poured immediately into a 250-ml beaker containing 100 ml of freshly prepared saturated solution of calcium hydroxide (limewater). The precipitated $CaCO_3$ may be collected by filtration, dried at 105° C, and weighed. The experiment is repeated selecting other approximate final pressures between 1 and 2 atm. The weights

---

[2] *Teacher should exercise care in this experiment.*

of $CaCO_3$ and thus the amount of dissolved CO_2 are shown to be proportional to the partial pressure of CO_2 in the gas bottle.

Calculation of the partial pressure of CO_2 in the gas bottle at equilibrium may be approached as follows:

Initially, the pressure of the gas in the eudiometer is adjusted to that of the atmosphere.

$$P_{\text{eudiometer}} = P_{\text{atmosphere}}$$

The pressure in the eudiometer is equal to the sum of the vapor pressure of water (a constant at constant temperature) and the pressure of dry air at the beginning of the experiment.

$$P_{\text{eudiometer}} = {}_{H_2O} + (P_{\text{dry air}})_1$$

When the apparatus has reached room temperature after inserting the Dry Ice and the water surfaces again have leveled, then:

$$P_{\text{gas bottle}} = (P_{H_2O} + P_{CO_2})_{\text{gas bottle}} = P_{\text{eudiometer}} = P_{H_2O} + (P_{\text{dry air}})_2 \quad (1\text{–}3)$$

where it is assumed that the air originally in the gas bottle has been flushed out by the gaseous CO_2.

According to Boyle's law:

$$(P_{\text{dry air}})_2 = \frac{V_1}{V_2} (P_{\text{dry air}})_1$$

where V_2 and V_1 are the final and initial volumes of gas in the eudiometer, respectively, and $(P_{\text{dry air}})_1$ is the initial pressure of dry air in the eudiometer; i.e., $P_{\text{atmosphere}} - P_{H_2O}$. If we assume that the partial pressure of water in the CO_2 solution is effectively equal to that of the water in the eudiometer, we can subtract P_{H_2O} from both sides of equation (1–3) yielding:

$$(P_{CO_2})_{\text{gas bottle}} = (P_{\text{dry air}})_2 = \frac{V_1}{V_2} (P_{\text{dry air}})_1 = \frac{V_1}{V_2} (P_{\text{atmosphere}} - P_{H_2O})$$

Thus, the equilibrium partial pressure of CO_2 can be found from knowledge of the eudiometer readings, the atmospheric pressure, and the vapor pressure of water (tabulated value).

RATE OF DIFFUSION

Loss of gas by leakage through small openings is a persistent problem in spacecraft. The rate of this loss is determined by several factors, including the mass of the gas particles, the size of the orifice, and the difference in pressure on opposite sides of the orifice. This activity examines the rate of loss of a gas from a container as a function of differences in the external pressure.

Into a petri dish are placed 20 ml of distilled water and 2 drops of phenolphthalein solution. Sufficient 1.0 *N* NaOH (2 to 3 drops) is added to impart an intense pink color to the solution. This dish is placed under a bell jar as shown in Figure 1–5. It may be helpful to set the dish on a piece of white paper to facilitate observa-

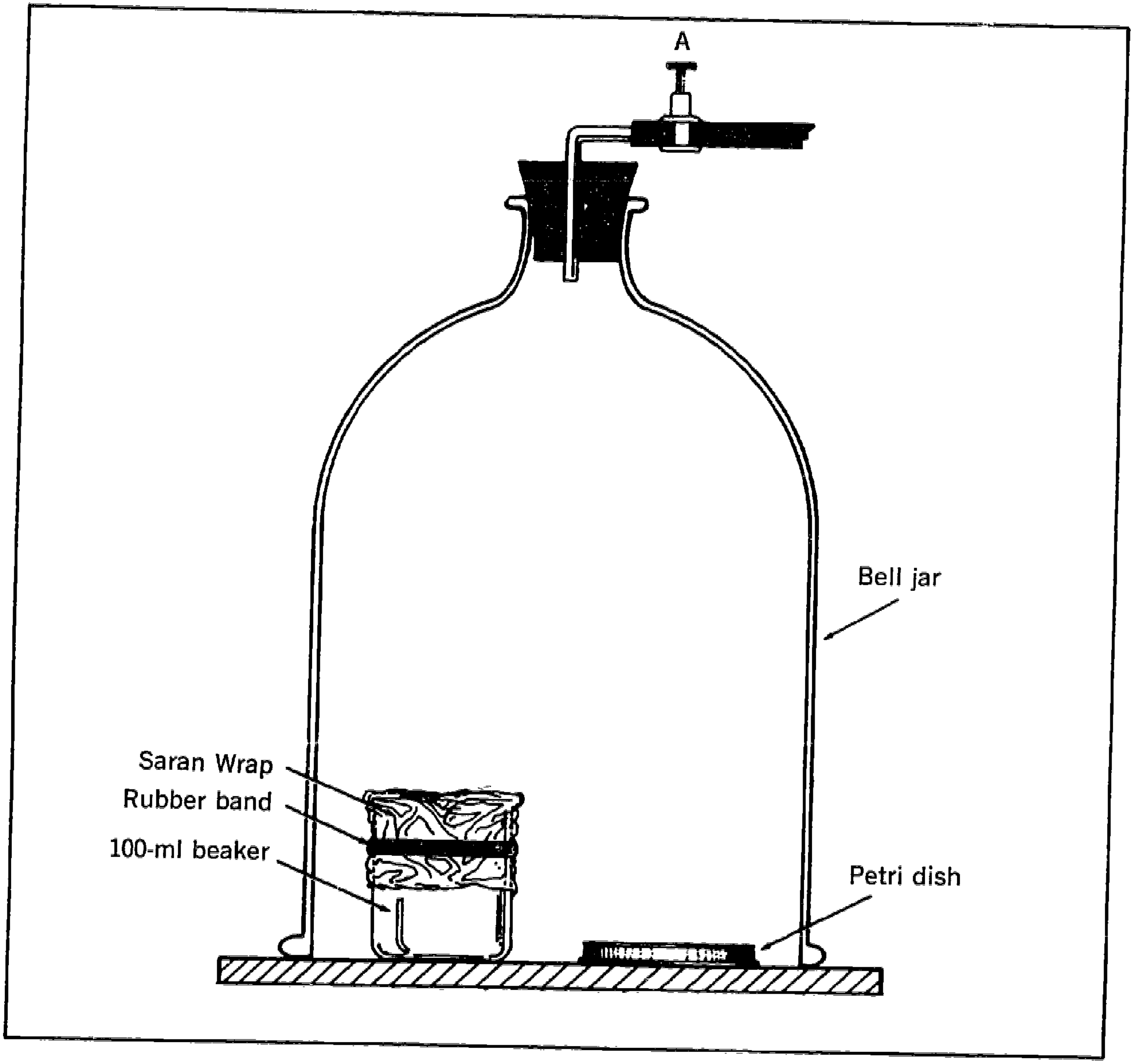


FIGURE 1–5. *Apparatus for investigating rates of diffusion. Gases escape from the covered beaker and diffuse at different rates depending on the pressure in the bell jar.*

tion. Ten ml of concentrated HCl (ca. 12 N) (CARE)[3] are poured into a 100-ml beaker. The beaker is covered securely with a piece of Saran wrap held in place with a rubberband. The Saran wrap is punctured with a common pin and the beaker is then placed under the bell jar next to the petri dish. Valve A is closed, and the time necessary for sufficient HCl to dissolve in the base solution to cause the pink color to just disappear is recorded.

To demonstrate the effect of external pressure on the rate of gas loss, the experiment is repeated but with a reduced pressure in the bell jar. After inserting the acid solution, the bell jar is partially evacuated by means of an aspirator, and the time for color change is noted to be less than that required at higher initial pressure.

LITERATURE CITED

1. Sanders, H. J. 1966. Chemistry and the atmosphere. Chemical and Engineering News 44 (13):1A.

2. Konecci, E. B. 1959. Manned space cabin systems, pp. 174–256. *In* F. I. Ordway, Advances in space science, Vol. 1. Academic Press, Inc., New York.

3. Welch, B. E. 1963. Ecological systems, pp. 310–332. *In* J. H. U. Brown, Physiology of man in space. Academic Press, Inc., New York.

4. Anderson, A. L. 1953. Essentials of physiological chemistry, p. 330. John Wiley & Sons, Inc., New York.

5. Kleiner, I. S., and J. M. Orten. 1966. Biochemistry, 7th edition, p. 703. C. V. Mosby Co., St. Louis.

6. Billingham, J. 1964. Physiology of man in the space environment, pp. 105–106. *In* P. E. Purser, M. A. Faget, and N. F. Smith, Manned spacecraft: engineering design and operation. Fairchild Publications, Inc., New York.

7. Dianov, A. G., and A. G. Kuznetsov. 1964. Substitution of He for N_2 in cabins of spacecraft, pp. 138–140. *In* V. V. Parin, Aviation and space medicine (transl). NASA TT–F–228. NTIS N65–13626#.

---

[3] *Teacher should exercise care in this experiment.*

8. Henry, J. P. 1966. Biomedical aspects of space flight, pp. 92–105. Holt, Rinehart & Winston, Inc., New York.

OTHER REFERENCES

National Aeronautics and Space Administration. 1966. Significant achievements in space bioscience 1958 to 1964, pp. 92–96. NASA SP–92. GPO, $0.55.

*Roth, E. M. 1964. Space-cabin atmospheres, part I: oxygen toxicity. NASA SP–47. GPO, $0.40.

*Roth, E. M. 1967. Space-cabin atmospheres, part III: physiological factors of inert gases. NASA SP–117. GPO, $1.

*Roth, E. M. 1967. Space-cabin atmospheres, part IV: engineering tradeoffs of one- versus two-gas systems. NASA SP–118. GPO, $1.

Wunder, C. C. 1966. Life into space, pp. 106–119. F. A. Davis Co., Philadelphia.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70–12345#).

**Recommended general sources of information.*

unit 2

unit 2

LIFE-SUPPORT SYSTEMS

Topics that may be enriched by use of this unit:

- Chemical equations
- Stoichiometry
- Oxidation-reduction
- Ionic reactions
- Adsorption
- Chromatography

Man is far from being an independent creature. He is dependent upon his environment for food, oxygen, water, and other basic necessities as well as for the dissipation of many of the toxic byproducts of his existence. In choosing to venture into space, man has intensified the problem of providing systems capable of supplying these needs.

The task of developing these systems is part of the work of the life-support divisions of NASA. The problem is complicated by the fact that the life-support systems must meet rather stringent criteria including simplicity of design and operation, reliability, efficiency, and compactness. Furthermore, although nonregenerative systems using storage techniques are adequate for short-term missions, those of longer duration will require regenerative systems that can use waste materials as sources of water, oxygen, and perhaps even food.

All space flights to date have been of relatively short duration; and sufficient food, water, and oxygen have been provided largely by prestorage aboard the spacecraft. The development of freeze-dried foods has been instrumental in permitting adequate storage of this commodity. Water has been prestored on all the manned flights to date, but was also produced as a byproduct of a fuel-cell reaction aboard the Gemini and Apollo spacecraft. Oxygen, like food, has been provided solely by prestorage on all manned flights to date. Carbon dioxide, a major waste product of man, has been removed from the cabin atmosphere by reaction with lithium hydroxide.

Anyone who has seen a manned spacecraft is acutely aware of its limited storage capacity. The Gemini spacecraft, for example, had an internal volume of approximately 80 ft^3 for its two occupants and their equipment. The three-man Apollo spacecraft (internal volume approximately 300 ft^3), although larger than either of the two previous types of spacecraft, is still extremely limited in storage space. Consequently, when missions of several months or more are considered, physical storage of the necessary quantities of food, water, oxygen (Table 2-1), and absorbents becomes increasingly difficult or even impossible. For such missions, either regenerative systems or a series of space stations along the route must be established. The former approach presently is considered more realistic, and space scientists are now attempting to develop regenerative life-support systems.

Both chemical and biological types of regenerative systems are being examined. The biological systems employ algae, bacteria, green plants, or some combination of these, to establish an ecological cycle that mimics that existing on Earth. In one such system, photosynthetic organisms use carbon dioxide and water to produce food and oxygen, while a species of bacteria uses hydrogen, oxygen, carbon dioxide, and urine to produce water and bacterial cells. The major disadvantage of most biological systems is their size: they are simply too bulky. For this and other reasons, chemical regenerative systems are considered superior for interplanetary space travel. These systems use sequences of relatively simple chemical processes to establish an artificial ecological cycle.

TABLE 2-1

MAN'S DAILY BALANCE

Commodity	Material Balance, lb	Water Balance, lb
Output:		
Urine (95 percent H_2O)	3.24	3.08
Feces (75.8 percent H_2O)	.29	.22
Transpired H_2O	2.20	2.20
CO_2 (1.63 lb O_2)	2.24	....
Other losses	.14	....
Total	8.11	5.50
Input:		
Food (dry weight)	1.5	0.15
O_2	1.92	....
Metabolic H_2O	....	.66
H_2O	4.69	4.69
Total	8.11	5.50

The values given in the table are from Popma and Collins (1) and are the nominal amounts of substances consumed and excreted by a moderately active man of average size. The amounts of water and oxygen potentially recoverable from man's waste products are also indicated.

In this unit we shall examine the chemical aspects of life-support systems that have been used on missions in the past or that appear most promising for use in the future.

CARBON DIOXIDE REMOVAL

Carbon dioxide is one of the major contaminants encountered in manned spacecraft. It is formed as an end product of the oxidation of foodstuffs in man and is expired into the cabin atmosphere. The carbon dioxide output of an average individual is about 2.2 lb/day. The minimum allowable concentration of carbon dioxide in a space cabin has been estimated to be approximately 3 parts per hundred (2) or a partial pressure of about 7.6 mm Hg (3). Continuous exposure to concentrations in excess of this amount produces varying degrees of headache, dizziness, confused thinking, and eventually will cause death.

Removal of carbon dioxide from the cabin atmosphere on all flights to date has been accomplished by its absorption with lithium hydroxide. Alkali metal hydroxides react readily with carbon dioxide in the presence of water vapor according to the following general equation (M represents any alkali metal):

$$2MOH\ (s) + CO_2\ (g) \rightarrow M_2CO_3\ (s) + H_2O\ (aq)$$

A simple weight-weight calculation shows that to absorb the 2.2 lb of carbon dioxide released per man per day requires about 2.4 lb of LiOH, 4.0 lb of NaOH, or 5.6 lb of KOH. Thus, the use of LiOH gives the smallest weight penalty per pound of carbon dioxide absorbed.

The $LiOH/CO_2$ reaction is essentially irreversible and is of little use if the carbon dioxide is to be used subsequently in a regenerative life-support system. In such a system, the carbon dioxide must be removed from the cabin atmosphere and concentrated by some mechanism that will allow its easy recovery for subsequent treatment. One potential regenerative system uses a bed of synthetic zeolite (metal-ion alumino silicates, e.g., $NaAlSiO_4$) to absorb the carbon dioxide as cabin air is circulated through the bed. Zeolite, however, reacts readily with moisture and loses its ability to absorb carbon dioxide. The airstream, therefore, must be predried to a dewpoint of about −57° C by passage through a desiccant such as silica gel. The carbon dioxide absorbed on the zeolite can be desorbed easily by heating the zeolite to 340° C (4), by exposing it to a vacuum, or by using a combination of heat and vacuum.

Another regenerative system for concentrating carbon dioxide that is currently under investigation at NASA Ames Research Center uses metallic oxides, particularly silver oxide, as the absorbent. The general equation for the reaction may be written as follows:

$$Ag_2O\,(s) + CO_2\,(g) \rightleftarrows Ag_2CO_3\,(s)$$

The reaction is reversible; about 90 percent of the silver carbonate can be decomposed in 4 hr at a temperature of 180° C. An advantage of the Ag_2O system is that the airstream need not be predried as in the case of the zeolite system. In fact, evidence suggests that the reaction is catalyzed in both directions by water vapor.

A third system for the removal and concentration of carbon dioxide takes advantage of two properties of ions—their ability to undergo exchange reactions and their migration in an electric field. As illustrated in Figure 2–1, the cabin air flows through

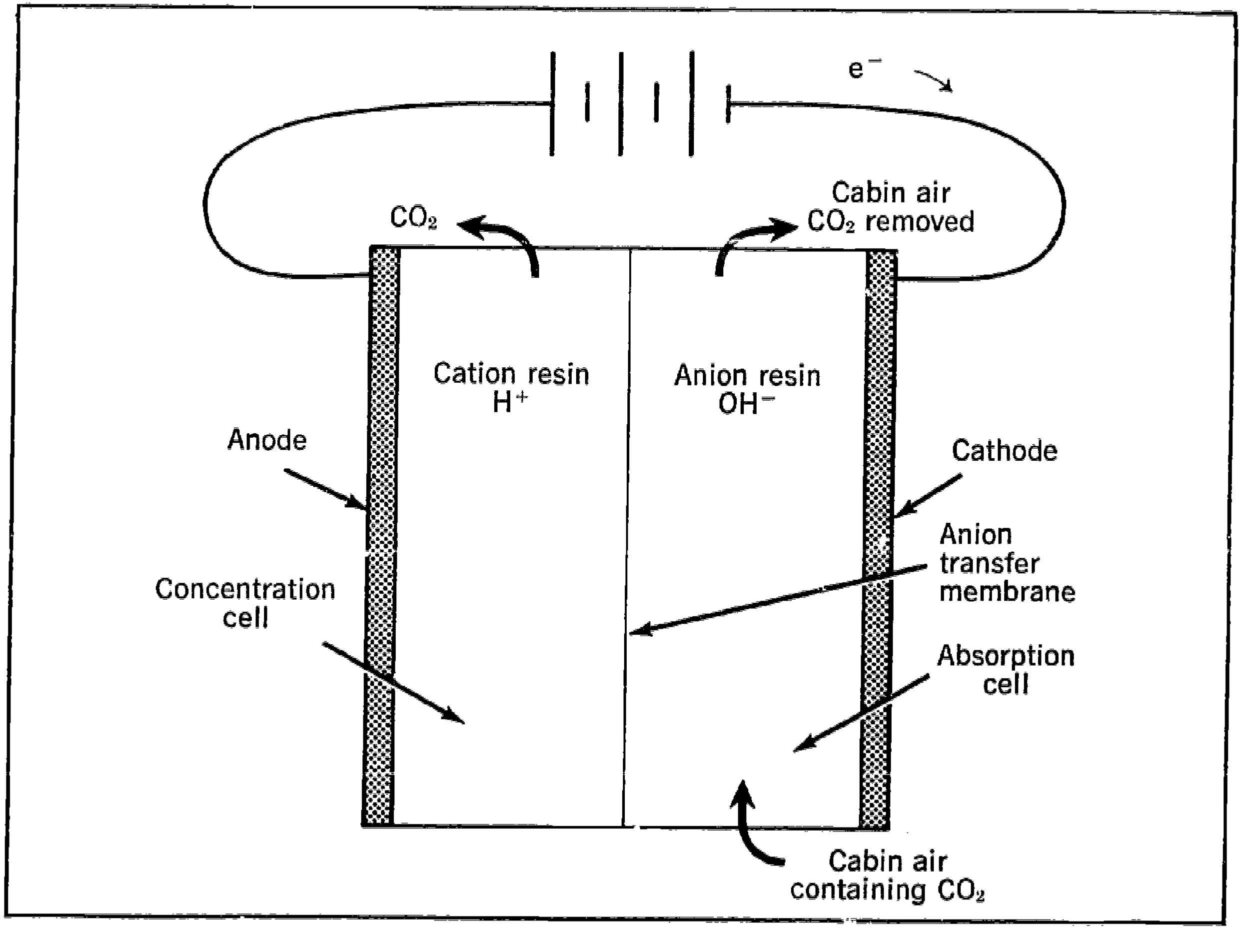


FIGURE 2–1. *Schematic representation of an ion-exchange system for concentrating carbon dioxide. Carbon dioxide, removed from the cabin air by reaction with hydroxide ions, migrates in the form of carbonate ions to the cation resin. There the carbonate ions react with hydrogen ions, and carbon dioxide is liberated as a gas.*

an anion-exchange resin containing hydroxide ions as the exchangeable ions. These react with the carbon dioxide to form carbonate ions.

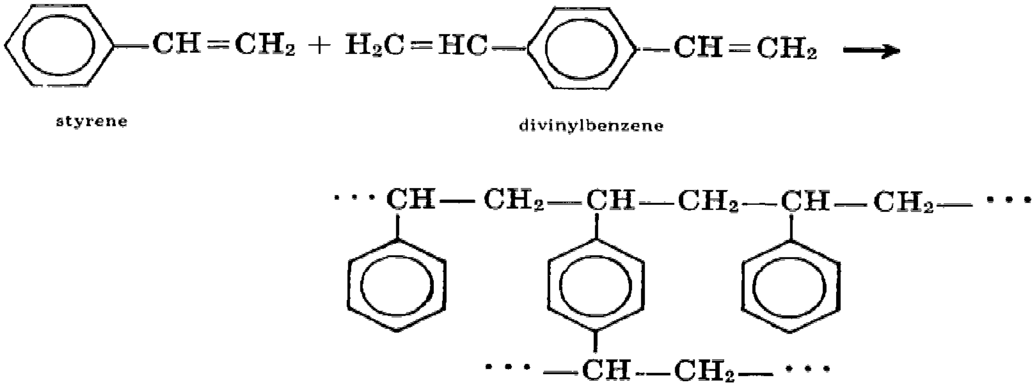
$$2OH^-\ (aq) + CO_2\ (g) \rightarrow H_2O\ (aq) + CO_3^{2-}\ (aq)$$

Under the influence of an electric field, the carbonate ions migrate from the absorption cell into the concentration cell containing a cation-exchange resin. Here hydrogen ions from the cation-exchange resin react with the carbonate ions to regenerate carbon dioxide.

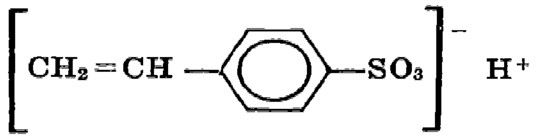
$$CO_3^{2-}\ (aq) + 2H^+\ (aq) \rightarrow H_2O\ (aq) + CO_2\ (g)$$

The carbon dioxide is then discharged as a more highly concentrated gas and is fed to an oxygen recovery system.

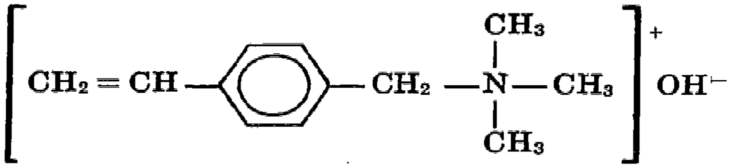
The commonly used ion-exchange resins are substituted copolymers of styrene and divinylbenzene:



The resins are crosslinked to varying degrees depending upon the amount of divinylbenzene used. Various functional groups may be introduced by beginning with substituted styrene molecules. If sulfonated styrene is used, for example, a strongly acidic cation-exchange resin is formed:



Similarly, an anion-exchange resin is formed if the starting styrene contains quaternary trimethylaminomethylene groups:



OXYGEN SUPPLY

Storage as Free Oxygen

Oxygen can be stored in a variety of forms, including high-pressure gas, supercritical fluid, cryogenic liquid, and oxygen-producing chemicals. Prestorage as a high-pressure gas was employed for the Mercury flights primarily because it is the simplest method. The gas, stored in heavy tanks under a pressure of approximately 7500 psi (4), is released at a rate sufficient to maintain the proper partial pressure of oxygen in the cabin. (See Unit 1, "Cabin Atmospheres in Space Vehicles.") Although it is the simplest method, high-pressure storage also provides the greatest weight penalty because sturdy, pressure-resistant tanks are required.

Liquid storage has several advantages over gas storage. The greater density and lower vapor pressure of oxygen in condensed form reduces the size and strength of the tanks required. Among the disadvantages of liquid storage are the need for maintaining the temperature below the critical temperature of oxygen, 154.8° K, and the continuous presence of two phases in the storage tank as a result of vaporization of the liquid. Removal of oxygen from the container as a gas is desirable from the standpoint of regulating both temperature and pressure within the storage tank. Discharging O_2 in the form of a gas removes larger amounts of heat energy from the tank than would the discharge of O_2 as a liquid; thus, the capacity of the cooling system needed to maintain the O_2 in the form of a liquid is smaller. In a zero gravity environment, however, it is difficult to prevent discharge of the liquid.

As a compromise solution, the Gemini and Apollo spacecraft carry oxygen in the form of a supercritical fluid (4). Stored as a supercritical fluid—that is, at a pressure greater than its critical pressure (49.7 atm) and at a temperature above its critical temperature—the oxygen exists as one phase, behaving as a compressed liquid. Thus, the density advantages of a liquid are combined with the single-phase advantages of a compressed gas. The oxygen is discharged from the tank at a pressure that is maintained constant by the regulated addition of heat.

Chemical Regeneration Systems

Numerous chemical methods of regenerating oxygen from waste products have been examined (5). Most of these systems are based on the reduction of carbon dioxide and the direct or subsequent recovery of the oxygen contained in the carbon dioxide. The processes that appear most promising involve the reduction of carbon dioxide with molecular hydrogen to form water, which is subsequently electrolyzed to produce oxygen (6). One variation of this process is known as the Sabatier or methanization reaction. The equation for this reaction is:

$$CO_2\ (g) + 4H_2\ (g) \xrightarrow[200°\text{-}260°C]{Ni} CH_4\ (g) + 2H_2O\ (g)$$

At a temperature of 200° C, about 99 percent of the carbon dioxide is converted. The methane from this reaction can be pyrolyzed, and the resulting hydrogen can be recovered and then recycled:

$$CH_4\ (g) \rightarrow C(s) + 2H_2\ (g)$$

The water from the methanization reaction can be electrolyzed to yield additional hydrogen and the desired oxygen:

$$2H_2O\ (aq) \xrightarrow{e^-} 2H_2\ (g) + O_2\ (g)$$

The sum of these three reactions gives the desired result—the recovery of oxygen from carbon dioxide:

$$CO_2\ (g) \rightarrow C\ (s) + O_2\ (g)$$

A modification of the hydrogen-reduction process, known as the Bosch or carbonization reaction, reduces carbon dioxide to elemental carbon and water:

$$CO_2\ (g) + 2H_2\ (g) \xrightarrow[590°\text{-}760°C]{Fe} C\ (s) + 2H_2O\ (g)$$

Again the water is electrolyzed in a subsequent step to obtain the desired oxygen. Although it requires one less step than the Sabatier method, the Bosch process is less efficient, achieving generally less than 25 percent conversion of the carbon dioxide per pass through the reactor (4).

Two electrolysis systems also might be mentioned as possible methods for the recovery of oxygen from carbon dioxide. One of these, under investigation at NASA Ames Research Center in California, employs a mixed solid oxide electrolyte consisting of a mixture of zirconium oxide and calcium oxide. Carbon dioxide is reduced at the cathode to carbon monoxide and an oxide ion:

Cathode reaction: $CO_2\ (g) + 2e^- \rightarrow CO\ (g) + O^{2-}\ (s)$

The oxide ions then migrate under the influence of the electrical field through the electrolyte to the anode where they give up electrons and form oxygen gas:

Anode reaction: $O^{2-}\ (s) \rightarrow 1/2O_2\ (g) + 2e^-$

The carbon monoxide formed is subsequently converted to carbon and carbon dioxide, and the latter can be recycled through the electrolysis cell:

$$2CO\ (g) \xrightarrow{Ni} C\ (s) + CO_2\ (g)$$

A second electrolysis system for the recovery of oxygen from carbon dioxide involves the electrolysis of a molten solution of lithium carbonate formed by the reaction of lithium oxide with carbon dioxide. The reaction may be represented as follows:

$$3Li_2O\ (s) + 3CO_2\ (g) \rightarrow 3Li_2CO_3\ (s)$$
$$4Li^+\ (s) + 4e^- \rightarrow 4Li\ (s)\ \text{(cathode reaction)}$$
$$2CO_3^{2-}\ (s) \rightarrow 2CO_2\ (g) + O_2\ (g) + 4e^-\ \text{(anode reaction)}$$
$$4Li\ (s) + Li_2CO_3\ (s) \rightarrow C\ (s) + 3Li_2O\ (s)$$
$$CO_2\ (g) \rightarrow C\ (s) + O_2\ (g)\ \text{(overall reaction)}$$

Lithium carbonate is formed by reaction of lithium oxide and carbon dioxide. It is then electrolyzed to form metallic lithium at the cathode and oxygen at the anode. The metallic lithium reacts further with lithium carbonate, re-forming lithium oxide and carbon; the carbon then deposits on the cathode. In practice, lithium chloride is added to the cell to lower the melting point of the lithium carbonate, thus lowering the operating temperature of the cell (4).

Storage in Chemically Combined Forms

Oxygen-releasing chemicals generally cannot compete with other methods of oxygen storage for long-duration missions, but they are being considered as a possible source of oxygen for spacesuit backpacks (4). The compounds under investigation for this purpose are primarily peroxides, superoxides, chlorates, and perchlorates of alkali and alkaline earth metals. An illustrative example is the "chlorate candle," which has also been used on submarines and for emergency supplies of oxygen on aircraft. Sodium chlorate decomposes when heated according to the following equation:

$$2NaClO_3\ (s) \rightarrow 2NaCl\ (s) + 3O_2\ (g)$$

Theoretically, 0.451 lb of oxygen is available per pound of sodium chlorate. Actual production is only about 40 percent of theoretical production.

A combined carbon dioxide removal/oxygen supply system, which has also been used successfully in submarines, employs potassium peroxide. The sequence of reactions may be represented as follows:

$$2K_2O_2\,(s) + 2H_2O\,(g) \rightarrow 4KOH\,(s) + O_2\,(g)$$
$$4KOH\,(s) + 2CO_2\,(g) \rightarrow 2K_2CO_3\,(s) + 2H_2O\,(g)$$

FOOD AND WATER SUPPLIES

Man needs about 5.5 lb of water per day. Some of this water can be obtained in the food he consumes; even freeze-dried foods have a residual water content of about 10 percent by weight. In addition, some water is formed as a product of the oxidation of these foods within the body. The remainder must be supplied as drinking water. (See Table 2–1.)

Hydrogen/oxygen fuel cells, such as those used aboard the Gemini and Apollo spacecraft, can provide drinking water as a byproduct of their production of electrical current. (See Unit 4, "Electrochemical Cells for Space Power.") On longer missions, fuel cells probably will be replaced by other power sources (1), and stored water will be the only source available. Because man does not chemically alter the water he consumes, recovery of the water contained in his waste products (Table 2–1) will greatly reduce the amount of water that must be stored on board the spacecraft.

Numerous water reclamation systems have been examined (1). No single system appears applicable to all situations. For example, a modified vacuum distillation system (4, 6) appears most feasible for recovery of water from urine. The basic principle—vaporization followed by condensation—is the same as that commonly used in the laboratory to obtain "pure" water. On the other hand, transpired water—water lost through respiration and perspiration—is already in the vapor phase and is recovered most easily by cooling the cabin air below its dewpoint and allowing the water vapor to condense. This is the same principle employed in household dehumidifying systems. The production of potable water often requires treatment to remove contaminants such as micro-organisms, volatile solutes, and dissolved gases.

Man's daily food intake weighs considerably less than the water he requires, averaging about 1.5 lb "dry" weight per day (1). (As indicated earlier, "dry" foods contain some residual water. The value given is based on use of freeze-dried foods containing a residual water content of about 10 percent by weight.) Presently, this need is met in space largely in the form of stored freeze-dried foods. Recently, the feasibility of regenerating foods, particularly carbohydrates, from metabolic waste products has been studied (7, 8, 9; and NASA scientists, NASA Ames Research Center) The available starting materials for such a synthesis are carbon dioxide, hydrogen, and water. Direct synthesis of carbohydrates from these materials has been considered but is difficult; the synthesis can be accomplished, however, by starting with intermediate products such as formaldehyde, CH_2O.

Formaldehyde can be prepared by first reacting carbon dioxide with hydrogen in the presence of the oxides of chromium and zinc to form methanol:

$$CO_2\,(g) + 3H_2\,(g) \xrightarrow[400^\circ\text{ C, 1-68 atm}]{Cr_2O_3 + ZnO} CH_3OH\,(g) + H_2O\,(g)$$

Methanol, in turn, is readily oxidized to formaldehyde by air in the presence of a silver or copper catalyst:

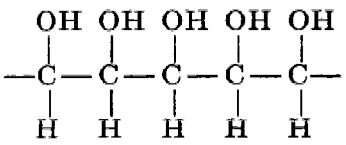
$$2CH_3OH\,(g) + O_2\,(g) \xrightarrow[500^\circ\text{-}600^\circ\text{ C}]{Cu} 2CH_2O\,(g) + 2H_2O\,(g)$$

Another synthesis of formaldehyde involves the oxidation of the methane formed in the Sabatier reaction. Barium peroxide serves as the catalyst:

$$CO_2\,(g) + 4H_2\,(g) \xrightarrow[180^\circ\text{ C}]{Ni} CH_4\,(g) + 2H_2O\,(g)$$

$$CH_4\,(g) + O_2\,(g) \xrightarrow{BaO_2} CH_2O\,(g) + H_2O\,(g)$$

Formaldehyde can be polymerized under alkaline conditions to give polyalcohol structures of the type:



$$\begin{array}{ccccccccccc} & OH & & OH & & OH & & OH & & OH & \\ & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & \\ & H & & H & & H & & H & & H & \end{array}$$

This reaction makes possible the synthesis of carbohydrates; the net reaction may be represented as:

$$CH_2O\,(aq) \xrightarrow[37^\circ\text{-}130^\circ\text{ C}]{Ca(OH)_2} C_nH_{2n}O_n\,(aq)$$

where n is any integer greater than 2. Studies by Sinyan (7) and at the NASA Ames Research Center have shown that a mixture of carbohydrate and noncarbohydrate products generally is formed. Furthermore, this mixture was found to be toxic when fed to rats at levels equivalent to 30 to 40 percent of their caloric requirement. Identification and elimination of any toxic material may make this process of primary importance for production of carbohydrates for consumption during extended missions in space.

Work on the synthesis of fatty acids from simple hydrocarbons such as methane is also being supported by NASA. Whether methods such as these can be used as sources of edible food remains to be demonstrated.

TRACE CONTAMINANT REMOVAL

Numerous potentially hazardous materials might be encountered in the atmosphere of a space vehicle (10). Such materials might arise from any number of sources including metabolic wastes, internal structural components, lubricants, stored materials, rocket propellants, and combustion processes (11). Data regarding the nature and quantity of trace contaminants are presently quite sparse. Until such data are available, effective control systems cannot be developed.

As an interim measure, manned spacecraft have been equipped with an activated carbon adsorbent. As the cabin air is circulated through this adsorbent, contaminants are concentrated onto the surface of the carbon particles. The principle is the same as that employed in some cigarette filters and gas masks. Numerous low-boiling materials (e.g., carbon monoxide and methane) are not adsorbed appreciably on carbon; therefore, long-term missions in the future undoubtedly will require additional control systems for contaminants.

ACTIVITIES

CARBON DIOXIDE REMOVAL WITH A SILVER OXIDE SYSTEM

Removal of carbon dioxide from the atmosphere of the cabin of a manned spacecraft is one of the major functions that the life-support system must perform. The carbon dioxide may be stored simply in combination with an absorbent for the duration of the mission (nonregenerative system). Alternately, the absorbent may serve simply as a concentrating medium from which the carbon dioxide subsequently can be desorbed and treated to recover the combined oxygen (regenerative system).

This experiment simulates a regenerable carbon dioxide removal system, utilizing silver oxide as the absorbent:

$$Ag_2O\ (s) + CO_2\ (g) \underset{180^\circ C}{\rightleftharpoons} Ag_2CO_3\ (s)$$

Desorption of the CO_2 is achieved by heating.

The apparatus is set up using two Erlenmeyer flasks as shown in Figure 2–2. Flask I contains alternating layers of glass wool and silver oxide, prepared as follows. A layer of glass wool is placed in the bottom of the flask. About 1 g of Ag_2O is sprinkled over the surface of the glass-wool layer. A second layer of glass wool is placed in the flask, and 1 g of Ag_2O is sprinkled over the surface. This layering process is continued until a total of about 5 g of Ag_2O have been introduced into the flask. The top layer should be glass wool. The flask and its contents are weighed; and the weight recorded. The inlet and exit tubes are inserted through a two-hole rubber stopper. The inlet tube should extend as close to the bottom of the flask as possible without touching it; the exit tube should terminate above the uppermost layer of

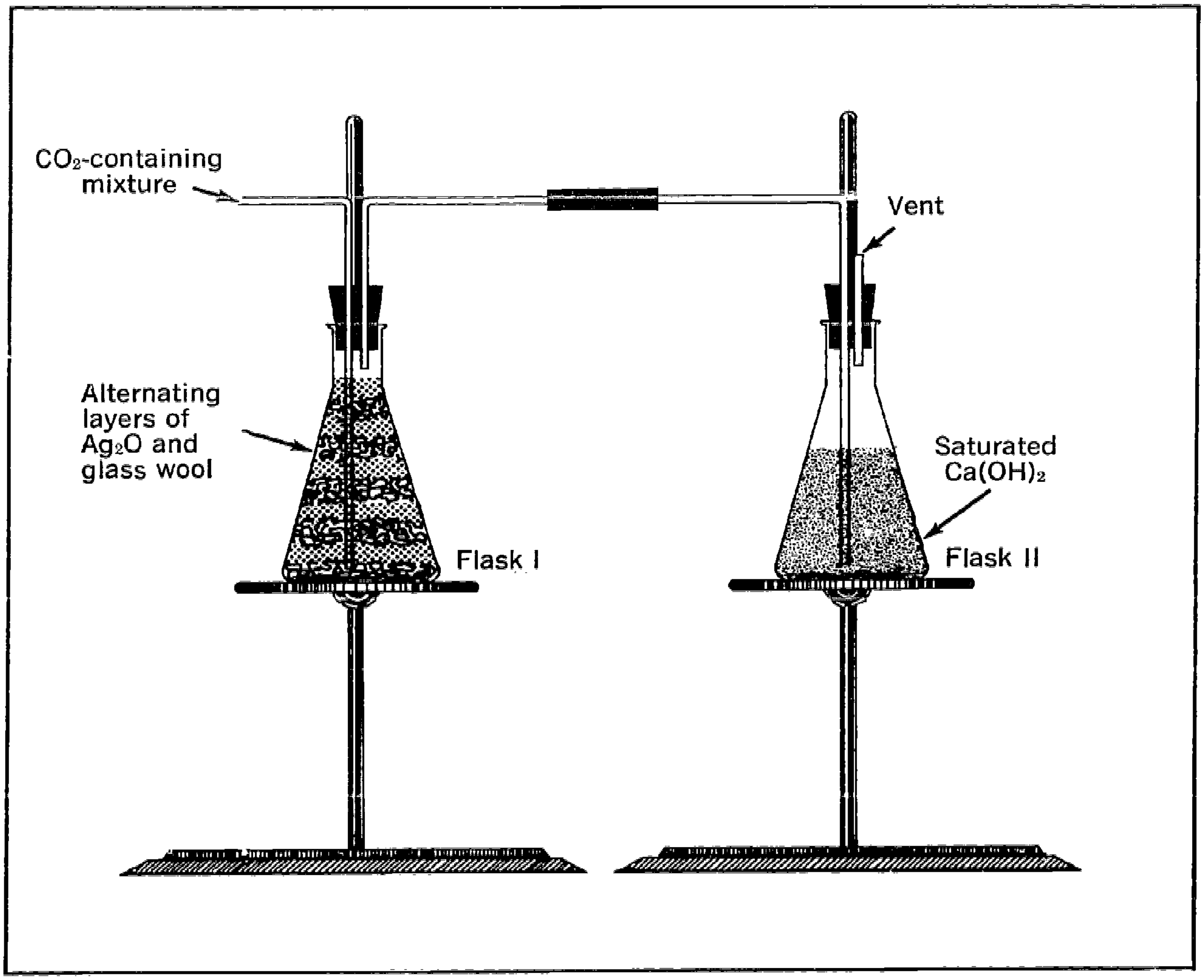


FIGURE 2–2. *Apparatus for absorption of CO_2 by Ag_2O. A gas containing CO_2 is passed through layers of Ag_2O supported on glass wool. Any carbon dioxide not absorbed in flask I is precipitated as carbonate in flask II.*

glass wool. Flask II contains a freshly prepared saturated solution of $Ca(OH)_2$ (limewater), and serves as an indicator of the efficiency of the Ag_2O absorbent. Should the flowrate of CO_2 be excessive for the apparatus, precipitation of $CaCO_3$ will be observed in flask II. If this occurs, the flowrate should be decreased and/or flask I should be repacked.

A piece of tubing is attached between the inlet of flask I and a source of CO_2, such as the breath of a person. Allow CO_2 to pass slowly through the Ag_2O system for a period of about 10 min. Then flask I and its contents are reweighed *under the same conditions as before.* The difference in weight represents the amount of CO_2 absorbed by the Ag_2O, plus any water vapor trapped within the glass wool matrix or on the Ag_2O. An estimate of the amount of water adsorbed on the glass wool may be obtained by passing an equivalent amount of gas through a similar system but omitting the Ag_2O absorbent. An alternate approach in measuring the amount of CO_2 absorbed by the Ag_2O is to recover the $CaCO_3$ from flask II by means of filtration in both the test system and control system, and then dry and weigh it. The difference in weights indicates the amount of CO_2 absorbed by the Ag_2O. The reversibility of the Ag_2O reaction may be demonstrated by heating the Ag_2O. The stopper is removed from flask I, and the flask is placed into an oven having a temperature of about 180° C. At intervals of 1 hr, the flask is removed from the oven, covered with a glass plate, allowed to cool to room temperature, and weighed. This process is repeated until two successive weighings give the same value. A plot of the weight of desorbed CO_2 versus time can be made, and the time necessary to desorb a fraction (e.g., 90 percent) of the CO_2 can be found. The Ag_2O used in this activity can be heated at about 180° C for several days and retained for future use in this experiment. It should be noted, however, that the reused Ag_2O will appear to lose up to 100 percent of the absorbed CO_2 upon being reheated.

ACTIVATED CARBON FOR CONTAMINANT REMOVAL

As indicated in the text, an activated carbon adsorbent has been employed as a general method for the removal of trace contaminants in the space cabin atmosphere. The effectiveness of this system varies with the nature of the substance to be adsorbed. The present experiment examines the effectiveness of activated carbon for the removal of ammonia, a contaminant that might arise from metabolic waste products.

The apparatus for this activity is shown in Figure 2–3. Flask I, a 250-ml Erlenmeyer flask, contains alternating layers of glass wool or cotton and powdered, activated carbon (charcoal). The total amount of carbon used should be about 30 g. The inlet tube

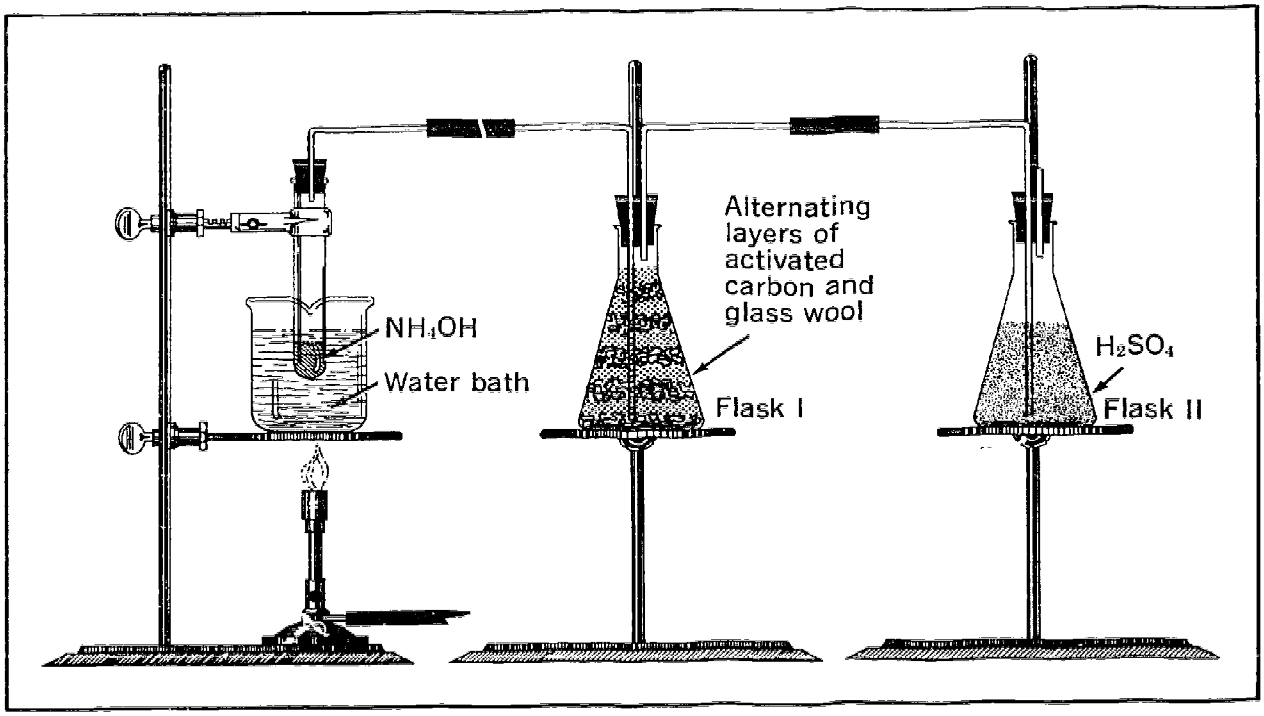


FIGURE 2–3. *Apparatus for measuring the adsorption of gases on activated carbon. Ammonia is passed through flask I where part of it is adsorbed on the carbon. The remainder reacts with the acid in flask II.*

should extend into the lowest layer of glass wool. Flask II contains 200 ml of 0.05 M H_2SO_4. About 10 ml of concentrated NH_4OH is placed in the test tube, and the test tube and flasks are connected as shown. The apparatus should stand at room temperature for 10 to 15 min. Then, preferably using an electric hot plate, the water bath is slowly heated to about 50° C. The heating is stopped, and flask II is *disconnected immediately*. A 25-ml portion of the contents of flask II is titrated with standardized 0.1 M NaOH using phenolphthalein as an indicator.

These results can be compared with a control system treated in the same manner, using only the glass wool in flask I. Comparison of the two results gives the amount of NH_3 adsorbed by the activated carbon.

CHEMICAL SYNTHESIS OF CARBOHYDRATES

Although prestorage is presently the most satisfactory solution to the problem of providing adequate amounts of food during manned space missions, synthetic techniques of food production probably will be used on long-duration missions and remote space stations. Systems capable of regenerating foodstuffs from simple inorganic materials such as CO_2 probably will be most suitable for this purpose because the starting materials are readily available in the form of metabolic waste products.

Many biological regenerative systems are being considered, but NASA scientists believe that systems based on reliable chemical procedures should also be considered at least as backup systems for the biological processes, which may be unreliable under space conditions. In this experiment, we shall examine one of the methods being tested by space scientists for the chemical synthesis of carbohydrates: the condensation of formaldehyde under alkaline conditions.

About 0.1 g of powdered $Ca(OH)_2$ is added to 40 ml of a 4 to 5 percent aqueous solution of formaldehyde in a 125-ml round-bottom flask. A condenser is attached to the flask (Figure 2–4) to reduce loss of formaldehyde during subsequent heating. The flask is placed in a water bath maintained between 80° and 100° C and shaken occasionally during heating. The heating is continued until the solution turns yellow. The reaction is autocatalytic, and the exact time required to reach completion depends in part upon how soon the reaction initiates itself. On the average, a heating period of 30 min is required.

The reaction mixture is filtered to remove any $Ca(OH)_2$, and the filtrate is neutralized with dilute formic acid. (CAUTION: Formic acid can produce severe skin burns.) The yellow liquid is concentrated to a small volume having the consistency of a viscous sirup. This is accomplished most readily with a rotary evaporator if available; if not, the solution may be poured into an evaporating or petri dish and placed in a vacuum desiccator over concentrated H_2SO_4. Whatever technique is employed, the temperature should be kept below 50° C to prevent caramelization of the products.

Five to ten ml of ethanol are added to the concentrated sirup to precipitate any dissolved inorganic materials; and the precipitate, if any, is removed by filtration. Further evaporation of the filtrate will yield a yellow solid, which is a mixture of carbohydrates and noncarbohydrate contaminants.

If desired, the nature of this mixture of carbohydrates can be examined by chromatographic techniques. A strip of Whatman filter paper (preferably No. 1 or No. 3), about 1 in. wide and 6¼ in. long, is prepared. Touching only one end of the strip, the student draws a light pencil line about 1 in. from the other end. A wire or string is inserted through the paper about ¼ in. from the handled end and as near the center of the strip as possible

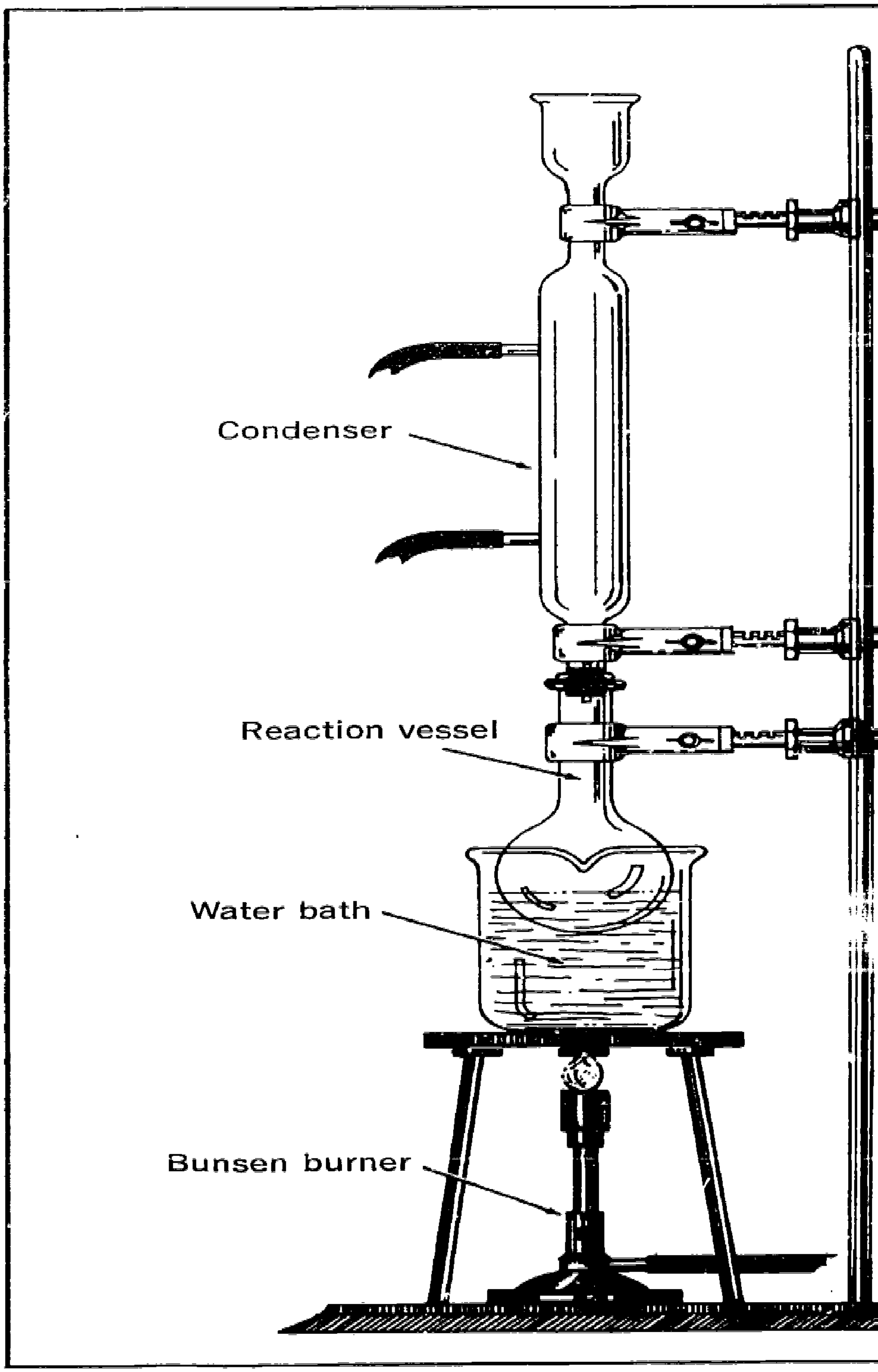
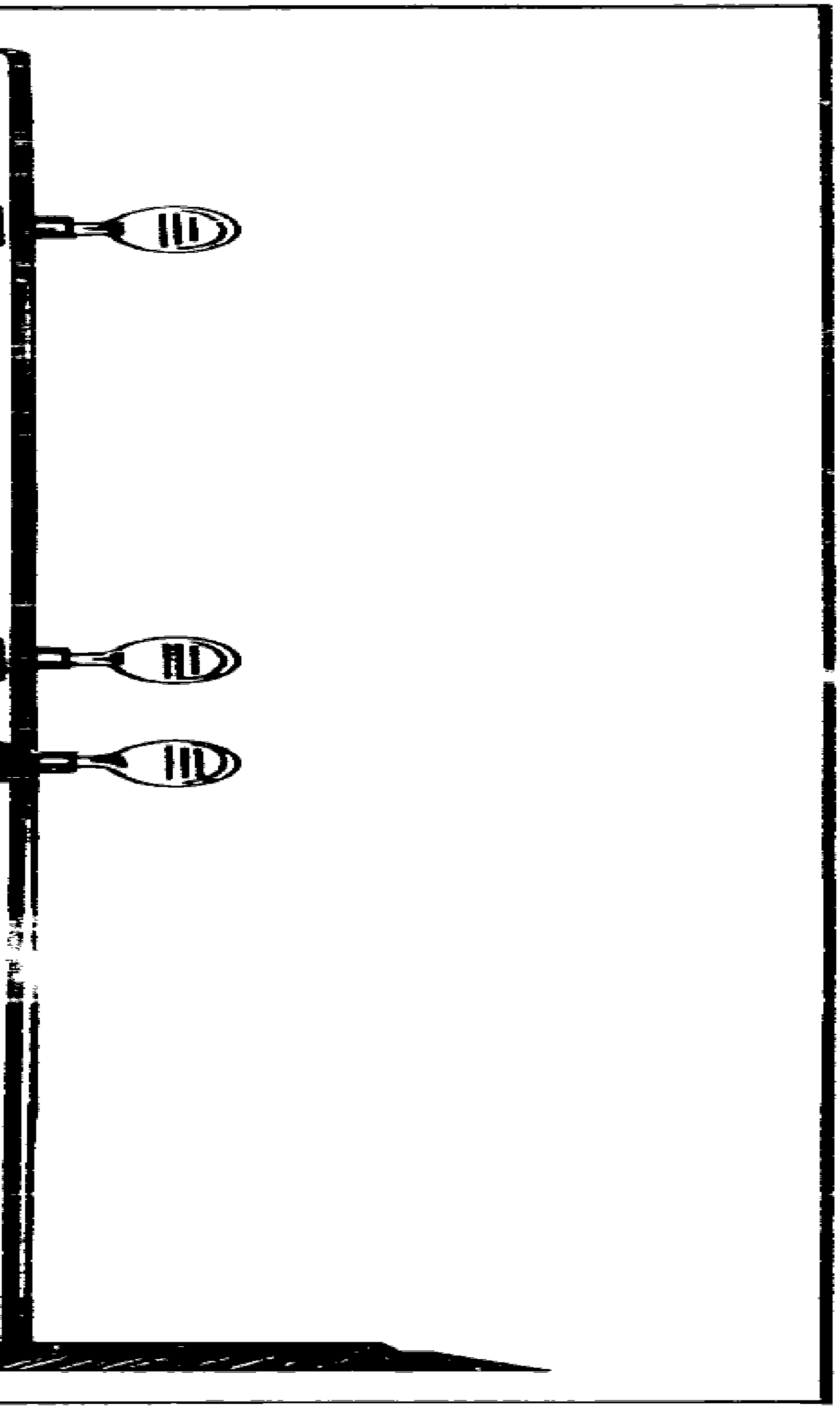


FIGURE 2–4. *Apparatus for the synthesis of carbohydrates. A mixture of aq and calcium hydroxide is heated in a flask fitted with a con turns yellow, indicating the formation of a mixture of carbol*



*queous formaldehyde
ndenser. The solution
hydrates.*

(Figure 2–5). This will serve to support the paper during the chromatography.

A clean, dry 500-ml Erlenmeyer flask fitted with a cork may be used for the chromatography vessel. A long-pronged staple or half a paper clip from which to hang the strip of filter paper is inserted into the bottom of the cork. The developing solvent is prepared by thoroughly mixing (preferably in a separatory funnel) *n*-butanol, glacial acetic acid, and water in the ratio 4:1:5 by volume. The mixture separates into two phases on standing. The upper butanol phase is used for the chromatography. About 30 ml of the developing solvent is placed in the Erlenmeyer flask, and the flask is stoppered immediately to prevent evaporation.

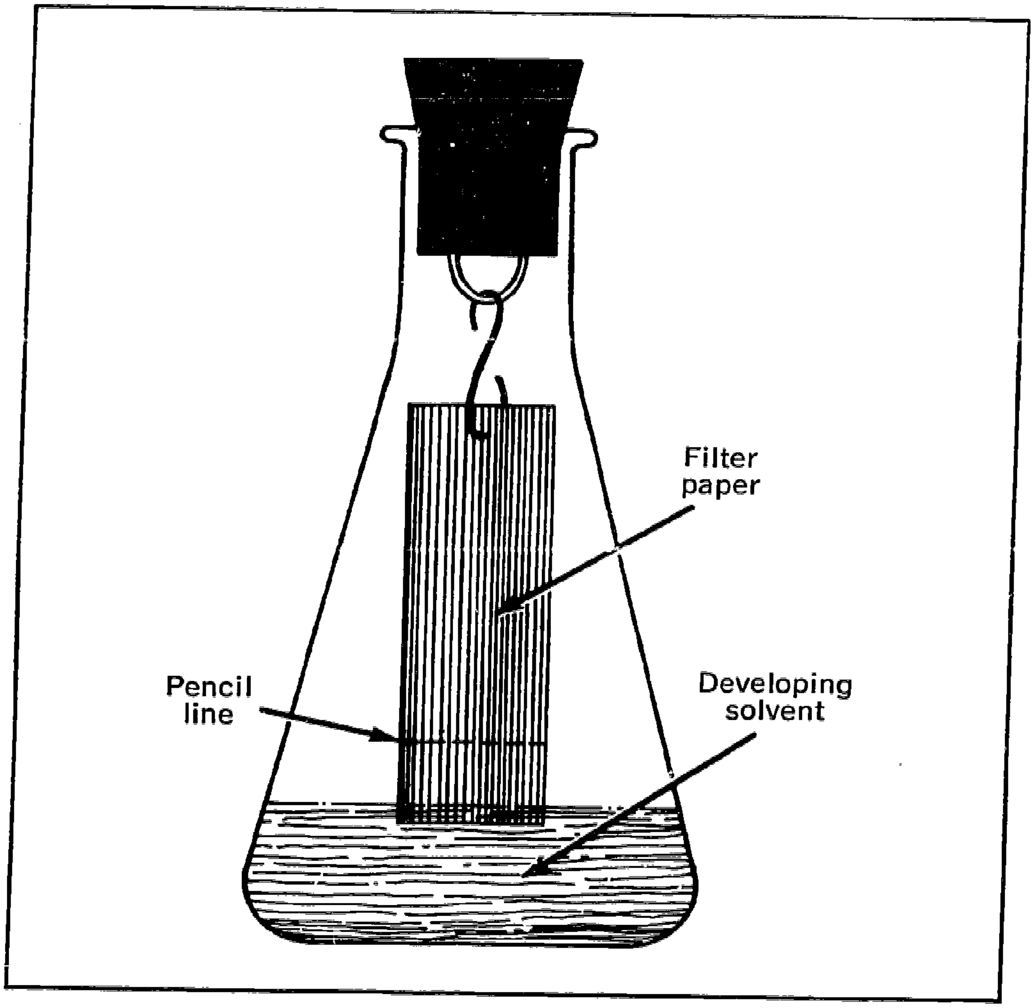


FIGURE 2–5. *Apparatus for chromatography of carbohydrates. A small amount of sugar solution is spotted at the level of the pencil line on the filter paper, and the mixture of sugars is resolved chromatographically.*

A very small amount of the solid carbohydrate mixture is dissolved in as small a volume of ethanol as possible. By means of a capillary tube drawn out to a fine point, a small amount of the sugar solution is deposited on the center of the pencil line on the strip of paper. (The volume of solution drawn into the tube by capillary action should provide sufficient material for the chromatography.) The spot should be kept as small as possible. (If the liquid is applied in several small doses with sufficient time for complete drying between each dose, a small, compact spot is obtained.) After allowing the spot to dry for 5 to 10 minutes, suspend the paper from the cork with the lower edge of the paper dipping into the solvent (Figure 2–5). The solvent level should not reach the pencil line, and the edges of the paper should not touch the sides of the flask. When the solvent has climbed to within ½ in. of the upper edge, the paper is removed from the flask and allowed to dry. The flask should be restoppered immediately to prevent evaporation of the solvent. Much better resolution of the components is achieved by returning the dried paper to the flask and repeating the solvent migration step.

After the final drying, the paper is sprayed uniformly with or dipped quickly into an aniline phthalate reagent (0.93-g aniline, 1.66-g phthalic acid, and 100-ml water-saturated butanol) and is dried at 105° C (drying oven) for 5 min. With this reagent, triose sugars produce a yellow color, pentose sugars give a crimson color, and hexose sugars give a brown color. In this manner, several components in the sugar mixture are characterized.

LITERATURE CITED

1. Popma, D. C., and V. G. Collins. 1965. Space vehicle water reclamation systems. NASA Langley Research Center. NTIS. N66–17221#.

2. Henry, J. P. 1966. Biomedical aspects of space flight, pp. 92–105. Holt, Rinehart & Winston, Inc., New York.

3. Welch, B. E. 1963. Ecological systems, pp. 310–332. *In* J. H. U. Brown, Physiology of man in space. Academic Press, Inc., New York.

4. Smylie, R. E., and M. R. Reumont. 1964. Life-support systems, Chapter 15. *In* P. E. Purser, M. A. Faget, and N. F. Smith, Manned spacecraft: engineering design and operation. Fairchild Publications, Inc., New York.

5. National Aeronautics and Space Administration. 1966. Significant achievements in space bioscience 1958 to 1964, pp. 77–78. NASA SP–92, 1966. GPO, $0.55.

6. Smylie, J. W. 1964. Evaluation and application of chemically regenerative atmospheric control systems, p. iv. Office of Technical Services, U.S. Dept. of Commerce. NTIS N64–31979#.

7. Sinyan, Y. Y. 1964. Possibility of physicochemical synthesis of carbohydrates in a space cabin, pp. 443–453. *In* N. M. Sisakyan and V. I. Yazdovskiy, Problems of space biology. Joint Publication Research Service, Washington, D.C. NTIS N64–23774.

8. Akerlof, G. C., and P. W. D. Mitchell. 1963. Study of the feasibility of regeneration of carbohydrates in a closed circuit respiratory system. FMC Corp., Princeton, N.J. NTIS N64–11801#.

9. Rosenberg, S. D., and G. A. Guter. 1964. Synthesis of foodstuffs from simple inorganic materials, pp. 69–74. Second annual meeting of the working group on extraterrestrial resources. NASA. NTIS N67–20418.

10. Wunder, C. C. 1966. Life into space, pp. 106–119. F. A. Davis Co., Philadelphia.

11. Quattrone, P. D. 1964. Trace contaminant removal, pp. 269–285. *In* Symposium on toxicity in closed ecological systems. Lockheed Missiles & Space Co., Palo Alto, Calif. NTIS N64–24626#.

OTHER REFERENCES

*Bioregenerative systems. 1968. NASA SP–165. GPO, $1.50.

*The closed life-support system. 1967. NASA SP–134. NTIS N67–34583#.

*Conference on nutrition in space and related waste problems. 1965. NASA SP–70. GPO, $2.75.

**Recommended general sources of information.*

FILMS

Living in space, part I: the case for regeneration. 1966. 12 min, sound, color. NASA.

Living in space, part II: regenerative processes. 1966. 22 min, sound, color. NASA.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70-12345#).

unit 3

unit 3

CHEMICAL ROCKET PROPELLANTS*

Topics that may be enriched by use of this unit:

Heat of combustion
Temperature
Periodic law
Enthalpy
Stoichiometry

It is the nature of man to move himself and his goods from place to place, to explore his surroundings, and to extend the limits of his abilities. It is natural, therefore, that man in his present stage of technological development is sending vehicles on missions into space. Because the atmosphere in space is far too rarefied to allow use of conventional engines, these space vehicles must be powered with rocket engines that produce thrust by expelling large amounts of gases at high velocities (1, 2). In the case of chemical rocket engines, the high-velocity gases that are expelled are the products of highly exothermic chemical reactions (3). A continuing problem for rocket scientists is to optimize the thrust produced by these rocket engines through choice of propellants, reaction conditions, and rocket-engine design.

SOLID PROPELLANTS

Chemical rockets are classified as solid or liquid based on the physical state of the stored reactants. The first rockets, called "arrows of flying fire," were made in the 13th century by the Chinese. They used heterogeneous solid propellants possibly composed of tow (fibers of hemp), pitch, turpentine, sulfur, charcoal, naphtha, petroleum, incense, and saltpeter. The first recorded attempt at manned rocket flight occurred about the year 1500 when a Chinese man named Wan Hoo strapped himself between two kites in front of 47 gunpowder rockets. Ignition of the rockets annihilated both the vehicle and its pilot. More

---

**The chemical compositions of several rocket propellants are stated in this unit. It is not suggested that these substances be prepared or obtained from other sources for purposes of experimentation because of the inherent danger involved.*

recently, heterogeneous solid propellants were composed of mixtures of an inorganic oxidizer with an organic fuel, such as the mixture of potassium chlorate and asphalt used in World War II jet-assisted takeoff rockets. This mixture is cast inside a rocket case; the asphalt gives the charge sufficient strength to withstand the stress associated with the rocket's acceleration and the pressures resulting from combustion. Most recently, elastomeric materials have replaced asphalt as the organic fuel in heterogeneous solid propellants. A mixture is formed of a monomer and oxidizer particles, and then the monomer is polymerized. Ammonium perchlorate commonly is used as an oxidizer; and often finely divided metals, such as powered aluminum, are added to increase the efficiency of combustion. In addition, other additives may be included to improve the physical properties of the propellant. The Polaris is an example of modern rockets using improved types of heterogeneous solid propellants.

A second type of solid propellant, termed "homogeneous" or "double-base propellant," is formed from gelatinized colloidal mixtures of nitrocellulose, nitroglycerine, or diethylene glycol dinitrate. Plasticizers, modifiers, and stabilizers are added to give homogeneous propellants more suitable physical properties. The Nike booster used such a propellant.

Data for two representative solid rocket propellants are given in Table 3-1 (4). Propellant I is a homogeneous propellant composed by weight of 52 percent nitrocellulose, 43 percent nitroglycerine, and 5 percent additives. Propellant II is a heterogeneous propellant composed of 80 percent ammonium perchlorate and 20 percent resin and additives.

A solid propellant is packed or molded inside a rocket case in the general shape of a tube, thus a cavity runs the entire length of the center of the solid charge (5). The initial cross-sectional shape of this cavity is selected with a view to controlling the area of surface that will be burning at any given time. The rocket is maintained at sufficiently low temperatures to retard reaction

TABLE 3-1

COMPARISON OF TWO SOLID PROPELLANTS

Property	Propellant I	Propellant II
Density, g/cm^3	1.61	1.72
Flame temperature, °C	1760	1530
Average particle mass, g/mole	27.8	25.5
Heating velocity, cm/sec	1.65	0.8–2.0
Specific impulse, lb-sec/lb	230	236

From Jaukovic (4).

or decomposition of the charge during storage. For ignition, the surface of the propellant along the cavity is brought to a sufficiently high temperature to sustain combustion. Ignition is accomplished by igniting small pyrotechnic devices placed near the charge or by introducing substances that spontaneously react together or with the solid propellant. Burning then occurs along the entire inner surface of the tubular charge; the remainder of the solid propellant and rocket case act as the combustion chamber. Heat from the combustion process melts, sublimes, and boils the reactants close to the surface; and the vapors react as they are carried along in the gas stream. Additives and polymeric binders keep large chunks of propellant from being dislodged by the vaporization or foaming action within the solid propellant.

The rate of combustion per unit of surface area of the solid charge is dependent on the pressure in the combustion chamber and on the propellant temperature. The pressure in the combustion chamber is related in turn to the amount of material burning per unit of time and to the size of the exhaust opening or throat. The surface temperature of the solid charge is determined by its specific heat and thermal conductivity. The rate of penetration of the heat into the solid charge is regulated by additives, such as soot or pigments. Solid propellants usually are consumed at 0.1 to 5 cm/sec in the absence of extreme erosive effects. Two examples of rates of combustion (or heating velocity) are listed in Table 3–1. Certain additives called inhibitors regulate the rate and direction of the consumption of the propellant, thus delaying exposure of the rocket case to high temperatures. Structural parts that have extensive exposure to the hot gases, such as nozzles, are protected by coatings of ceramics or ablating materials. (See Unit 8, "Ablative Materials for High-Temperature Thermal Protection.")

Solid-propellant rockets have the advantages of simplicity and reliability along with the disadvantage that the solid propellant may decompose or react prior to launching. Homogeneous propellants are also very sensitive to shock. Solid-propellant rockets, however, have the further disadvantage that once the combustion process is initiated, it cannot be throttled easily and continues until all of the propellant in the engine is consumed. Thus, solid-propellant rockets are more difficult to use for some functions, such as maneuvering space vehicles.

LIQUID PROPELLANTS

A second type of rocket propellant that is used extensively in our space efforts is stored in the liquid state. Rocket engines using liquid propellants have the advantage that the combustion process in the engine can be throttled by the pilot or ground control because the storage and combustion sites of the propellants are separated. The liquid propellants are forced or pumped from storage tanks through pipelines to a combustion chamber. The complex systems required for the storage and movement of liquid propellants, however, impose penalties of increased mass of a rocket and create realiability problems. Furthermore, many liquid propellants must be handled and stored at very low temperatures.

The first use of liquid propellants occurred in the year 1895 when Paulet in Peru operated a bipropellant rocket using gasoline as the fuel and liquid oxygen as the oxidant. The work of Robert Goddard, both in theoretical analysis of space flight (1919) and in experiments with liquid-oxygen rockets (first flight, 1926), was important early pioneering work. By World War II German scientists had perfected a liquid-oxygen/alcohol rocket called the V–2. More recently, nitrogen tetroxide and aerozine (hydrazine that has been stabilized by mixing it with unsymmetrical dimethyl hydrazine) were used in Titan II boosters to launch the Gemini series of manned satellites. Nitrogen tetroxide and hydrazine have the advantage that they can be stored at temperatures just below room temperature, but the disadvantage that they are very toxic. In addition, hydrazine can be dangerous to handle because it can burn alone as a monopropellant. Another example of a liquid-propellant rocket engine is the F–1 engine, five of which provide the 7,500,000-lb thrust for the first stage of the Saturn V-Apollo. The propellants of the F–1 engine are RP–1 (a type of kerosene) and liquid oxygen. (See Figure 3–1.) More energy per pound of propellant and a larger specific

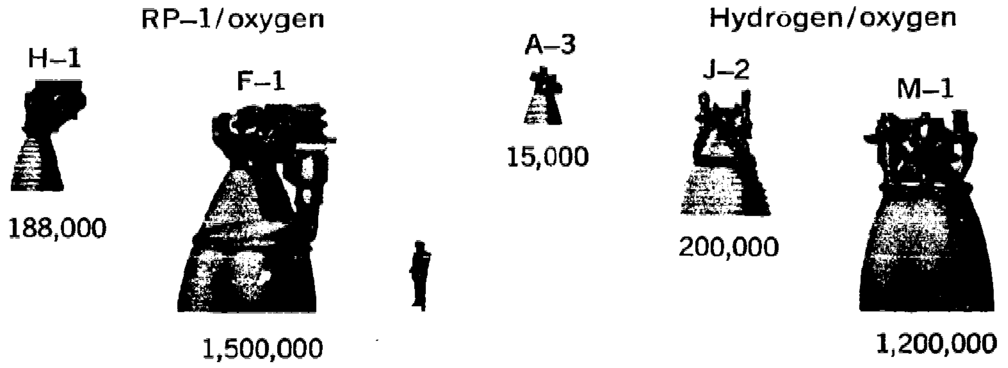


FIGURE 3–1. *Some liquid-propellant engines and the pounds of thrust produced by each. RP–1 is a type of kerosene; five F–1 engines using this fuel power the Saturn V rocket. The size of a man is given for comparison.*

impulse (ratio of the thrust produced by a rocket motor to the mass of the propellants reacting per unit time) are obtainable from the reaction of hydrogen and oxygen. These propellants are used to power the 200,000-lb thrust J–2 engines in the second and third stages of the Saturn V-Apollo. Table 3–2 lists some of these biopropellant combinations and the approximate storage temperatures of each fuel and oxidant.

The combustion chamber of a liquid-propellant rocket (Figure 3–2) is much smaller and lighter in weight than that of solid-propellant rocket of comparable thrust. In many liquid-propellant rocket engines, the liquid fuel is circulated through the tubular walls of the combustion chamber and nozzle. This procedure, called regenerative cooling, warms the fuel to the proper temperature for ignition and protects these surfaces from the effects of the high temperatures. The liquid fuel and oxidant of a

TABLE 3–2 **COMMON PAIRS OF LIQUID PROPELLANTS**

Oxidant (O)	Liquid fuel (F)	Best weight ratio (O/F)	Specific impulse lb-sec/lb
Oxygen: O_2, −183° C	Alcohol: C_2H_5OH, 16° C	2.00	287
Nitrogen tetroxide: N_2O_4, 16° C	Hydrazine: N_2H_4, 16° C	1.30	291
Oxygen: O_2, −183° C	RP–1: kerosene, 16° C	2.60	301
Oxygen: O_2, −183° C	Hydrogen: H_2, −253° C	4.00	391

Specific impulse is calculated here assuming ideal expansion of the combustion products from a pressure of 1000 psi to 1 atm. Units are the conventional pounds-force divided by weight flowrate (pounds per second); specific impulse is, of course, independent of gravity.

From Burrows (6).

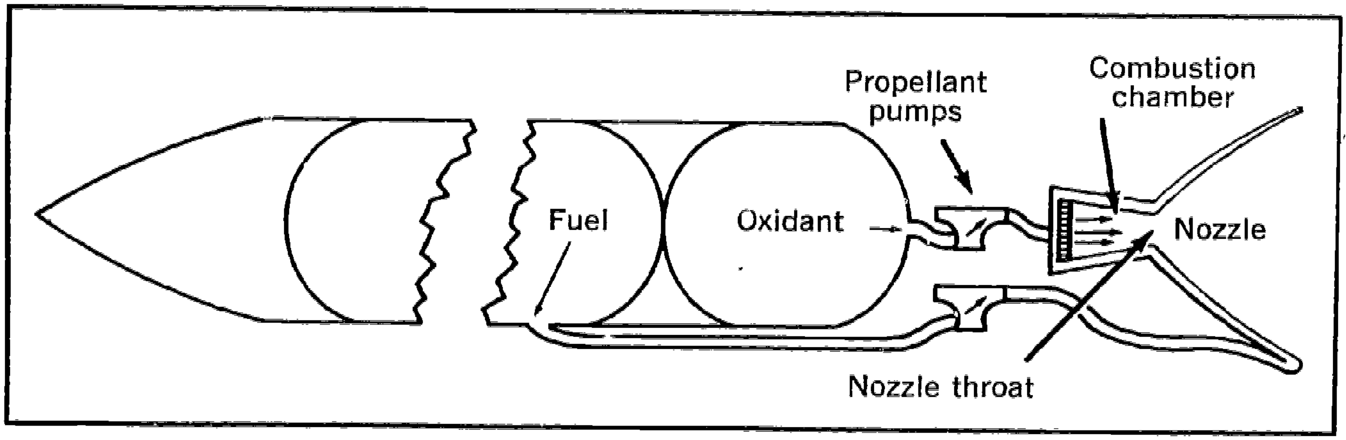


FIGURE 3–2. *Components of a typical liquid bipropellant rocket. Fuel and oxidant are pumped from their storage tanks to the combustion chamber. Circulation of the fuel through the walls of the combustion chamber and nozzle cools the surfaces of these structures.*

bipropellant rocket are metered, atomized, and mixed upon injection into the combustion chamber. Some propellants such as N_2O_4 and N_2H_4 ignite spontaneously on mixing (hypergolic); whereas other propellants such as H_2 and O_2 must be ignited initially by a glow plug, spark plug, injection of a small amount of hypergolic fuel, or a pyrotechnic igniter.

The temperature of the droplets of liquid propellant rises rapidly when they are injected into the hot combustion chamber. Vaporization occurs at their surfaces and the average droplets exist for only several microseconds as they are accelerated to the speed of the surrounding gases. The gaseous reactants begin to burn after they reach a sufficiently high temperature under the prevailing pressures. Burning occurs downstream from the fuel injectors, thus preventing convective heating and erosion of the fuel injector plates. Although these plates are also heated by radiation from the burning gases, excessive damage to the plates is prevented by the cooling effect of the liquid propellants being injected.

The location of fuel injectors in a rocket engine is one of several variables that affect the stability of the combustion process. Critical regions of instability in an engine develop wherever large gradients in temperature, pressure, and composition exist. These can cause pulsations to arise with frequencies ranging from less than 100 to several thousand cycles per second that would vibrate the entire rocket. In addition, the high-frequency oscillations can cause erosion of the combustion chamber and fuel injector (Figure 3–3). Elimination of this instability is still an art and often is achieved by making changes in the geometry of the combustion chamber through modification of the fuel injectors and the baffles on the fuel injector plates (7) (Figure 3–4).

A combustion chamber must be of sufficient size to complete the process of atomizing, mixing, igniting, and burning the propellants by the time the gases enter the nozzle (Figure 3–2). The area of the nozzle throat determines the combustion pressure, which in turn determines the speed of the reaction and, therefore, the size of the combustion chamber. These and other parameters have no optimum magnitudes but are calculated by NASA space scientists for a given set of conditions including the nature of the propellants, external pressures, and the thrust expected from the engine.

Heating of the rocket nozzle provides still another problem for combustion scientists. The heat-transfer rate in the nozzle may be three to four times that occurring in the combustion chamber; and in the throat, three to four times that in the nozzle. In addi-

FIGURE 3–3. *Erosive effects from high-frequency "screaming." Instabilities in a combustion chamber caused severe erosion of this fuel injector plate. Burnout of this plate occurred in about 0.5 sec.*

tion to employing the regenerative cooling mechanism mentioned previously, these structures may be protected by fabricating them from superalloys and coating them with ceramics or ablating materials. (See Unit 8, "Ablative Materials for High-Temperature Thermal Protection.") The walls may also be sprayed with liquid fuel to cover their surfaces with a vapor shield of relatively cool gases.

Some liquid-propellant rockets derive thrust from the thermal decomposition of a single substance. The hardware design of

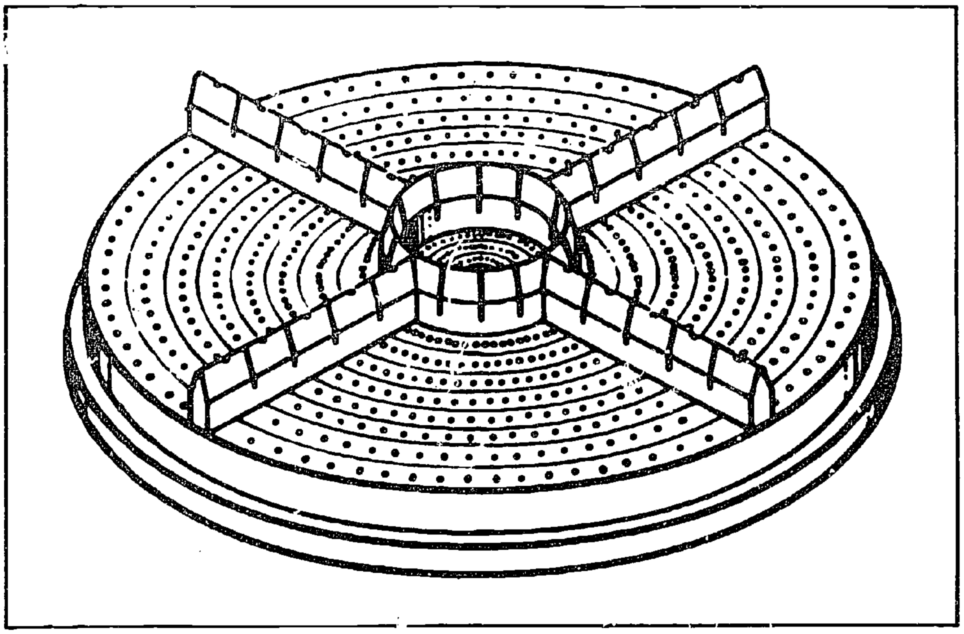


FIGURE 3–4. *Injector with baffles. Baffles discourage the rotary motion of a pressure wave near the fuel injector plate thus preventing damage of the type shown in Figure 3–3.*

these monopropellant liquid rockets is essentially the same as for a rocket of the bipropellant type. The monopropellant is ignited initially by a glow plug, spark plug, or the simultaneous injection of a small amount of a substance with which it reacts spontaneously. For instance, the midcourse propulsion system on the Ranger Moon probe was a monopropellant hydrazine engine. A small amount of N_2O_4 was injected to initiate the decomposition of the hydrazine. At the resulting higher temperatures, the decomposition of injected hydrazine was continued, catalyzed by Al_2O_3 present on the walls of the reaction chamber.

ROCKET PROPULSION

The purpose of a rocket engine is to provide the accelerating force or thrust needed to place a space vehicle into an orbit or an interplanetary trajectory. The thrust arises as a result of expelling small particles, called propellants, at high speeds from the rocket engine. The amount of acceleration produced is directly proportional to the thrust, which, in turn, is directly proportional to the amount of propellant ejected per unit time and the velocity of the ejected propellant. If m_p is the mass of propellant ejected at a velocity V_p in an interval of time t, then the thrust F is given by

$$F = \frac{m_p V_p}{t} \qquad (3\text{–}1)$$

For a rocket having a gross mass of m_g, the acceleration produced by the thrust is

$$a=\frac{F}{m_g} \tag{3-2}$$

The gross mass of the rocket may be considered as the sum of the mass of the vehicle m_V and that of the propellant m_p.

$$m_g=m_V+m_p$$

Substituting this expression in Equation (3-2), we have at any instant

$$a=\frac{F}{m_V+m_p} \tag{3-3}$$

As shown in Equations (3-1) and (3-3), large accelerations are achieved by expelling large amounts of propellant at high speeds from a space vehicle of the smallest possible mass.

ROCKET PROPELLANTS

While rocket engines are rated in terms of thrust, propellants often are rated in terms of specific impulse. Specific impulse I_{sp} is the ratio of the thrust produced to the mass of propellant expelled per unit time. The equation for this relationship is

$$I_{sp}=\frac{F}{(m_p/t)}$$

or

$$I_{sp}=\frac{Ft}{m_p} \tag{3-4}$$

(It can be seen from the latter equation that specific impulse is simply the impulse, Ft, per unit mass of propellant.)

Specific impulse is often expressed in the units of pounds of thrust per pound of propellant consumed per second; that is, pounds per pound per second, or pound-seconds per pound. (In the literature, the mass of rocket propellants commonly is given in pounds.) The importance of this quantity is that it is directly proportional to the velocity with which the propellant is ejected from the engine and to the rate of acceleration of the rocket (Equations (3-1) and (3-3)).

Typical values of the specific impulse of propellants in chemical rockets range from 200 to 450 lb-sec/lb. For nuclear or electrical rockets, the value of specific impulse may be several hundred to several thousand pound-seconds per pound (2). The relatively small values of specific impulse for chemical propellants result from the fact that the energies for accelerating the propellants come from chemical reactions involving the propellants themselves. The energies produced are limited to those of the most exothermic chemical reactions and are much less than can be produced with nuclear or electrical devices. Chemical rockets, however, will continue to play an important role in space missions by maximizing the specific impulse of propellants through the use of highly exothermic chemical reactions, minimizing the masses of vehicles, and using large masses of propellants. Chemical rockets will continue to be especially useful in launching vehicles from the surface of planets because their total thrust can be made very large.

SELECTION OF CHEMICAL PROPELLANTS

A fundamental and often limiting characteristic of chemical rockets is that all of the energy used in accelerating the propellants comes from the energy released in the combustion reaction. Therefore, the chemical propellants selected are those that undergo highly exothermic reactions. These highly exothermic combustion reactions result in increased temperatures in the combustion chamber, ejection of the propellants at higher speeds, and increased thrust. The relationship among these quantities can be understood by noting that the average velocity of the particles of propellant in the combustion chamber V_c is directly proportional to the square root of the ratio of the absolute temperature T_c to the average mass of the particles of propellant m:

$$V_c \propto \sqrt{\frac{T_c}{m}} \tag{3-5}$$

Furthermore, the directed velocity of the propellant V_p ejected from the nozzle of a rocket engine is directly proportional to the random velocities of the gases in the combustion chamber; therefore

$$V_p \propto \sqrt{\frac{T_c}{m}} \tag{3-6}$$

This relationship is quite important to the rocket scientist because it states that the average velocity of the molecules of the ejected propellant, and hence the thrust of the rocket engine, is increased by increasing the combustion temperature and by decreasing the average molecular mass of the combustion products. Higher combustion temperatures are achieved by selecting propellants with large heats of reaction (large negative values of ΔH) under the conditions of temperature and pressure found in combustion chambers. Because the combustion temperature is directly proportional to the heat of reaction and because the specific impulse of propellants is directly proportional to the velocity of the propellants, it follows from Equation (3–6) that (3, 8, 9)

$$I_{sp} \propto \sqrt{\frac{\Delta H}{m}} \qquad (3\text{–}7)$$

This important proportionality shows that the specific impulse of the propellant, and thus the thrust of a rocket, is related to the heat of reaction of the propellants and to the average mass of the particles ejected from the rocket engine. Rocket scientists therefore must select combinations of propellants and a combustion chamber geometry that yield large values of specific impulse.

HEATS AND PRODUCTS OF REACTIONS OF ROCKET PROPELLANTS

Chemical reactions involve electrons in the outer or valence shells of atoms, and the number of these electrons varies periodically with increasing atomic number. Therefore, as might be expected, the amount of energy released in the reaction of 1 mole of any element with sufficient atoms of a given element, such as oxygen, varies in a periodic manner with increasing atomic number. Because the mass of the propellant is very important in achieving maximum acceleration from rocket engines (Equation (3–3)), the energy released per unit mass of product is of even more significance in selecting propellants (3). A representative plot of the heats of reaction of various elements with oxygen is shown in Figure 3–5. It is apparent from the figure that the elements having atomic numbers nearly equal to those of beryllium, aluminum, and scandium upon reaction with oxygen release the most energy per unit mass of the oxide formed. Thus, if oxygen is chosen as the oxidant, potential elemental rocket fuels would include these substances. However, the oxides of beryllium, boron, magnesium, aluminum, calcium, scandium, and titanium have very high boiling or sublimation points; and thus these oxides would tend to aggregate in the gas flow and even condense on the walls of the combustion chamber. Therefore, use of these elements as fuels would give high heats of reaction but would yield low values of specific impulse (Equation (3–7)). A compromise is made: typical oxidants used are oxygen and fluorine (an oxidizing agent in the broad sense of the term); and typical fuels include hydrogen and compounds containing boron, carbon, nitrogen, and hydrogen. Combustion temperatures for these substances are in the range of 2500° to 4000° C.

The average mass of the combustion products depends on the nature of the fuel/oxidant pair, the reaction conditions, and the thermal stabilities of the product molecules. For a given fuel/

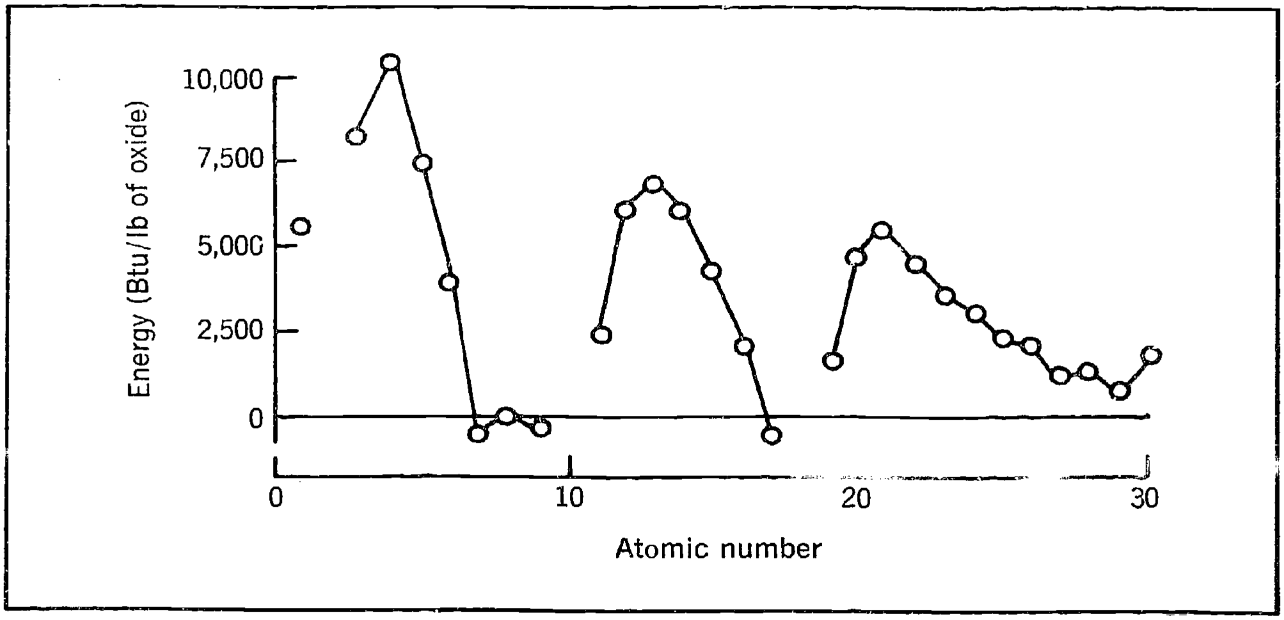


FIGURE 3-5. *Reaction energy with oxygen. The heat released per pound of oxide formed in the reactions of various elements with oxygen is seen to vary periodically with atomic number. Maxima occur for the elements beryllium, aluminum, and scandium.*

oxidant pair, the average mass of the product molecules often can be made smaller by injecting excess fuel into the combustion chamber. That is, the ratio of fuel to oxidant is made larger than its value calculated on the basis of a balanced stoichiometric equation. This is illustrated in Table 3-2. For instance, if hydrogen reacts with oxygen at room temperature, the balanced equation for the reaction is

$$2H_2 + O_2 \rightarrow 2H_2O$$

Under these conditions the only product molecules are those of water. At the temperatures found in combustion chambers, however, small amounts of free radicals such as H and OH would also be present in the reaction mixture. Furthermore, if the reaction mixture is made fuel rich, the proportion of small molecular weight molecules is increased. Although less heat is released per mole of reactant under these conditions, smaller particle masses and a higher specific impulse result (Equation (3-7)). For use in rocketry a typical weight ratio of oxygen to hydrogen is 4 to 1 (Table 3-2). Under these fuel-rich conditions, the reaction at high temperature can be written approximately as

$$4H_2 + O_2 \rightarrow 1.98H_2O + 1.97H_2 + 0.06H + 0.03OH$$

Similar equations apply to other fuel/oxidant combinations. For instance, if hydrocarbons are burned in insufficient oxygen, some of the hydrogen appears as H and H_2 rather than as water. Again, this results in a higher specific impulse than could be achieved with stoichiometric amounts of the reactants.

The chemical composition of the combustion products continues to change as the products pass through the throat and nozzle of the rocket engine. If one considers the composition of these gases to be fixed at that found in the combustion chamber (a "frozen" equilibrium), illustrative calculated values of specific impulse for various combinations of oxidants and reactants are shown in Figure 3–6 (from Rothrock (3)).

Although specific impulse is a measure of the performance of propellants, several other factors need to be considered in selecting a fuel/oxidant pair. For instance, although the specific impulse of the hydrogen/oxygen reaction is relatively large, the density of liquid hydrogen is relatively low compared to other fuels. As a consequence, larger storage tanks are required, and this results in an added weight penalty for the rocket. Therefore, not only is the energy released per unit mass of reactant important in rocketry but also the specific gravity of the reactants. In addition, a number of other factors may be relevant to the choice of the propellants, such as their stability, the difficulty

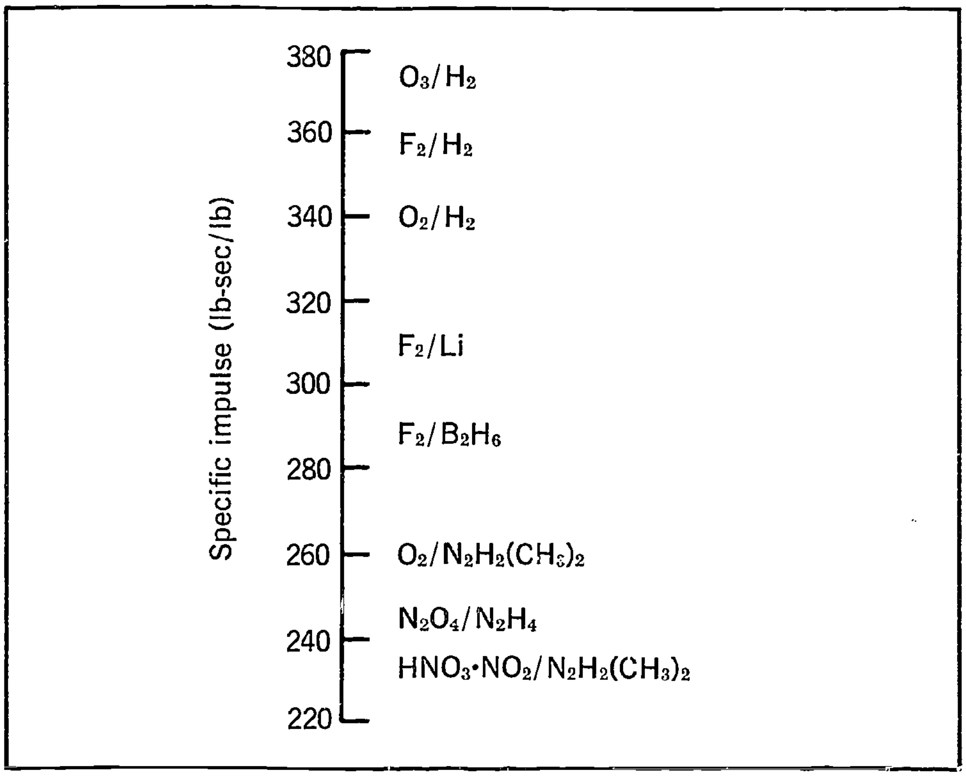


FIGURE 3–6. *Performance of representative rocket propellants (3).*

in handling and storing them, and the toxicity of the propellants or of the combustion products. (See Unit 2, "Life-Support Systems.")

Although much information about propellant performance can be determined through combustion experiments, such trials are very costly and time consuming. A potentially more efficient and revealing method is to predict the performance of a propellant in a given combustion chamber from thermodynamic data. By statistical thermodynamic methods, one calculates the molecular contribution to quantities such as enthalpy, heat capacity, transport properties, and equilibrium constants. From knowledge of molecular-energy levels and the distribution of molecules among these levels, one can calculate thermodynamic quantities at any combustion temperature and pressure. Such data have been compiled for almost 20 elements and more than 200 chemical combinations of these elements at the NASA Lewis Research Center. Through use of high-speed computers, these thermodynamic data can be used to solve combustion problems including atomization and vaporization of propellants, heat transfer, chemical composition of the reaction mixtures, and values of specific impulse (9).

ACTIVITIES

HEAT OF REACTION FOR THE CATALYTIC OXIDATION OF ETHANOL

Chemical reactions that yield gaseous products and large amounts of heat are of particular interest for use in propelling space vehicles. For reactions occurring at moderate temperatures and pressures, the heat released can be measured experimentally. Often, the fuel under study is oxidized with excess oxygen in a bomb calorimeter. Such measurements can be illustrated in a simple open system by burning ethanol in air. Because large losses of heat will occur in this experiment, the measured value will be only about 60 to 70 percent of the actual heat of combustion.

A calorimeter is made by insulating the inner surfaces of a 1-liter beaker with paper towels and inserting an 800-ml beaker in a nested arrangement. The inner beaker is filled with a measured quantity of water (about 600 ml). A 125-ml Erlenmeyer flask, containing about 10 ml of ethanol, is used as the reaction vessel. The amount of ethanol in the flask can be determined by weighing the empty flask and reweighing the flask after adding the ethanol.

A copper catalyst is prepared by cutting a 1- by 4-cm strip of copper screen and bending it into a cylinder. A piece of uninsulated wire is attached to either side to make a harness arrangement as shown in Figure 3–7. The catalytic cylinder is hung from a glass rod so that when inserted into the reaction flask, it extends to within 2 cm of the surface of the ethanol.

The reaction flask is placed in the calorimeter and the initial temperature of the water in the calorimeter is recorded. The reaction is initiated by heating the copper catalyst in the flame of a bunsen burner until it is glowing and quickly transferring it to the reaction flask. During the reaction, the water in the calorimeter is stirred slowly. The reaction is allowed to proceed until a change in water temperature of 1 to 2 C° is observed. The

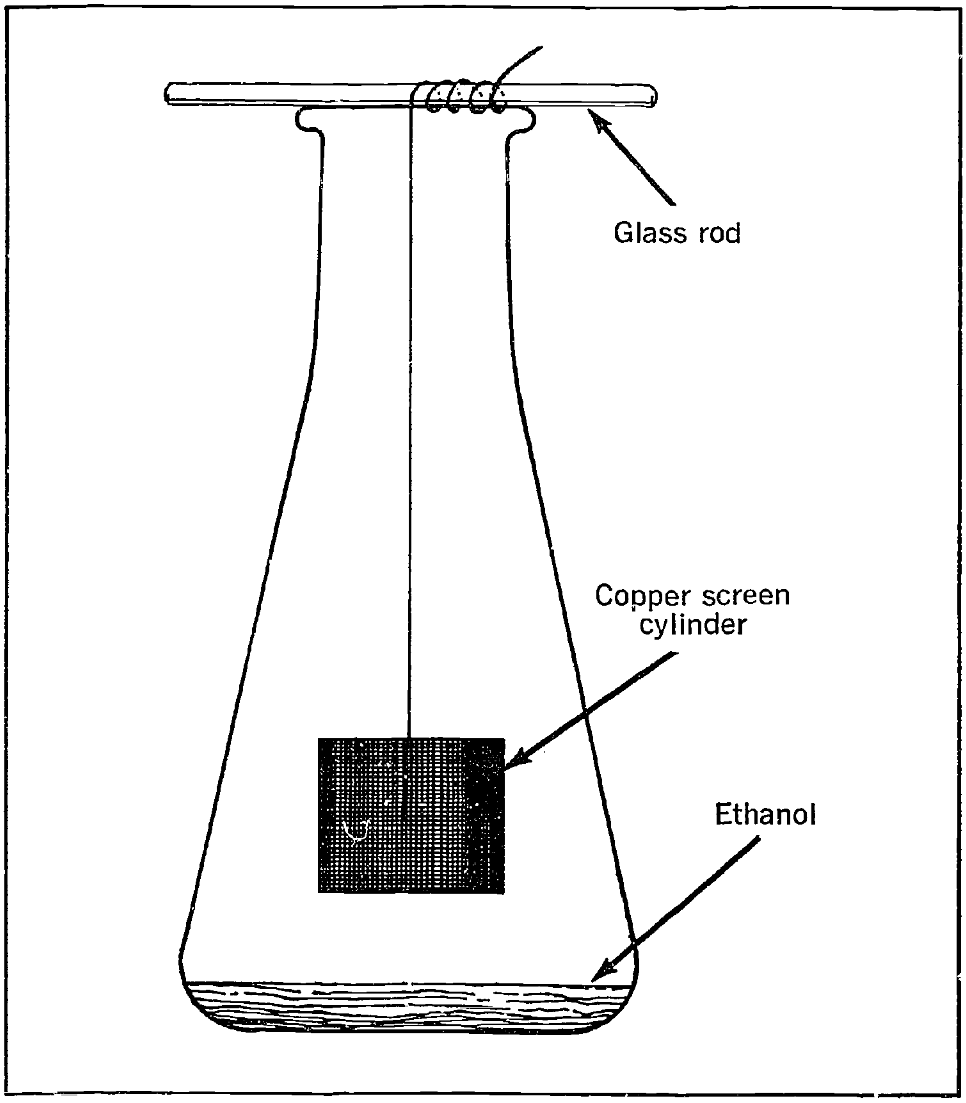


FIGURE 3–7. *Copper-screen catalyst and reaction vessel. Ethanol is catalytically oxidized on the hot copper screen.*

copper screen is removed and the flask is weighed again to determine the amount of alcohol that reacted. Assuming that the only products of the reaction are carbon dioxide and water, one divides the heat absorbed by the water in the calorimeter by the number of moles of ethanol consumed to obtain a very rough value of the heat released in the reaction:

$$C_2H_5OH + 3O_2 \xrightarrow[\text{cat}]{\text{Cu}} 2CO_2 + 3H_2O$$

The experimentally determined value can be compared with the ΔH calculated from tabulated enthalpies or directly with the tabulated heat of combustion for ethanol, −327 kcal/mole.

EFFECT OF TEMPERATURE AND MOLECULAR WEIGHT ON SPECIFIC IMPULSE

The performance of rocket propellants is rated in terms of specific impulse. Their performance increases with increase in specific impulse, which in turn is directly proportional to the square root of the ratio of the temperature in the combustion chamber T_c to the average molecular mass of the gases in the chamber m. (See Equation (3–7).) Direct calculation of specific impulse requires rather detailed information about fuels and oxidants and is facilitated by high-speed calculating machines. However, there is another quantity—the speed of sound in gases—that depends on T/m and that can be studied in a qualitative manner. The speed of sound in gases is approximately equal to $\sqrt{\gamma T/m}$, where γ is the ratio of the heat capacity of the gas at constant pressure to that at constant volume. In the experiments described, the values of γ are sufficiently similar for various mixtures of gases to consider the speed of sound as being dependent only on the value of T/m. The speed of sound in this experiment is determined qualitatively by listening to the pitch of notes produced by singing tubes.

Two similar setups are made by clamping large diameter tubes in ringstands as depicted in Figure 3–8. Two gas jets are formed by heating the ends of approximately 5-in. lengths of 6-mm glass tubing until only a small hole remains. Rubber tubing is attached to the 6-mm tubes and to sources of a single gas such as methane. The gas pressure is adjusted and the gas issuing from the jets is ignited so that a *very* small flame (about 2 mm high) burns on each tube. Then the tubes are clamped into the lower ends of two glass or metal tubes of nearly the same size (1 to 5 cm by 30 to 60 cm). The positions of the flames are adjusted to produce a singing sound. Considerable patience may be needed in sustaining a loud sound, but the small flames are quite stable if the jet is withdrawn slightly from the position producing maximum

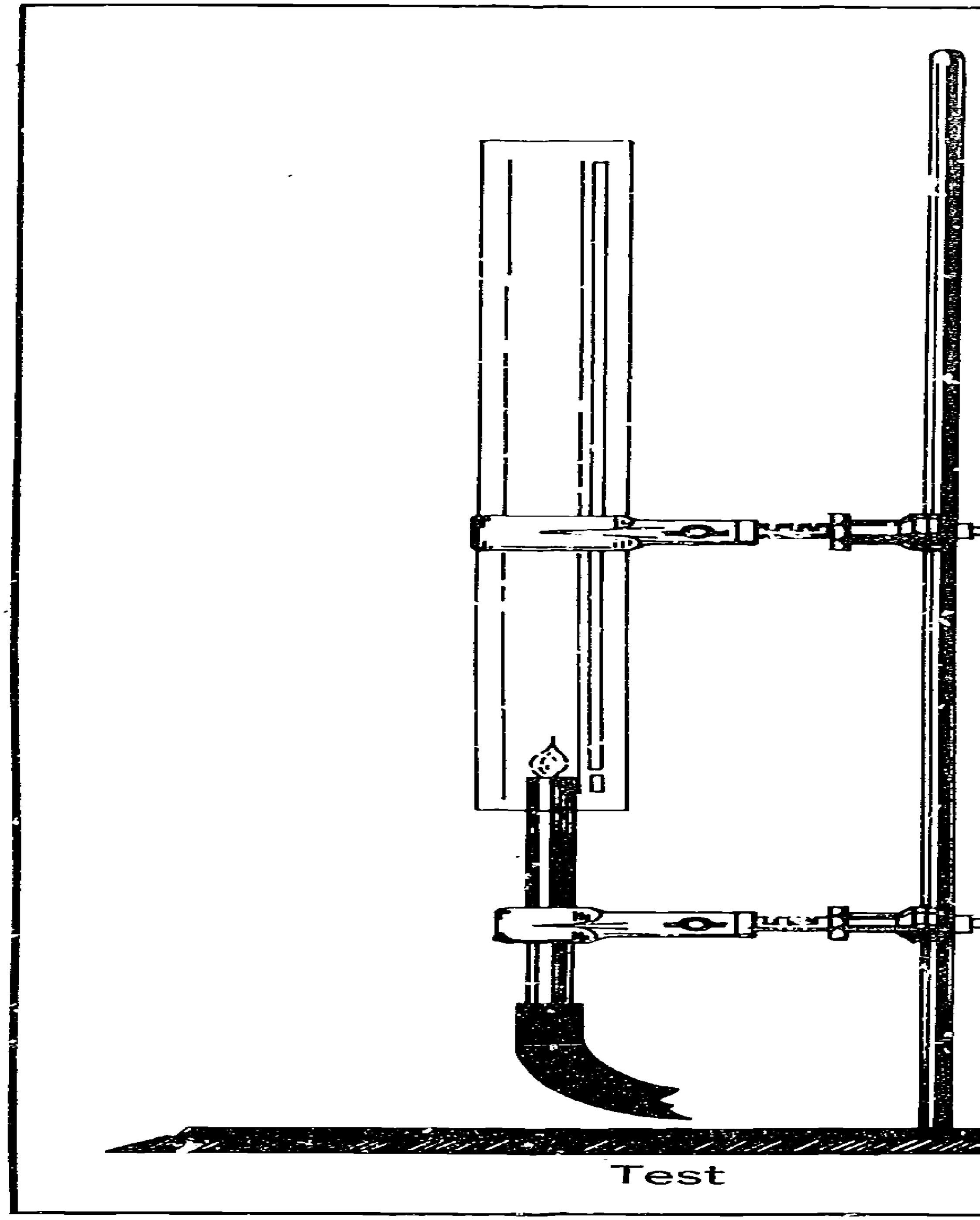
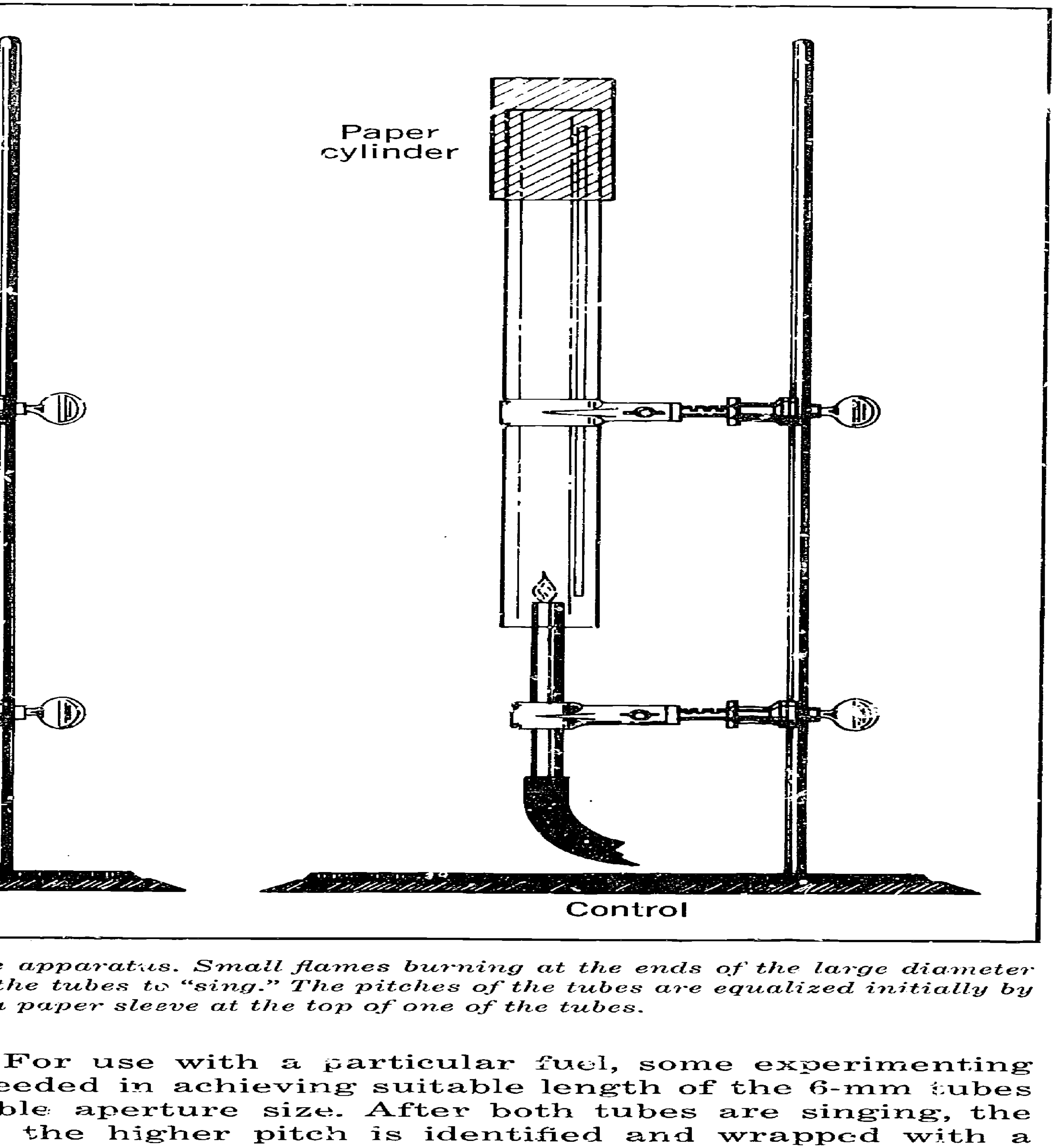


FIGURE 3–8. *Singing tube a*
tubes cause th
positioning a p

loudness. F
may be nee
and suitabl
tube with
cylinder of



apparatus. Small flames burning at the ends of the large diameter
the tubes to "sing." The pitches of the tubes are equalized initially by
paper sleeve at the top of one of the tubes.

For use with a particular fuel, some experimenting
eeded in achieving suitable length of the 6-mm tubes
ble aperture size. After both tubes are singing, the
the higher pitch is identified and wrapped with a
f paper held in place with a rubberband. By sliding

the paper cylinder beyond the end of the tube, the frequency is changed and thus the pitch can be adjusted to be the same as that of the second tube. In the experiment the pitch of the singing tube with the paper cylinder is used as a reference and the pitch of the second tube is varied.

With the control tube singing at the reference frequency, the T/m value in the second tube can be altered by warming the tube with a bunsen burner or by burning other fuels having different heats of combustion and different average molecular weights of the products. Because the second tube retains its length and thus its fundamental frequency, changes produced in its pitch are directly proportional to changes in the velocity of sound and the value of $\sqrt{T/m}$. Pairs of fuels, such as C_3H_8/CH_4 or H_2S/H_2, permit testing of relative values of T/m based on calculated heats of combustion and the molecular weights of the products of the reaction.

To make more valid inferences to the relative ΔH values of two fuels, the flowrates of the gases through the jets should be equalized eudiometrically; that is, by bubbling the gases into graduated tubes initially filled with water or some appropriate liquid so that the volumes of gas delivered per unit time can be measured and equalized. Equalization of the volumes of the gases passing through the jets per unit of time eliminates ambiguities in the relative values of T/m that might arise because [illegible] ter rate of consumption of fuel. Higher pitches thus [illegible] oted for the higher performance fuels; that is, those [illegible] er heats of combustion and/or those giving lower molec- [illegible] weight products.

THERMOCHEMICAL CALCULATIONS

Accurate measurement of the heats released in typical combustion processes requires special apparatus (such as a bomb calorimeter) and involves highly exothermic chemical reactions that are inherently dangerous. If appropriate thermodynamic data are available, however, one can perform *Gedanken*, or thought experiments, in which the heats of particular reactions can be estimated.

Heat of Reaction

In the conventional manner, the change in enthalpy or heat content ΔH can be calculated for an isothermal reaction of an oxidant such as O_2, F_2, or Cl_2 with fuels such as N_2H_4 or H_2. For instance, for the reaction

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) \rightarrow H_2O\ (g)$$
$$\Delta H^\circ_{298} = H_{H_2O} - \tfrac{1}{2}H_{O_2} - H_{H_2} = -57.58 \text{ kcal}$$

The enthalpies of elemental substances (in their standard states) are taken to be zero by convention. (Tabulated values for enthalpies are included in Appendix C.)

The change in enthalpy also can be found for the decomposition of a monopropellant such as hydrazine. Considering the reaction to be given by the equation

$$N_2H_4\ (l) \xrightarrow{cat} N_2\ (g) + 2H_2\ (g)$$

then

$$\Delta H^\circ_{298} = H_{N_2} + 2H_{H_2} - H_{N_2H_4} = -12.05 \text{ kcal}$$

In any case, a balanced stoichiometric equation is requisite to the calculation of a value for ΔH from tabulated values of enthalpies. However, the thermodynamic principles involved can be illustrated even with balanced equations that involve only predicted products occurring in estimated amounts. For instance, if we predict

$$3N_2H_4\ (l) + N_2O_4\ (g) \rightarrow 4N_2\ (g) + 4H_2O\ (l) + 2H_2\ (g)$$

then

$$\begin{aligned}\Delta H^\circ_{298} &= 4H_{N_2} + 4H_{H_2O} + 2H_{H_2} - 3H_{N_2H_4} - H_{N_2O_4}\\ &= 4(0) + 4(-68.32) + 2(0) - 3(12.05) - (2.31)\\ &= -311.74 \text{ kcal}\end{aligned}$$

Thermodynamic data generally are available in the range from zero to several hundred degrees Celsius only, and not at the temperatures found in combustion chambers. Without additional information, therefore, one can only state that according to Le Chatelier's principle, the ΔH of typical combustion reactions would be smaller at higher temperatures. The ΔH values of highly exothermic reactions are likely to have negative values for equilibrium mixtures of the reactants and products. According to Le Chatelier's principle, therefore, high temperatures would favor the formation of the reactants and would reduce the extent of the reaction.

Other Factors Affecting the Heat Released in Combustion Processes

Several other factors affect the total amount of heat available for accelerating the propellant in a chemical rocket. For instance, the heat consumed in warming and subliming or vaporizing solid or liquid reactants would reduce the amount of energy available to accelerate the propellant. Heats of sublimation and vaporization along with heat capacity data can be used to predict this effect. In addition, at high temperatures, considerable dissociation of the gaseous products occurs with a further decrease in the heat that would be released if the products were cooled. A chemical equation describing a typical combustion process occurring in a combustion chamber would include high-temperature products such as CO and the free radicals H and OH. Actual combustion processes in rocket engines are further complicated by the fact that the fuel and oxidant are not mixed in stoichiometric amounts. Calculation of the ΔH of the H_2/O_2 reaction mentioned previously in the text is as follows:

$$4H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (g) + 2H_2\ (g)$$

where for simplicity the products are taken to be those that are stable at room temperature. For this reaction

$$\Delta H^\circ_{298} = 2H_{H_2O} + 2H_{H_2} - 4H_{H_2} - H_{O_2} = -115.60 \text{ kcal}$$

It is seen that the ΔH per mole of fuel consumed (−28.90 kcal) is just one-half that calculated for reaction of stoichiometric amounts of H_2 and O_2. Nevertheless, the flame stability and specific impulse of the fuel-rich mixture are superior to the stoichiometric mixture. The *Gedanken* experimenter can be inventive in selecting potential reactants and in predicting products and still illustrate some of the typical problems confronting rocket thermodynamicists.

Heat of Reaction Per Unit Weight of Product Formed

The ΔH values of the several combustion reactions can be compared per mole of fuel consumed or product formed. Because of the importance of the mass of the propellant (Equation (3–3)), it is more informative to calculate the ΔH per unit of mass of the reactants. For instance, the ΔH for the reaction $2B\,(s) + 3/2\, O_2(g) \rightarrow B_2O_3(s)$ is −302.0 kcal, and 69.62 g of oxide is produced. The ΔH per pound of oxide formed is −302.0 kcal × (453.6 g/lb)/69.62 g or −1968 kcal/lb. This value can be compared to that found in Figure 3–5, if it is noted that there are 3.968 B[illegible]lorie. The small amounts of dissociated molecule[illegible] exist at the high temperatures of exhaust gases are difficult to include in such comparisons, and it is suggested that the *Gedanken* experimenter write chemical equations for products that are stable at room temperature.

Potential rocket propellants also are compared on the basis of specific gravity. Low specific gravity fuels such as H_2 require greater amounts of tankage than higher specific gravity fuels such as ammonia, and the additional mass provides an added weight penalty.

The Periodicity of Heat of Reaction

For a fuel/oxidant pair to be of potential use in rocketry, the combustion reaction must release large amounts of energy. Because chemical reactions involve primarily outer electrons in atoms, one might correctly anticipate that the heat of combustion of elements varies periodically with atomic number. Selected enthalpy data are available for a variety of binary oxides, fluorides, and chlorides (Appendix C) and can be used to plot the ΔH of the combustion of elements with one of these oxidants versus atomic number. The periodicity of ΔH and the overall decrease of ΔH with increasing atomic number is noted. From the point of view of rocketry, a more informative plot results by considering the mass of the reactants (Figure 3–5).

LITERATURE CITED

1. Kuentz, C. 1964. Understanding rockets and their propulsion, Chapters 1–4. Rider Publishing, Inc., New York.

*2. National Aeronautics and Space Administration. 1969. Propulsion for deep space. NASA EP–41. NASA Lewis Research Center.

*3. Rothrock, A. M. 1961. Spacecraft propulsion, pp. 333–339. *In* L. Broglio, Current research in astronautical sciences, Vol. 6. Pergamon Press, New York.

4. Jaukovic, D. 1964. Solid rocket propellants (transl.), p. 5a. Foreign Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. NTIS N65–14027#.

*5. Hunter, M. W. 1966. Thrust into space, p. 40. Holt Rinehart & Winston, Inc., New York.

6. Burrows, M. C. 1967. Exploring in aerospace rocketry, Chapter 4. NASA Lewis Research Center. NTIS N68–19840#.

7. National Aeronautics and Space Administration. 1962. Chemical rocket propulsion, p. 45. NASA SP–19. GPO, $0.40. NTIS N63–11509#.

8. Rattin, E. J. 1965. Rocket propulsion, p. 258. *In* J. C. Meitner, Astronautics for science teachers. John Wiley & Sons, Inc., New York.

9. National Aeronautics and Space Administration. 1965. Chemical propellant performance. Educational Brief 3001. NASA Manned Spacecraft Center.

**Recommended general source of information.*

OTHER REFERENCES

Brokaw, R. S., F. E. Belles, B. J. Clark, and F. J. Zeleznik. 1966. Combustion, Section I. *In* Conference on selected technology for the petroleum industry. NASA SP-5053. GPO, $1.25.

Lange, O. H., and R. J. Stein. 1966. Space carrier vehicles: design, development, and testing of launching rockets, Chapter 6. *In* F. I. Ordway, Advances in space science and technology, Supplement 1. Academic Press, Inc., New York.

National Aeronautics and Space Administration. 1966. Space: the new frontier. Revised edition, Chapters 8 and 10. NASA EP-6. GPO, $0.50.

FILMS

Basics of propulsion. 1965. 15 min, sound, color. Aerojet-General Corp., P.O. Box 3925, Glendale, Calif. 91201.

Saturn propulsion systems. 1962. 15 min, sound, color. NASA Marshall Space Flight Center.

Two-dimensional grain design for solid rocket motors. 1962. 18 min, sound, color. Aerojet-General Corp., P.O. Box 3925, Glendale, Calif. 91201.

Spacecraft propulsion and power. 1966. 30 min, sound, color. NASA Manned Spacecraft Center.

Solid propellant rocketry. 12 min, sound, color. Thiokol Chemical Corp., Rocket Operations Center, 3340 Airport Road, Ogden, Utah 84403.

Visualization studies of combustion instability in a hydrogen-oxygen model combustor. 1963. 14 min, sound, color. NASA Lewis Research Center.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70-12345#).

unit 4

unit 4

ELECTROCHEMICAL CELLS FOR SPACE POWER

Topics that may be enriched by use of this unit:

Galvanic cells
Batteries
Fuel cells
Oxidation and reduction
Electromotive series

Man makes varied and extensive use of electrical energy to operate and control the multitude of systems aboard space vehicles. These systems include cameras, telescopes, data recorders, propulsion devices, clocks, radios, directional antennas, temperature sensors, telemetry devices, and many, many others (1). To meet the need for electrical power, space scientists are designing and fabricating converters that can change nuclear, solar, and chemical energies into electrical energy.

Nuclear fuels will be used in space to produce large amounts of electricity over long periods of time. These fu[illegible] consumed in reactors [illegible] generated heat will be absorbed by a liquid, such as mercury or potassium, which is then changed into a superheated vapor. This vapor, on expanding and cooling, will drive fans or turbines that, in turn, will drive electric generators. Although large amounts of electricity can be produced in this manner, nuclear-power systems have inherently large masses and present a radiation hazard. The radiation will not only be a hazard on manned missions but also on unmanned missions because radiation would degrade materials in the space vehicles. These hazards can be reduced sufficiently by shielding the reactor from the remaining components of a space vehicle but the use of such massive shielding would provide a prohibitive weight penalty for most missions. At the present time, therefore, electrical energy is provided in space through conversion of solar and chemical energies into electrical power. Our discussion will be limited to chemical batteries.

ELECTROCHEMICAL CELLS

Chemical batteries are used extensively in space missions because of their inherent convenience and high efficiency The efficiency of conversion of chemical energy directly into electrical energy is commonly 70 percent or more depending on the constituents of the cell and the conditions of current draw. (The efficiency of an electric cell is sometimes considered as $(\Delta G/\Delta H) \times 100$, where ΔG is the maximum electrical energy available from the cell and ΔH is the amount of heat released if the reactants were simply mixed.) A second advantage of electrochemical cells is that some chemical reactions that occur at negligible rates when the reactants are simply mixed occur rapidly in cells. This fact extends the choice of potential cell constituents. For instance, the rate of the highly exothermic, gas-phase reaction of hydrogen and oxygen is effectively zero at room temperature, even in the presence of a catalyst. That is, the activation energy of the hydrogen/oxygen reaction under these conditions is too high for the reaction to occur at a noticeable rate. Nevertheless, hydrogen and oxygen react rapidly in appropriately constructed electrochemical cells. The increased rate of reaction primarily results from first adsorbing the hydrogen and oxygen gases on the electrodes of the cell. Oxidation or reduction of the adsorbed atoms yields hydrogen ions and hydroxyl ions, which rapidly combine in the electrolyte. In both the gas-phase and cell reactions the product is water; but the activation energy for the cell reaction is much smaller, and consequently the rate of the reaction is much faster.

A wide variety of substances can be used in the construction of practical electrochemical cells (2). (Theoretically, any spontaneous reaction can be used to produce a flow of electrical current.) Some cell constituents are evident from the names of the cells, such as lead storage, silver/zinc, and mercury batteries. Commonly, cell electrolytes are aqueous solutions or pastes made of solids mixed with water. Because many high-energy-density substances (i.e., substances common to chemical reactions in which relatively large amounts of energy are released) of potential interest for constructing cells react with water, extensive research is underway at laboratories such as NASA Lewis Research Center to find suitable cell constituents using nonaqueous electrolytes.

Almost every space vehicle launched has made use of batteries to store and help supply the electrical power for instrumentation, telemetry, communications, and onboard housekeeping. The Alouette, Explorer, Gemini, Mariner, and Ranger satellites, to name a few, all used silver/cadmium or nickel/cadmium batteries. In Table 4–1 some of the characteristics of these two cells are contrasted with those of silver/zinc batteries that potentially offer higher energy densities but have other problems (3).

TABLE 4-1

SOME CHARACTERISTICS OF 3 CONVENTIONAL BATTERIES WITH EXTENSIVE AEROSPACE APPLICATION OR POTENTIAL

System	Primary Battery			Secondary Battery	
	Power Density, W-hr/lb			Actual Power Density, W-hr/lb	Shallow Discharge Life, cycles
	Theory	Actual	Expected Maximum		
$AgO \mid KOH \mid Zn$	193	80	95	40	80–100
$AgO \mid KOH \mid Cd$	118	33	40	30	2000–3000
$NiOOH \mid KOH \mid Cd$	99	17	20	7–10	1000–11,000

Secondary cells differ from primary cells in that the former are rechargeable.

Although the amount of electrical power a battery can deliver is an important consideration for its use in space, other factors must also be considered. These include the cell's weight, volume, operating temperature, efficiency, and need for maintenance. In addition, it is important that a cell be able to operate in many positions, under zero gravity, and possibly in a vacuum. If a cell is to be recharged in its normal use, the number of recharge cycles it can undergo and the recharging time are also significant. (See Table 4–1.)

The electrical needs of some spacecraft are served by both solar cells and electrochemical cells. Before the solar cells are deployed, when the spacecraft is in the dark, or during peak loads, batteries supply the electrical energy. Solar cells can supply electrical energy when the spacecraft is in direct sunlight, and they recharge the secondary electrochemical cells. Especially large numbers of these cycles occur in communications, weather, and Orbiting Geophysical Observatories (OGO's) as they orbit the Earth. For missions that involve interplanetary travel, combinations of solar cells and electrochemical cells also are used. For instance, 792 solar cells having an area of about 9 ft^2 maintained the charge of the silver/zinc batteries on board the Surveyor 1 spacecraft and supplied 85 W during the cislunar phase of the mission and on the lunar surface (4).

HIGH- AND LOW-TEMPERATURE ELECTROCHEMICAL CELLS

Because man is exploring and inhabiting hot and cold regions on Earth and in space, there is increased interest in batteries that can operate at temperatures beyond the liquid range of the aqueous electrolytes found in most electrochemical cells. Cells capable of delivering electrical current at temperatures near 500° C are being studied by several private companies and Government laboratories that are providing the hardware for solar probes and missions such as landings on Venus. Presently, these cells are constructed with alkaline earth metal anodes and heavy metal oxide or halide cathodes submerged in a molten mixture of alkali metal halides or carbonates (5, 6). For example, one of these experimental cells, shown diagramatically in Figure 4–1, is composed of electrodes of magnesium metal and mixed copper oxides placed in a molten mixture of lithium and potassium chlorides. The container, made of pure copper or nickel, does not react significantly with the molten electrolyte.

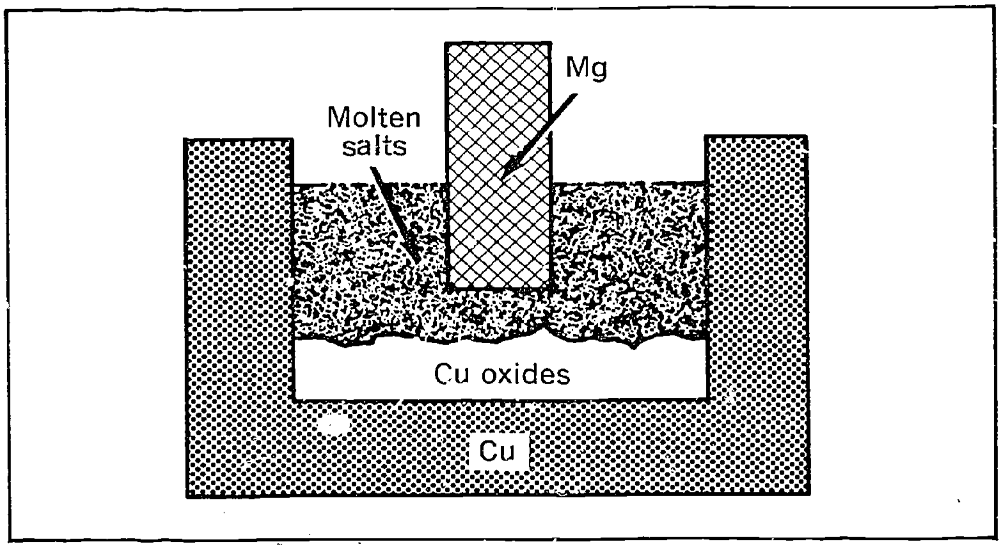


FIGURE 4–1. *Components of an experimental high-temperature cell. During operation of the cell the magnesium anode is oxidized, and the magnesium precipitates as magnesium oxide. The mixture of copper oxides is reduced liberating copper metal and oxide ions.*

When the cell is delivering a current, the metal atoms of the magnesium anode are oxidized to the +2 oxidation state, liberating electrons. The electrons pass through the external electrical circuit to the cathode and reduce the copper oxides, yielding copper metal. The oxide and magnesium ions combine in the electrolyte to give magnesium oxide, which is sparingly soluble in the molten salts and thus precipitates. Although the electrodes and electrolyte of discharged cells have been analyzed, the detailed nature of the reaction is not known. The open-circuit voltage of this cell is 1.55 V, 0.5 V less than predicted by calculations. Because of their short life after the electrolyte is melted, these cells are stored at low temperatures. When a high-temperature cell is to be placed in use, it can be activated by a pyrotechnic device ignited with an electric match (Figure 4–2).

Batteries that can operate at low temperatures, such as those temperatures found on the Moon and on Mars, must also use

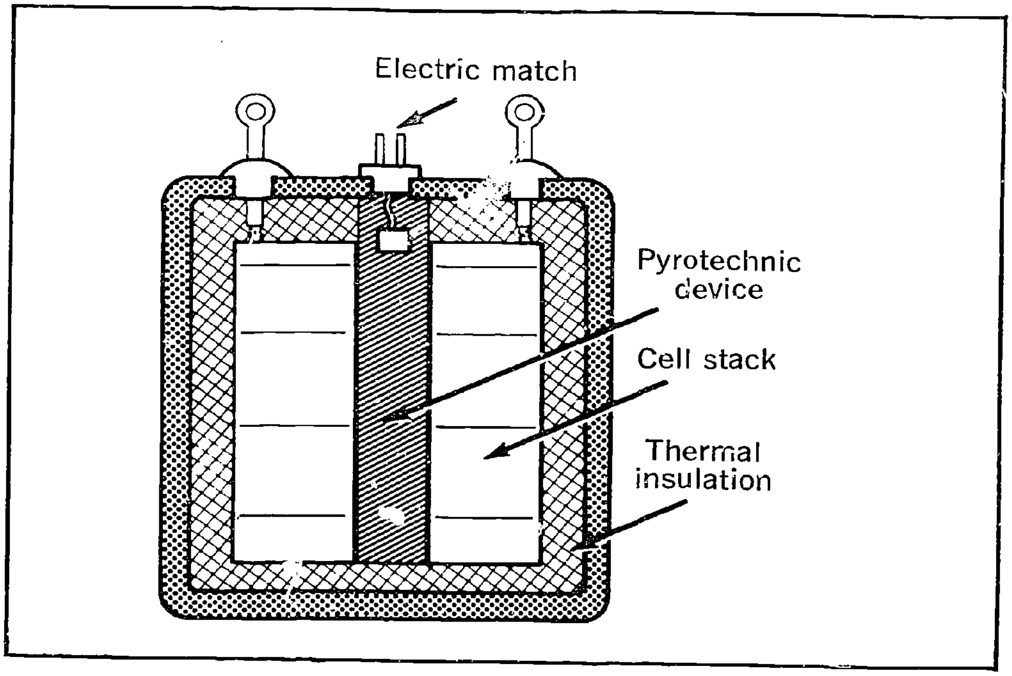


FIGURE 4–2. *Diagram of a typical high-temperature battery; service life, 5 min; operating temperature, 430° C. Similar cells may be used in the high-temperature environments of Mercury and Venus.*

nonaqueous systems. To supply electrical current at low temperatures, electrochemical cells constructed of a magnesium anode and a mercury(II) sulfate, sulfur, or silver chloride cathode with an ammonia solution as the electrolyte have been developed under a NASA Lewis Research Center contract. An electrolyte composed of a 34-percent solution of potassium thiocyanate in ammonia permits operation of the cell in the neighborhood of −50° C (6). (See Figure 4–3.) This cell can be activated at the appropriate time during a mission by puncturing the reservoir of liquid ammonia thus bringing the electrolyte in contact with the electrodes.

FUEL CELLS

The electrochemical cells discussed thus far have the property of going "dead" in use. During the production of electrical current, the composition of the electrolyte changes, and one or both of the electrodes are consumed. Other electrochemical cells, called fuel cells, are characterized by the constant addition of reactants and the removal of products during cell operation (7, 8, 9). Thus, the composition of the electrolyte remains unchanged. As in the case of primary and secondary batteries, fuel cells are important sources of power because of their efficiency in converting chemical energy directly into electrical energy. Furthermore, many potential reactants for fuel cells

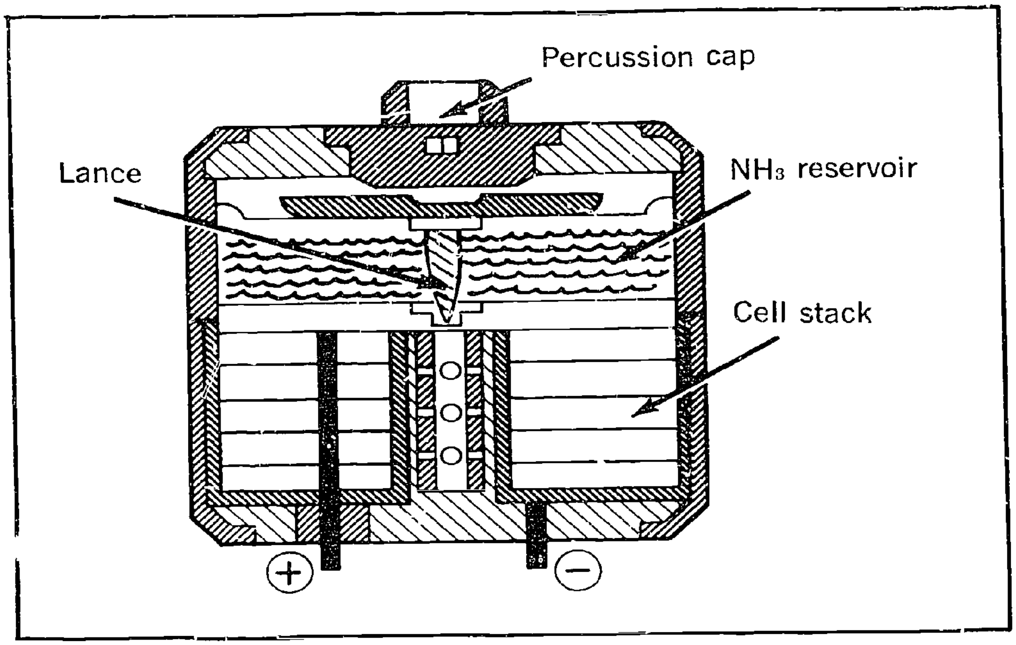


FIGURE 4–3. *Diagram of a typical low-temperature battery; service life, 36 hr; operating range, −54° to 72° C.*

are important rocket propellants; thus the technology of their storage and manipulation are familiar to rocket scientists.

The Gemini space vehicle was the first space vehicle to use fuel cells as a primary source of electrical energy. Each of its two cylindrical fuel-cell batteries measured 25 in. long by 12.5 in. in diameter, weighed 68 lb, and contained 96 cells connected in series (6, p. 23; 10). Each fuel cell produced 1 kW at peak load and 1 pint of water per kilowatt-hour of operation. Fuel cells with power capacities of 2 or 3 kW for 10 to 14 days are components of the service module of the Apollo spacecraft. Hydrogen and oxygen gases are the reactants in the fuel cells for both the Gemini and Apollo missions. Although these gases are difficult to store, easily storable substances such as N_2H_4 and N_2O_4 are potential sources of these reactants.

The simplicity of a hydrogen/oxygen fuel cell is evidenced by Figure 4–4. During operation, gaseous hydrogen and oxygen are fed to porous electrodes through which they diffuse. The gases come in contact with the electrolyte at the inner surface of the electrodes. The porous, wetproof electrodes are designed so that the gases do not bubble into the electrolyte and the electrolyte does not flood the gas compartments. The electrodes often are made of carbon, a substance that conducts electricity and that can be produced with uniform pore size. When the fuel cell is delivering an electric current, the hydrogen and oxygen gases

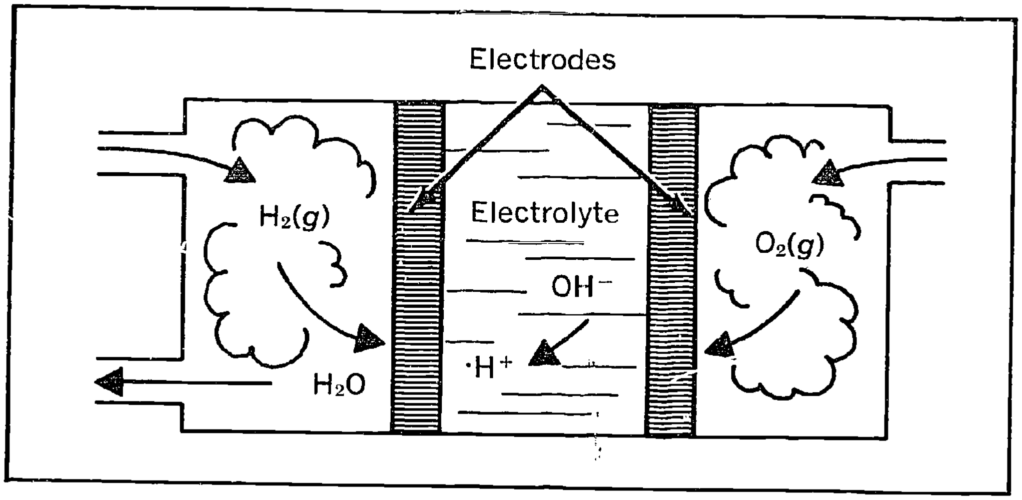


FIGURE 4–4. *Diagram of a typical hydrogen/oxygen fuel cell. Hydrogen and oxygen gases diffuse from their compartments through porous electrodes into contact with the electrolyte where they react. The resulting water escapes as steam.*

are fed continuously into the cell. At the cathode, the gaseous oxygen is reduced to the −2 oxidation state. It combines with the alkaline electrolyte and is transported rapidly as OH^- to the anode. At the anode, hydrogen gas is oxidized to hydrogen ions giving up electrons that pass through the external circuit to the cathode. The anode is impregnated with platinum, which acts as a catalyst and increases the oxidation rate of hydrogen by a factor of 10^3 to 10^6. The hydrogen ions rapidly combine with hydroxide ions to form water, which is removed continuously from the cell along with the heat liberated from the cell reaction. Both of these byproducts are potentially useful. For instance, the water can be purified and used for washing or drinking by an astronaut. In addition, the water can be electrolyzed by another source of electricity to regenerate the reactants of the fuel-cell reaction. For example, a nuclear-power station placed on the Moon could regenerate these fuel-cell reactants for space vehicles landing there. By careful design, the fuel cell itself can be used as the electrolytic cell in a regenerative fuel-cell system.

Although almost any oxidizable substance is a potential fuel for fuel cells, there are several considerations other than cost in choosing the reactants, as well as in choosing the electrodes and the design of these cells. These considerations are relevant to electrochemical cells in general. For instance, if relatively large currents are to be drawn at reasonable voltages, the reactants must combine rapidly in the cell without a large decrease in the open-circuit voltage. If migration of the reactants or products in the electrolyte and reactions at the electrodes are slow for any of a variety of reasons, the current delivered by the cell will be small relative to its weight. At the present time, most fuel cells are designed to consume hydrogen and oxygen gases because aqueous half cells involving these gases have been studied extensively and improved. Another reason for their extensive use is that hydrogen and hydroxide ions are many times more mobile than other ions, thus larger current densities can be obtained. Also, considerable energy is available from the hydrogen/oxygen reaction, and the product, water, is easily stored or regenerated into the reactants.

Fuel cells that can operate at higher temperatures than those having aqueous electrolytes are also being studied (11). For instance, a hydrogen/oxygen fuel cell has been constructed of a ceramic electrolyte and porous-platinum electrodes to operate at temperatures of about 1000° C. The ceramic is a mixture of zirconium(IV) oxide and calcium or yttrium(III) oxide, molded in a tubular form and coated inside and outside with a porous layer of platinum (Figure 4-5). The length of the tube is adjusted so that, considering the pressures of the gases and temperature of operation, most of the hydrogen passing through the tube is converted to water. During delivery of electrical current, molecules of oxygen, on combining with electrons at the surface of the cathode, are reduced to O^{2-} ions. The O^{2-} ions enter the crystal lattice of the ceramic and rapidly migrate to the anode where they react with adsorbed hydrogen, yielding water and liberating electrons.

As a result of the research by companies such as Allis-Chalmers, Pratt & Whitney, and General Electric, and by Government laboratories such as NASA Lewis Research Center, technology has developed to a level where tractors, cars, and space systems are now powered by fuel cells. Additional technological advances are needed, however, before fuel-cell batteries become competitive (on an economical basis) with other energy converters. In view of present rapid progress this could occur in the next few years.

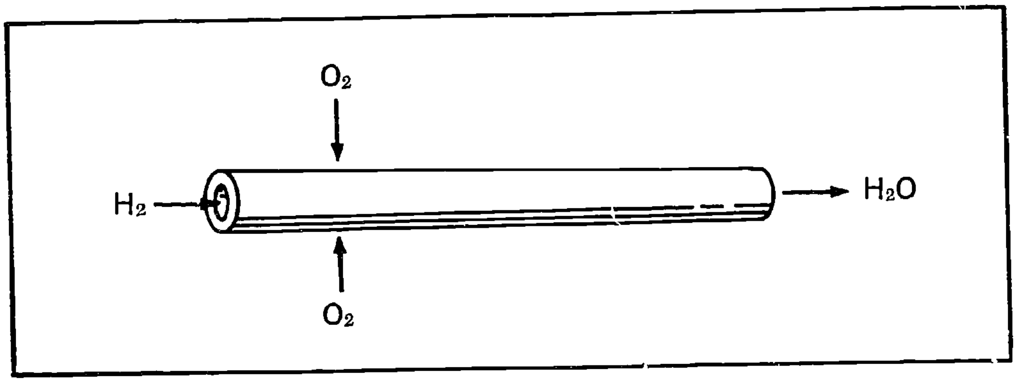


FIGURE 4-5. *High-temperature hydrogen/oxygen fuel cell. Use of a ceramic electrolyte allows operation of the cell at high temperatures.*

ACTIVITIES

HIGH-TEMPERATURE CELL

Exploration of space brings us in contact with environments of higher and lower temperatures than are found on the Earth's surface. NASA researchers and contractors are developing batteries that can supply our needs for electrical current over a wide range of temperatures. As a student activity, a cell that is capable of operating at 500° C can be constructed of a magnesium anode, a copper(II) oxide cathode, and an electrolyte composed of a mixture of alkali metal halides such as LiCl and KCl. (See Figure 4–1.)

About 5 [illegible] of copper(II) oxide is placed in the bottom of a copper dish. The dish can be made from a thin sheet of copper or can be obtained in the form of a 1- to 2-in. copper cap from a store selling plumbing supplies. The oxide is covered by a 30-g mixture of about equal weights of dry potassium and lithium chlorides. The dish is placed on a wire gauze over a bunsen burner, as shown in Figure 4–6. A wire gauze with an asbestos center

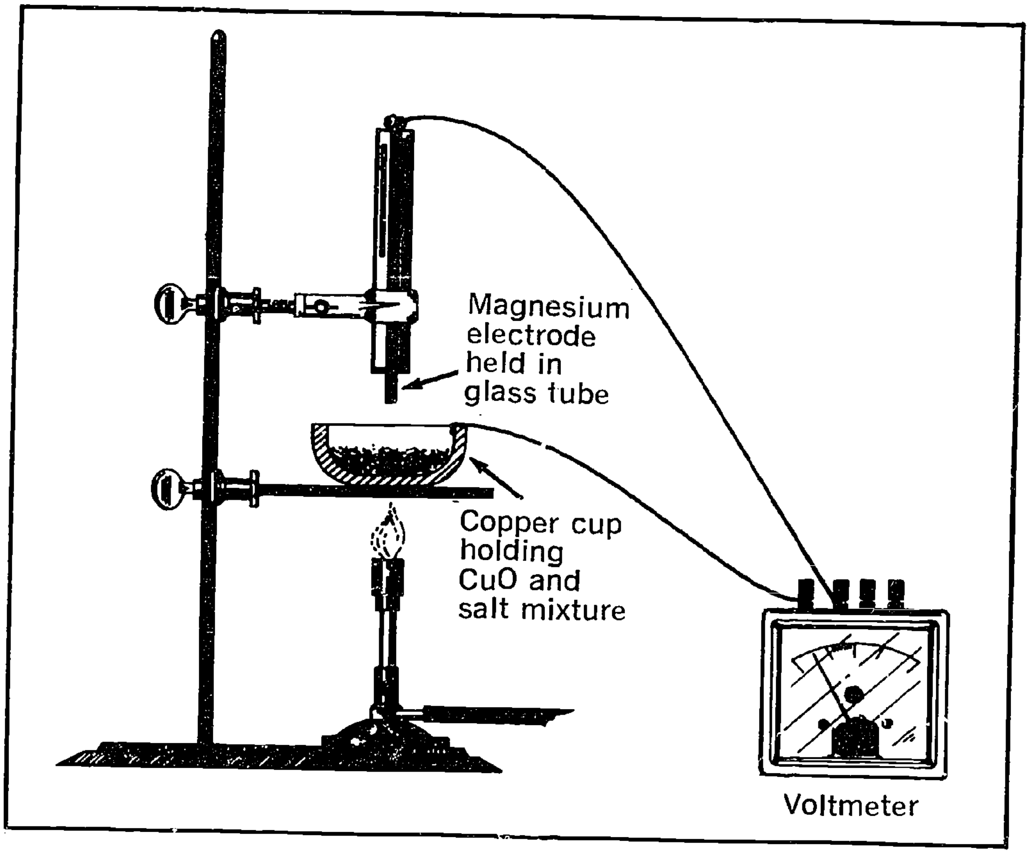


FIGURE 4–6. *Experimental setup of the high-temperature cell. During operation of the cell, the magnesium anode is fed through a glass tube into the copper cup containing CuO covered with a molten salt mixture.*

can be used if one wishes to electrically insulate the dish from the ringstand. The magnesium anode can be formed by folding several thicknesses of magnesium ribbon and twisting the strands together. An electrical lead is attached to one end of the anode, passed through a glass tube, and connected to a load (e.g., a 1.5-V electric light bulb) or voltmeter. The magnesium anode is pressed into the tube. The glass tube is held by a buret clamp so that the magnesium anode is suspended above the salt mixture. This anode assembly permits lowering the electrode as the metal is consumed. The electrical circuit is continued by attaching the second lead from the lamp or voltmeter to the ringstand or copper dish.

To place the cell in operation, the mixed-salt electrolyte is heated strongly until the salts fuse. (Water in the salts may cause some spattering of the electrolyte, and some minor popping might occur from water decomposition; safety glasses should be worn.) The anode is lowered into the molten electrolyte, completing the circuit.

LOW-TEMPERATURE CELL

The need for electrical power in low-temperature environments results in substituting conventional aqueous solution batteries with nonaqueous ones. A low-temperature cell using liquid ammonia as the solvent system can be constructed in this activity with a magnesium anode and a mercury(II) sulfate cathode. The electrolyte is an ammoniacal ammonium chloride solution. A working model of such a cell has an open-circuit voltage in the range of 1 to 2 V and delivers a current of less than 10 mA.

The ammonia generator is prepared by adding a mixture of 35 g of calcium oxide and 27 g of ammonium chloride to a 500-ml flask. The flask, drying tube, and low-temperature cell are arranged as shown in Figure 4–7.

The low-temperature cell is assembled by placing 5 g of mercury (II) sulfate or powdered sulfur in the bottom of a 200-mm test tube (Figure 4–8). The bare end of an *insulated* wire is submerged in the solid salt with the remainder of the wire extending over the lip of the test tube. The area of this electrode and the current delivered by the cell can be increased by attaching a circle of wire gauze to the buried end of the wire. Four g of ammonium chloride is added on top of the mercury(II) sulfate or sulfur.

The anode is formed by tightly coiling about 5 in. of an 8-in. piece of magnesium ribbon. The bare end of a second insulated wire is attached to the uncoiled portion of the ribbon. The magnesium

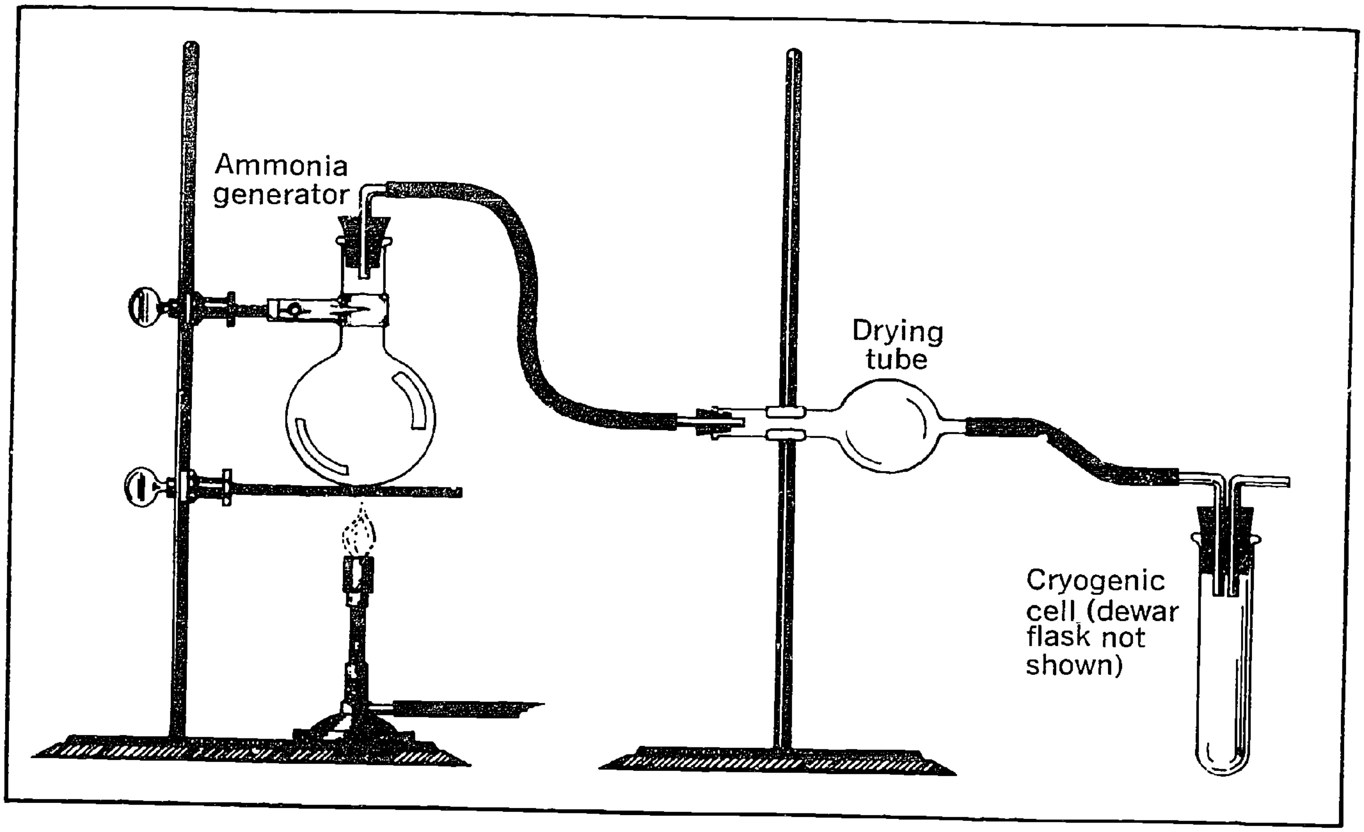


FIGURE 4–7. *Ammonia generator and cryogenic cell. Ammonia, the solvent in the low-temperature cell electrolyte, is produced from ammonium chloride, is dried by passing it through a bed of* $CaCl_2$*, and is condensed in the cryogenic cell.*

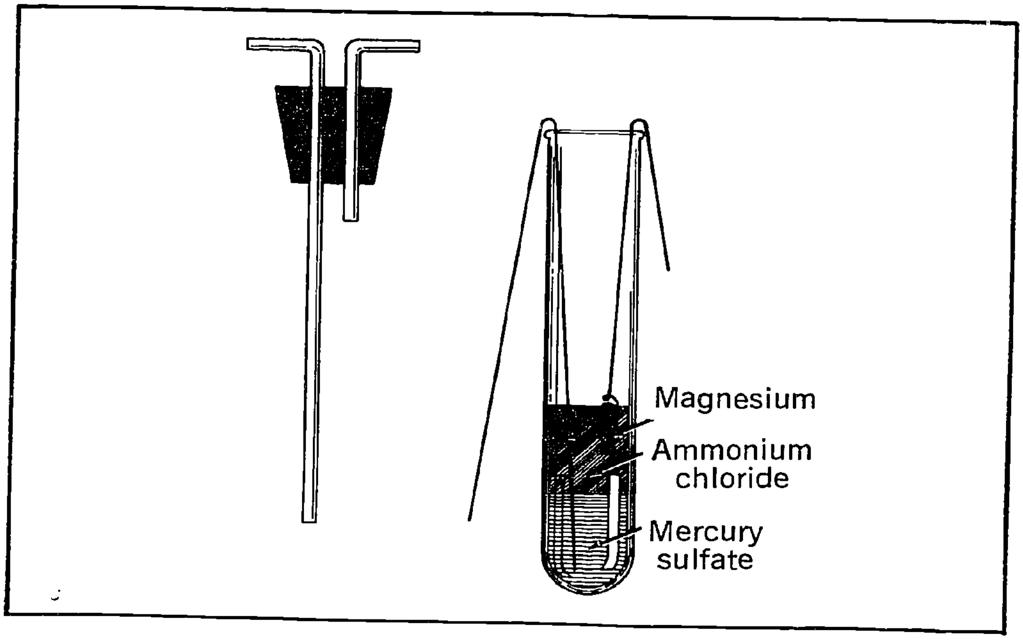


FIGURE 4–8. *Construction of the cryogenic cell. The magnesium anode is partially buried in the layer of ammonium chloride. An insulated wire passes through the ammonium chloride layer and makes contact with the layer of mercury sulfate.*

anode is inserted into the test tube so that it is partially buried in the solid ammonium chloride. The two electrical leads are crimped over the top of the test tube so insure that the electrodes remain at the proper height.

The rubber-stopper assembly (Figure 4–8) is then placed in the test tube. The longer tube should extend almost to the ammonium chloride layer, and its external end is attached to a piece (1 or 2 ft) of rubber tubing that in turn is connected to the drying tube of the ammonia generator. The test tube is placed in a freezing mixture of Dry Ice (CARE)[1] and acetone or ethyl alcohol in a Dewar flask or a beaker wrapped with paper towel. The electrical leads are connected to a dc voltmeter on a 2- to 3-V range. (CAUTION: The freezing mixture should be placed as far as possible from the generator because of the flammability of acetone.) The bunsen burner is then lighted, and the ammonia generator is heated strongly. As soon as sufficient ammonia condenses in the test tube to form an ammoniacal ammonium chloride solution, the cell will begin to operate and its voltage can be read.

HYDROGEN/OXYGEN FUEL CELL

Cells that maintain constant electrolyte composition by continuous intake of reactants and removal of products are called fuel cells. Cells of this type have been constructed for a variety of applications where lightweight and efficient sources of electrical power are needed and bulk fuels are available. The technology developed for storage and manipulation of rocket fuels makes the fuel cell an important potential source of electricity for missions in space. A demonstration model of this type of electrochemical cell can be constructed for many combinations of fuels and oxidants. This activity involves the construction of a simple hydrogen/oxygen fuel cell.

A 25- by 200-mm test tube from which the closed end has been removed can serve as the body of the cell (Figure 4–9). Two circular electrodes 25 mm in diameter are cut from copper screen. The efficiency of the cell is improved by platinizing the electrodes in a solution of platinic chloride for 10 to 15 min. Each electrode is attached to an electric wire about 5 in. in length. A "sandwich" is made of the electrodes by stacking six to eight disks of 25-mm-diameter filter paper between them. This stacking can be carried out conveniently in one end of the glass tube. The filter paper is saturated with concentrated KOH, and the electrodes are pressed together, thereby increasing the contact between the paper elements in the stack. The sandwich is then pushed to the center of the glass tube and is checked visually to see that no

---

[1] *Teacher should exercise care in this experiment.*

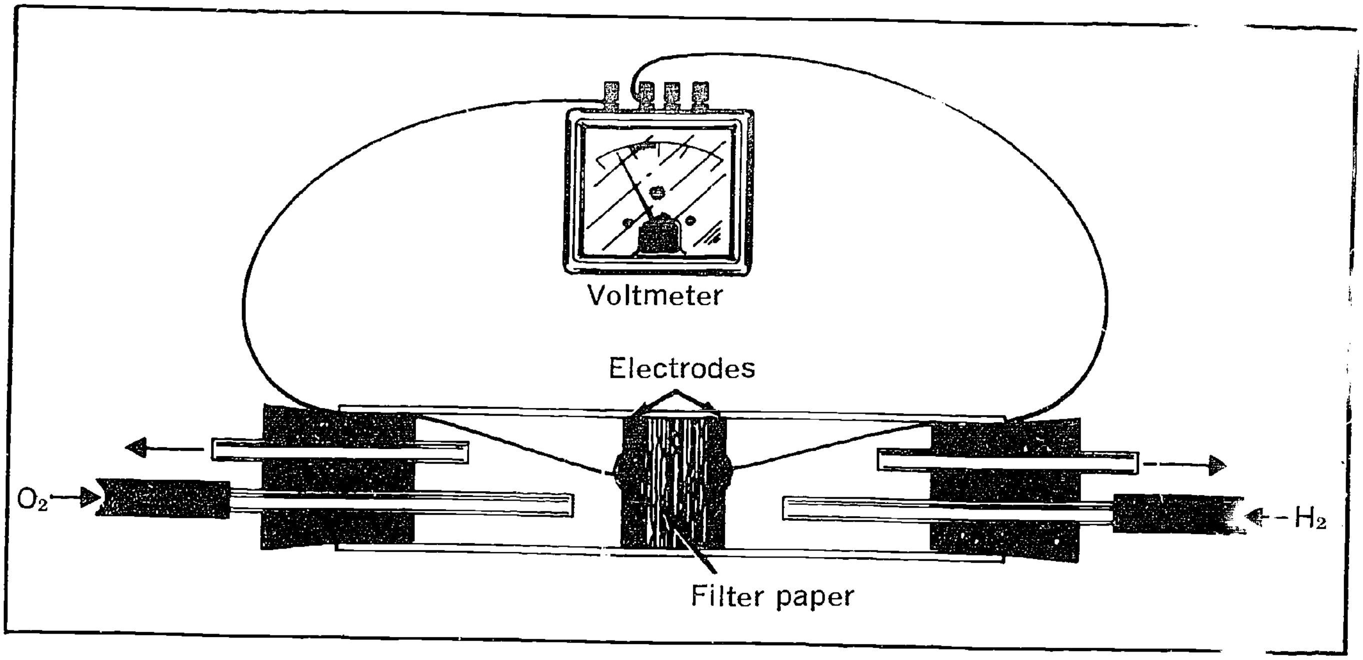


FIGURE 4–9. *Construction of the hydrogen/oxygen fuel cell. Hydrogen and oxygen gases are fed into their respective compartments where they come into contact with the copper-screen electrodes.*

direct contact exists between the metal electrodes. Glass tubes are inserted into two two-hole rubber stoppers that are then placed on the ends of the cell leaving the electrical leads protruding. The longer glass tubes should almost reach the copper-screen electrodes when the stoppers are in place. Sources of hydrogen and oxygen gases are connected to the longer glass tubes. The shorter tubes permit exit of the excess gases. With moderate flow of the reactants a potential of about 0.2 V can be read on a voltmeter connected across the cell.

TOPICS FOR THE DEVELOPMENT OF ADDITIONAL ACTIVITIES

In addition to the cells described, students can construct electrochemical cells using other combinations of electrodes and electrolytes. By referring to the periodic chart or tables of standard electrode potentials, they can predict and test the voltages obtained by pairing some redox couples. Nonaqueous electrolytes based on solvents such as H_2SO_4, HCl, or NH_3 can be used in cells where electrodes would otherwise react with water. The calculated change in enthalpy for a chemical reaction can be compared with the electrical energy produced by a cell, thus emphasizing the high energy density of the alkali metals and halogens of small atomic weight.

Many experiments with electrochemical cells can be performed with only a voltmeter, an ammeter, and a clock. For instance, the fact that a cell runs down even if it is not placed in use (so called self-discharge) can be investigated by measuring the voltage of a cell at intervals of several weeks over a period of several months. For cells delivering currents, the voltage or current draw can be recorded as a function of time. If a variable resistance load is used, the current draw can be made constant, and the easily determined area under the voltage-time curve can be multiplied by the current yield to show the amount of electrical energy delivered by the cell. Voltage-time curves found for different rates of current draw for a cell can lead to the concept of optimum drain rate. Also, the general forms of the voltage-time or power-time curves can be compared for cells constructed of different materials such as zinc/copper and mercury cells.

After a few milliseconds of operation, the rates of chemical reactions in all electrochemical cells are diffusion controlled. The rate of diffusion of the reactants can be changed by operating a cell at various temperatures, and the change in diffusion rate can be related qualitatively to other properties of the electrolyte. The internal resistance of a cell, one component of polarization, can be correlated with the cell's age, past history, and current draw.

For secondary cells, voltage-time curves also can be drawn for the recharging cycle. The change in the nature of a cell can be found as a function of the number of times the cell is recharged.

Because it is often necessary to sterilize the contents of space capsules, the stability of particular cells under typical conditions of sterilization can be investigated. This project might involve heating cells (CARE)[2] at about 140° C for three 36-hr periods and then comparing their performance to similar cells that were not heated.

LITERATURE CITED

1. National Aeronautics and Space Administration. 1964. The view from Ranger, pp. 32–34. NASA EP–38. (Out of print.)

2. Collins, J. R. 1963. Modern batteries. Electronic World 70: 34.

*3. Schwartz, H. J. 1962. Batteries, p. 7. *In* Power for spacecraft. NASA SP–21. GPO, $0.25.

---

[2] *Teacher should exercise care in this experiment.*

**Recommended general sources of information.*

4. National Aeronautics and Space Administration. 1966. Surveyor I, p. 4. NASA SP-126. NTIS N66-29481#.

5. Thaller, L. H. 1965. A long-life thermal cell. NASA TN D-2915. NTIS N65-27818#.

*6. Schwartz, H. J., J. S. Fordyce, R. B. King, J. M. McKee, D. G. Soltis, and L. H. Thaller. 1966. Batteries and fuel cells, pp. 9-51. *In* Space power systems advanced technology conference. NASA SP-131. NTIS N67-10261.

*7. Austin, L. G. 1967. Fuel cells. NASA SP-120. GPO, $2.75.

8. Austin, L. G. 1959. Fuel cells. Scientific American 201(4): 72.

9. Schwartz, H. J. 1965. Fuel cells for space power. NASA Lewis Research Center.

10. National Aeronautics and Space Administration. Gemini-Titan V. Educational Brief #10003.4. NASA Manned Spacecraft Center. (Out of print.)

11. Air Force Systems Command. 1963. An investigation of solid-electrolyte fuel cells. Report No. ASD-TDR-63-448, Wright-Patterson Air Force Base, Ohio. NTIS N64-16060#.

OTHER REFERENCE

Gardner, M. H. 1965. Chemistry in the space age, Chapter 6. Holt, Rinehart & Winston, Inc., New York.

FILMS

Power for the Moon ship. 1966. 28 min, sound, black and white. NASA.

Spacecraft propulsion and power. 1966. 30 min, sound, color. NASA Manned Spacecraft Center.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or repro-

**Recommended general sources of information.*

duced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70–12345#).

unit 5

unit 5

RATES OF HIGH-TEMPERATURE REACTIONS ASSOCIATED WITH SPACE VEHICLES

Topics that may be enriched by use of this unit:

Rates of chemical reactions
Combustion
Chemical kinetics
Reaction mechanisms
Chain reactions

The controlled inferno in a combustion chamber of a chemical rocket engine plays an important role in our ability to travel in space. (See Unit 3, "Chemical Rocket Propellants.") High-energy propellants and rocket-motor geometry are selected for optimum performance and reliability. To make these selections, rocket scientists need information concerning the rates at which propellants react in the combustion chamber and nozzle. One approach is to study the bulk rate of combustion for a given set of conditions, including the nature of the propellants, the fuel injection and ignition systems, the size and shape of the combustion chamber, the temperature, and the pressure. Such tests, however, are very costly in terms of personnel, materials, and time; and prediction of the rate of combustion for even slightly different conditions is difficult. Instead, rocket scientists are compiling kinetic and thermodynamic data for individual steps in these complex combustion reactions. From these data they can predict the performance of a chemical rocket engine.

Many of the experimental methods used and the chemical reactions studied in combustion research are the same as those of another area of concern to space scientists—the high-temperature, gas-phase reactions occurring around a space vehicle passing at hypersonic velocity through a planetary atmosphere. The resulting hot gas cap produces important effects with respect to communications, tracking, and heat transfer. (See Unit 8, "Ablative Materials for High-Temperature Thermal Protection.") The subject of aerodynamic and radiative heating of space vehicles will be treated after a brief discussion of the kinetics of combustion reactions in rocket engines.

KINETICS OF COMBUSTION REACTIONS

To predict the expected performance of a rocket engine, scientists need thermodynamic data (Unit 3, "Chemical Rocket Propellants") and kinetic data including the rate of ignition of the fuel/oxidant mixture and the rate of formation of products in the combustion chamber and nozzle. One of the most energy-rich reactions, that of gaseous hydrogen and oxygen, has been studied in great detail. Consequently, the hydrogen/oxygen pair is an important fuel/oxidant combination for rocket and ramjet engines. These ramjet engines are being developed for hypersonic aircraft, including those that may be used to shuttle personnel and supplies between the ground and spacecraft in orbit about the Earth. The complexity of combustion reactions in general can be illustrated by considering the hydrogen/oxygen reaction in detail.

The equation for the gas-phase reaction of hydrogen with oxygen at 298° K is written

$$H_2\ (g) + \tfrac{1}{2}O_2\ (g) = H_2O\ (g) \qquad \Delta H^\circ_{298} = -57.7979\ \text{kcal}$$

That is, the formation of one mole of gaseous water from gaseous hydrogen and oxygen is accompanied by the release of 57.7979 kcal of heat when all of the substances are at 1-atm pressure and 298° K. At equilibrium and near room temperature, the amount of hydrogen and oxygen left unreacted is insignificant. Nevertheless, under the conditions existing in rocket combustion chambers, even at equilibrium considerable hydrogen and oxygen are present in the form of molecular hydrogen and oxygen, H_2 and O_2, and the free radicals H, O, and OH. In addition, this chemical equation does not reveal the kinetics of the reaction; that is, the rate at which the reaction proceeds and the elementary steps in the reaction.

Reaction occurs when a mixture of hydrogen and oxygen gases is heated to a high temperature in the combustion chamber (Figure 5-1). The high temperature can originate from exothermic reactions already occurring there or from the presence of a shock wave such as that positioned between the diffusion and combustion chambers of a ramjet engine (Figure 5-2). It is believed (1, 2) that the reaction begins with the formation of small amounts of OH free radicals produced in bimolecular collisions involving molecular hydrogen and oxygen; that is,

$$H_2 + O_2 \xrightarrow{k_1} 2OH \qquad (5\text{-}1)$$

During the remainder of the induction period, H, O, and OH

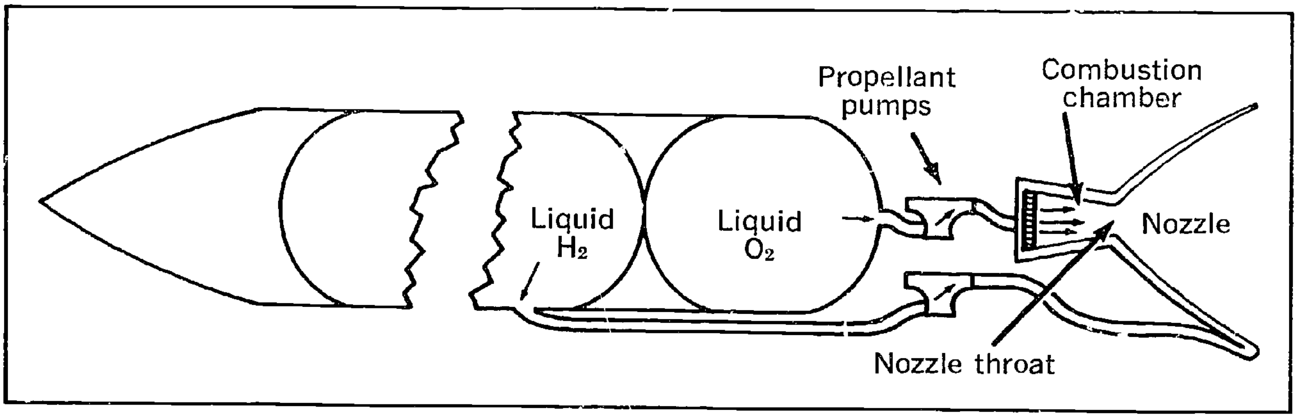


FIGURE 5–1. *Liquid bipropellant rocket hardware. The liquid propellants are pumped to the combustion chamber where they begin to react. The liquid fuel is passed through the tubular walls of the combustion chamber and nozzle to prevent high-temperature degradation of these surfaces.*

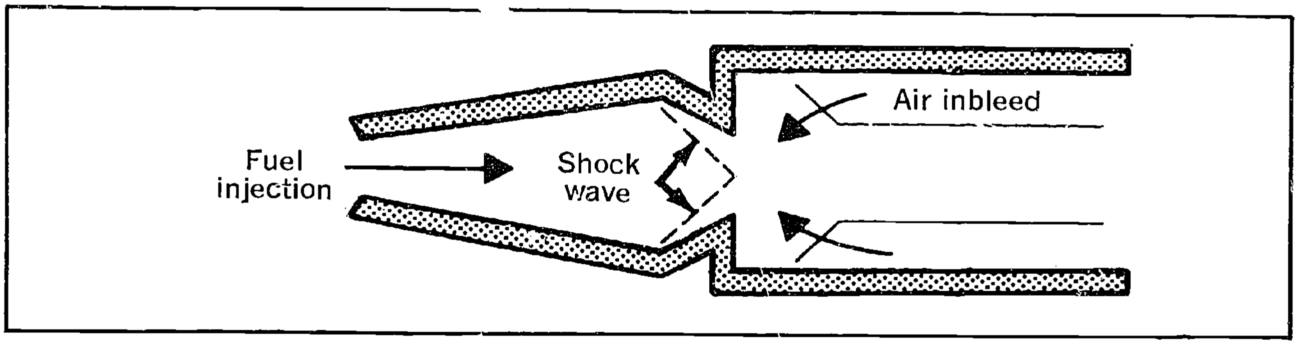


FIGURE 5–2. *Shock-wave-induced ignition in an airbreathing hypersonic ramjet engine. The fuel and air are heated to combustion temperatures as they pass through the shock wave.*

free radicals are formed in increasing amounts by branched-chain reactions:

$$OH + H_2 \xrightarrow{k_2} H_2O + H \qquad \Delta H_{1273} \sim -15 \text{ kcal} \qquad (5\text{–}2)$$

$$H + O_2 \xrightarrow{k_3} OH + O \qquad \Delta H_{1273} \sim 16 \text{ kcal} \qquad (5\text{–}3)$$

$$O + H_2 \xrightarrow{k_4} OH + H \qquad \Delta H_{1273} \sim 2 \text{ kcal} \qquad (5\text{–}4)$$

The hydrogen formed in Reaction (5–2) combines with molecular oxygen to give back a hydroxyl free radical and an atom of oxygen, Reaction (5–3). On collision with molecular hydrogen, the atom of oxygen reacts to yield another hydroxyl free radical and atom of hydrogen, Reaction (5–4). Thus, the concentration of atoms and free radicals increases exponentially with time. The ignition phase of the reaction is nearly thermoneutral as indicated by the approximate values of ΔH for these steps at 1273° K.

The ignition phase of the hydrogen/oxygen reaction at 1400° C is depicted in Figure 5–3. The concentration of H_2 remains effectively unchanged for about 8 μsec after the H_2/O_2 mixture is heated quickly to the ignition temperature. After the formation of some OH free radicals requiring only a fraction of a microsecond, the concentration of the atomic oxygen increases exponentially with time. This is followed by a rapid change in the concentrations of molecular hydrogen and oxygen, and the ignition phase of the reaction is completed.

Following the ignition phase of the reaction, highly exothermic recombination processes among the H, O, and OH free radicals prevail. These recombinations are of the termolecular type shown in Reaction (5–5) and therefore are much slower than the bimolecular processes occurring during ignition:

$$OH + H + M \xrightarrow{k_5} H_2O + M \qquad (5\text{–}5)$$

The symbol M refers to any species that removes sufficient energy in the three-body collision to stabilize the product molecule. These recombination reactions occur mainly in the combustion chamber, the length of which is predetermined on the basis of the speed of the combustion process. If the reactions are fast enough, further recombinations occur in the gases as they pass through the exhaust nozzle of the engine (3). The consequent additional release of energy contributes to the speed of the expanding gases and, thus, to the total thrust produced by the engine.

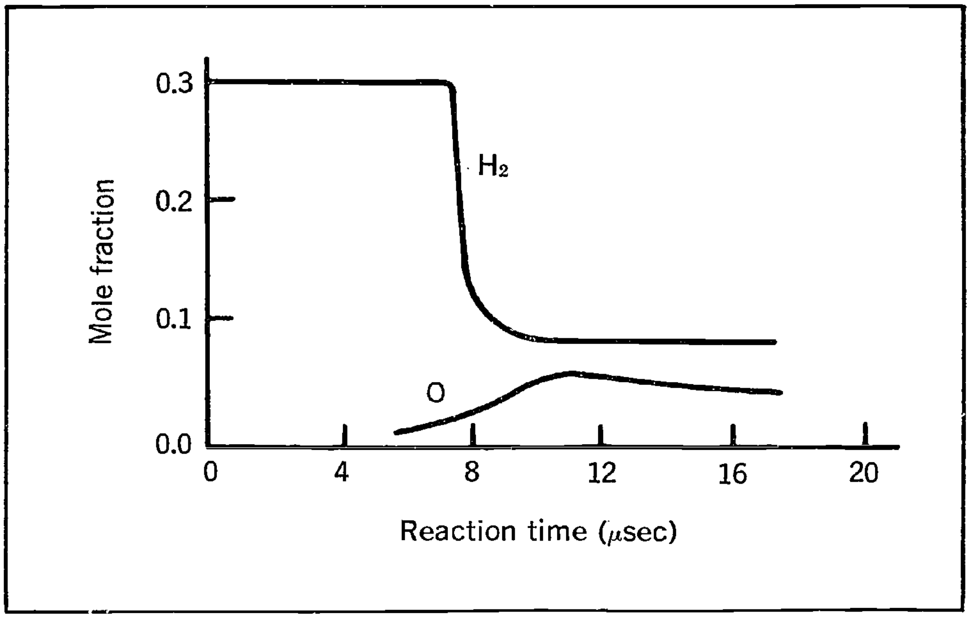


FIGURE 5–3. *Characteristics of hydrogen/oxygen ignition for hydrogen burning in air at 1-atm pressure and 1400° C (2).*

The performance of a rocket engine can be predicted from knowledge of the specific rate constants of the elementary steps in the reaction mechanism. For instance, using appropriate kinetic data, one can calculate the ignition delay at various temperatures, pressures, and fuel/oxidant mixtures. Such calculations yielded the results shown in Figure 5–3. Unfortunately, such data are available for only a few fuels other than hydrogen. Because sufficient information is not available for many reactions, the rate of a combustion process often is given merely in terms of an equation of the Arrhenius type; that is, rate $= k$ (fuel)^a (oxidant)^b $\exp(-E_a/RT)$ where the values of k, a, b, and E_a are chosen to yield the observed rate under given conditions of temperature and pressure. For these complex reactions, however, no detailed information can be gleaned from measurements of bulk rates. Instead, individual steps in a proposed mechanism must be studied so that the contribution of each to the overall rate of the process can be evaluated under the wide range of conditions found in rocket and ramjet engines. These studies are in progress in several NASA laboratories (4, 5, 6, 7), and some representative results are presented in Figure 5–4. In the figure, the specific impulse of the H_2/O_2 upper stage of the Centaur rocket is plotted as a function of the oxidant/fuel ratio. Specific impulse is the amount of thrust produced by a rocket

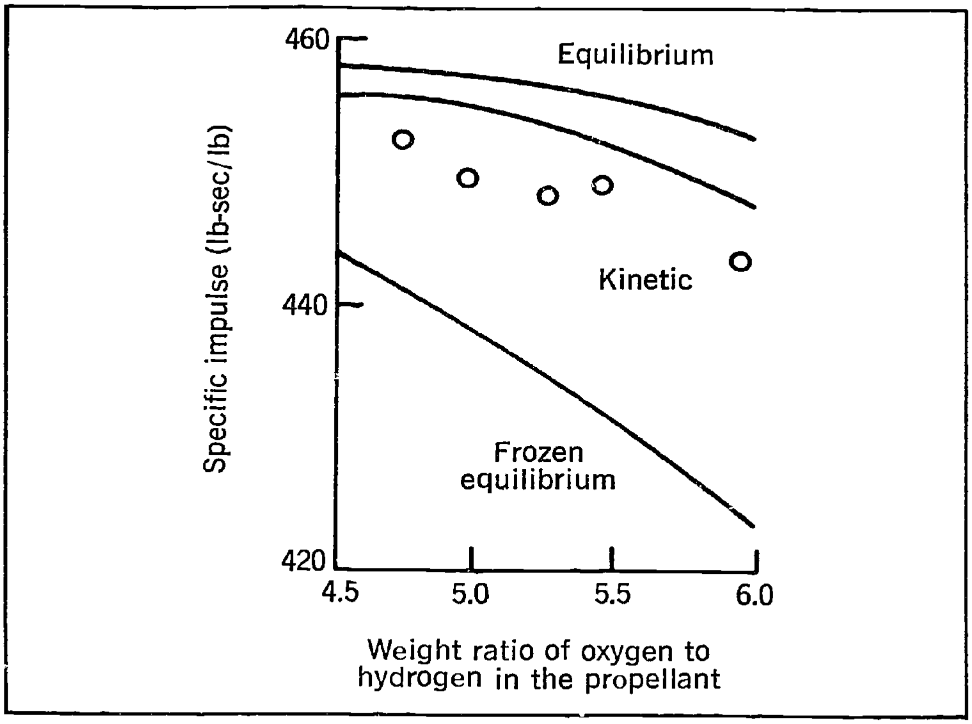


FIGURE 5–4. *Centaur rocket engine performance (2). The actual performance is shown by the open circles, and the predicted performance based on calculations is shown by solid lines.*

motor in burning a unit mass of propellant per unit time. (See Unit 3, "Chemical Rocket Propellants.") The values of specific impulse in Figure 5-4 were calculated on the basis of expansion of the exhaust gases into a vacuum.

If the exhaust gases are assumed to be in chemical equilibrium as they expand from the nozzle, the upper curve results. These values of specific impulse are based on the assumption that the steps in the H_2/O_2 reaction require much less time than that required for the gases to pass from the nozzle. Similar treatment yields values of specific impulse corresponding to the lowest curve in Figure 5-4, but in this case the rate of the reaction is taken to be so slow that the gases flow from the nozzle without further reaction, resulting in a "frozen" equilibrium. Experimentally determined values of specific impulse for the Centaur rocket engine lie between these two curves. By incorporating sufficient kinetic data, one should be able to calculate a curve that nearly passes through the observed values. Such a calculation yielded the smooth curve labeled "kinetic" in the figure. Although the kinetic curve does not seem to agree very well with the observed values of the specific impulse, it is seen to be a much better prediction of the actual performance of the Centaur engine than can be calculated from thermodynamic information alone. As more kinetic data are accumulated, better approximations of the performance of a rocket engine can be made for a wider choice of reactants.

AERODYNAMIC AND RADIATIVE HEATING OF SPACE VEHICLES

Another phenomenon that has prompted space laboratories to study gas-phase kinetics is the interaction between space vehicles and planetary atmospheres. When a space vehicle enters a stationary orbit about a planet or makes a landing on a planet, the vehicle's speed must be reduced. If rockets are used to slow the vehicle, then the braking rockets used for these maneuvers must have approximately the same capacity as those that would launch the vehicle from a parking orbit or from the surface of the planet, respectively. Such sizable rockets would provide a considerable weight penalty for any mission. Instead, the atmosphere of a planet, if any, can be used to brake the fall of space vehicles. Atmospheric braking is made possible by designing the shape of the vehicle so that the deceleration rate and aerodynamic heating are not excessive. If the vehicle is decelerated too rapidly, the stress on materials and living occupants in the vehicle could become too large; therefore, the vehicle is shaped so that some lift results as it passes through an atmosphere. The speed of the vehicle and the nature of the atmosphere determine the detailed shape of the vehicle for any specific mission.

The shape of the vehicle also is designed to reduce aerodynamic heating. If the kinetic energy of the fall to the surface of a planet were absorbed as heat, the vehicle would be destroyed. It has been found that a large portion of the kinetic energy of a pointed object passing through an atmosphere is absorbed by the object through a convective process of heat flow or "skin friction." If the object is blunt, like the Mercury and Gemini vehicles, a larger portion of its kinetic energy is dissipated by heating the surrounding air and less is absorbed by the body itself (8). For post-Apollo missions, however the velocities of the vehicles entering planetary atmospheres will be so great, 12 to 20 km/sec, that radiative heating also must be considered. That is, the air around a blunt vehicle would become so hot that the gaseous molecules would be dissociated and the resulting atoms ionized. At these temperatures, the gases will emit continuous radiation, part of which will be absorbed by the vehicle. To minimize the heat transferred to the space vehicle, therefore, a balance in the sharpness or bluntness of its shape must be achieved in each mission. Not only is the radiative flux important in terms of maintaining the temperature of the vehicle, but also the excited gases make radio communication with the vehicle impossible. Nevertheless, the dissipation of the kinetic energy of space vehicles by heating the surrounding air remains an important aspect of space travel, and the associated problems of heating and communications are being solved partly by studies in gas-phase kinetics.

REACTIONS IN SHOCK WAVES

When a blunt object such as a meteor or a space vehicle enters a quiescent gas, a shock wave (9) is formed in front of the object at a distance of about one-tenth the radius of curvature of the object. The shock wave is only three to four mean free paths thick. (Mean free path is the average distance a gaseous particle travels between successive collisions with other particles.) Passage of the shock wave through a quiescent gas heats the gas immediately behind the wave to temperatures in the vicinity of 100,000° K (based on the distribution of molecules among the translational and rotational energy levels). That is, after only three to four collisions, the molecules of gas become very excited in their translational and rotational degrees of freedom. In the region between the shock wave and the vehicle, the gas molecules continue to collide and become excited vibrationally at the expense of their translational and rotational energies. Excitation of the vibrational modes, occurring in a stepwise manner, requires 100 to 1000 collisions. The resulting temperatures are typically so high that the molecules are excited vibrationally to the point of dissociation into atoms. Further, the atoms become excited electronically and some are ionized. The sinking of energy into vibrational modes, dissociation of molecules, and electronic excitation of the particles yields temperatures in the range of 10,000° to 12,000° K between the shock wave and the vehicle. At these temperatures, an object entering the Earth's atmosphere would be surrounded by a high-temperature gas composed mainly of N, O, N^+, O^+, and electrons. Continuous radiation is emitted as recombinations occur in this mixture (10).

To predict the nature of the radiation emitted by the incandescent gas envelopes surrounding space vehicles entering atmospheres, the rates of gas-phase reactions at high temperatures are being studied at several NASA laboratories. These studies include gases such as N_2, Ar, CO_2, CO, and others that are prominent in the atmospheres of planets where we plan to orbit satellites or land space vehicles. Many of these kinetic studies are performed by observing the effects of shock waves on gases (11, 12, 13).

At NASA Ames and Lewis Research Centers, several shock tubes are used to study the kinetics of gas-phase reactions, aerodynamic heating, and other problems associated with reentry physics (2). One of the gaseous systems treated is that of carbon dioxide because this gas dominates the atmosphere of Venus and also is present in many combustion reactions. In a shock tube the changes in concentrations of various chemical species are observed as the test gas is disturbed by the passage of a shock wave. In a simple shock tube, the shock wave is generated by creating a large difference in pressure on either side of a diaphragm at one end of the tube. When the diaphragm bursts, a shock wave is propagated the length of the tube and the resulting chemical changes in the test gas are observed spectroscopically. For instance, the dissociation of carbon dioxide is observed by following the CO_2 concentration using the infrared emission from heated CO_2. (See Figure 5–5.) More complex shock tubes use a combination of compression and expansion waves. Such an instrument (Figure 5–6) has been used to observe the recombination of CO and O. The spectroscope is adjusted to receive the characteristic blue light from the reaction

$$CO + O + M \rightarrow CO_2 + M + h\nu$$

This light is responsible for the color of mantles of many flames including those of the bunsen burner.

At Ames Research Center a shock tube of impressive size and versatility was constructed of two 16-in. naval guns welded end to end. A nylon plug can be blown into a constriction at one end

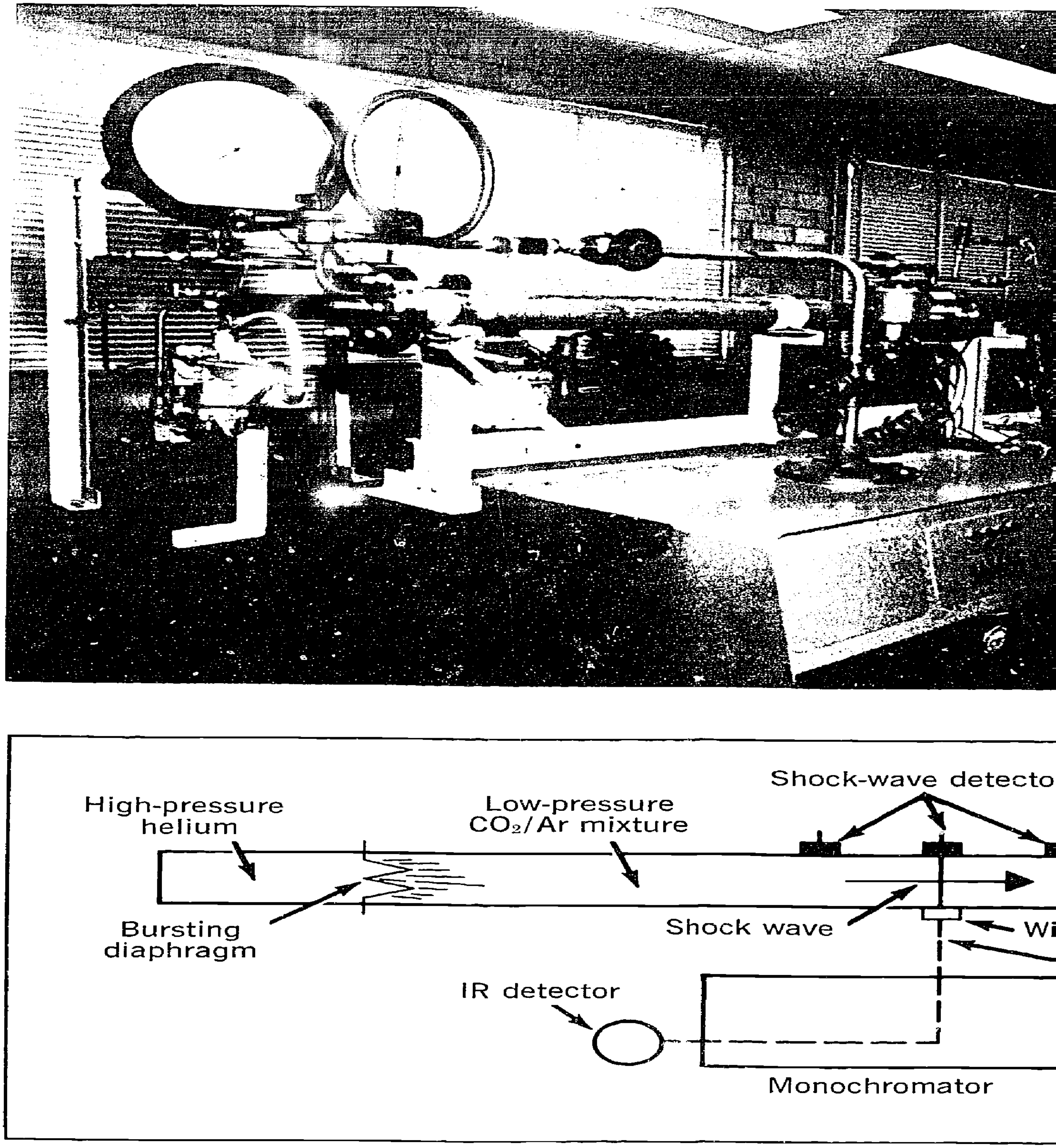
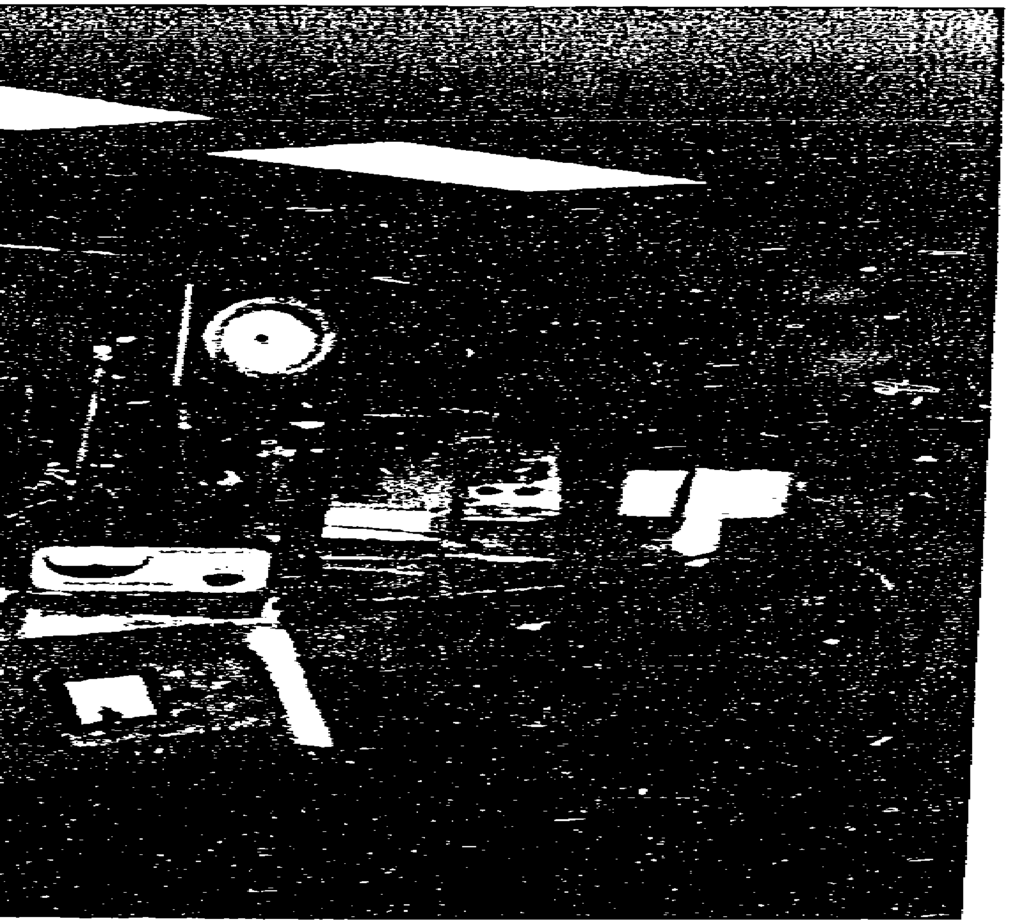
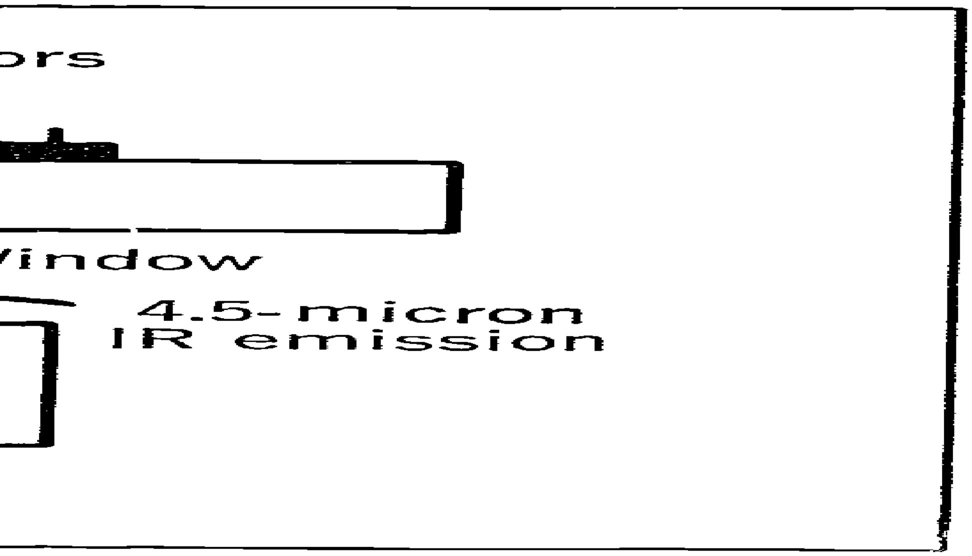


FIGURE 5–5. *Photograph and diagram of a shock tube used for the*
carbon dioxide (2). A shock wave, produced at one end of
through the CO_2/Ar mixture and causes dissociation of the
of CO_2 is followed by observing its characteristic emission





study of dissociation of
f the tube, is propagated
e CO_2. The concentration
in the infrared.

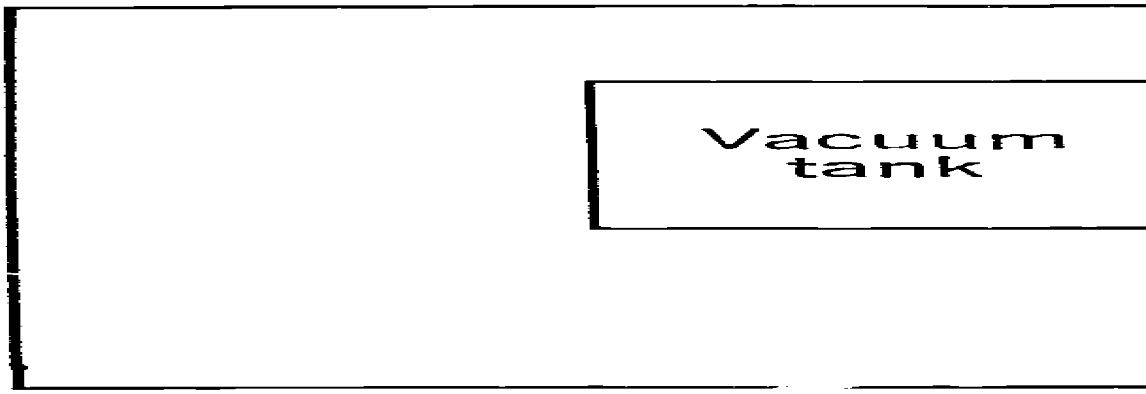
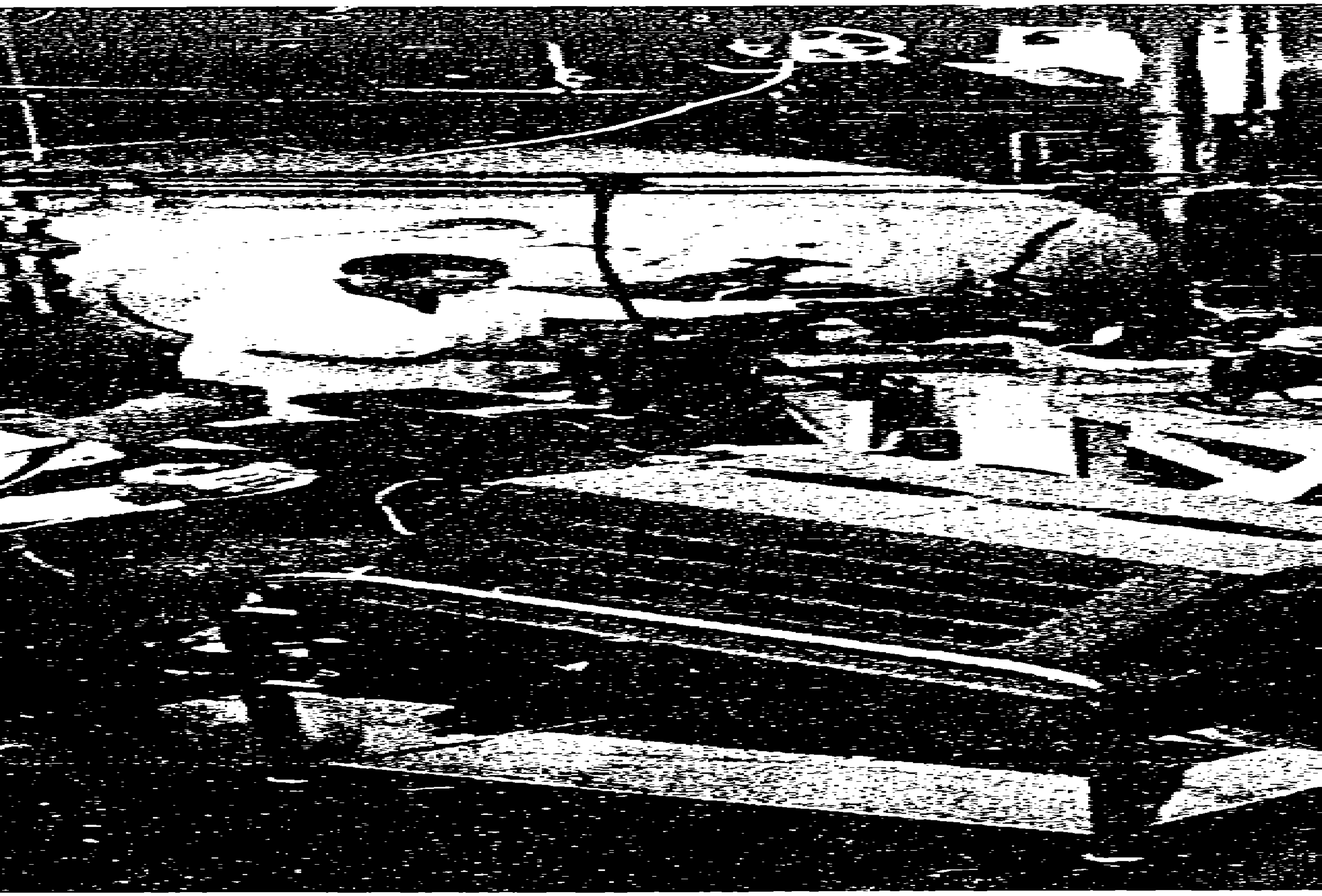
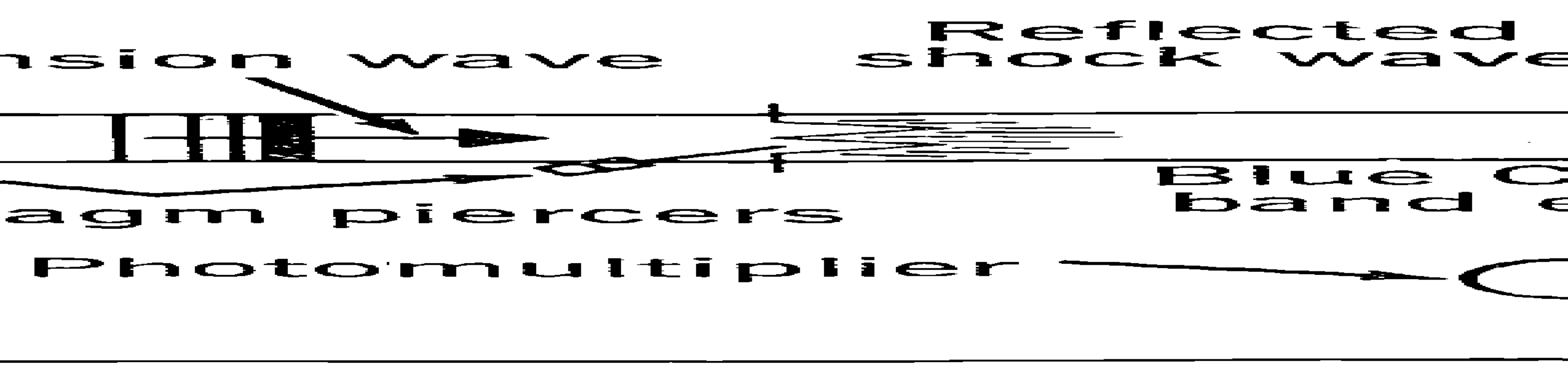


FIGURE 5–6. A
hi
re
bl

es of High-Temperature Re





used for studying recombin
techniques are combined to
the end of the shock tube. T
band emission.

acuum and
shock wave
serving the

of the shock tube yielding an airstream moving at speeds up to 16,000 ft/sec. From the other end of the tube, models can be fired by gas guns into the approaching shock wave, thereby achieving relative velocities of about 44,000 ft/sec or almost 15 km/sec, nearly the speed of an object executing free fall to the Earth on a return trip from Mars. The experiment in the tube lasts only several thousandths of a second, and during this time shadowgraph pictures and spectroscopic observations are made at as many as 16 points along the tube. From studies conducted with this shock tube, one can calculate the rate constants for gas-phase reactions, find the aerodynamic forces on model reentry vehicles, or observe the effects of radiative and convective heating on models. Air temperatures up to 9000° K and Ar and Ne temperatures up to 20,000° K can be achieved. The operator of this shock tube can exercise almost independent control of the enthalpy, the Reynolds number (which characterizes the nature of the gas flow through the tube as to the degree of turbulence), and the Mach number. Thus, ablative heat-shield materials can be tested under realistic radiation environments. This unique shock tube has also been used to study the effects of impacts of meteors with space vehicles. From these and similar studies, protective devices for space stations have been developed. Shock-tube experiments are also revealing the chemistry of the reactions occurring in the gases surrounding vehicles entering atmospheres. These studies may lead to methods of maintaining radio communications with a space vehicle during this important entry phase of a mission.

ACTIVITIES

Flames, their stability, the rates at which reactions occur within them, their temperatures, their support of standing waves and vibrations, and other facets of their nature are very much the concern of scientists who study combustion. Detailed studies require considerable instrumentation and complicated mathematical treatment of the resulting data. Nevertheless, the bulk rates of reactions in flames can be noted qualitatively by observing flames of ordinary burners. In the following activities, primarily using an ordinary bunsen burner, the nature of flames is examined. Subdued light and the absence of strong air currents will make the experiments more effective. (CAUTION: The experimenter should be more than usually cautious of burns because of the unusual manipulations made with the burners.)

FLAME IGNITION

Initiation of any combustion process requires ignition of a fuel/oxidant mixture. Some fuel/oxidant pairs ignite spontaneously on mixing (Unit 3, "Chemical Rocket Propellants"), whereas others require that a minimum volume of the fuel/oxidant mixture be brought to a minimum temperature. In addition, the pressure and the relative amounts of fuel and oxidant are important variables influencing ignition. One can illustrate these facts with an ordinary bunsen burner using natural gas as the fuel.

The fact that some fuel/oxidant mixtures are too fuel or oxidant rich to ignite can be demonstrated in the following manner. The air vents of a bunsen burner are closed and the gas is turned on. At a height of 2 ft or more above the burner, one substantiates the presence of natural gas by its characteristic odor. However, a burning wood splint inserted into the gas stream at such heights does not ignite the gas/air mixture. If one moves the burning wood splint closer to the burner, the point is reached where the gas/air mixture is sufficiently fuel rich to support combustion. Nevertheless, at this distance the flame flutters about the burning wood and does not become attached to anything. This effect illustrates the manner in which some flames are maintained by a pilot light. As the burning wood is brought closer to the mouth of the burner, the flame jumps to the lip of the burner and stabilizes there in the usual manner.

One can demonstrate that a certain minimum volume of heated fuel/oxidant mixture is necessary for ignition of a gas/air mixture. A tesla coil is turned on with the tip of the electrode in contact with the grill of an unlighted Meker burner. With the primary air vents at the base of the burner open and with sufficient gas flowing through the burner, the electrode of the tesla coil is backed off until a small spark is visible. As long as the spark gap remains small, the burner fails to light; but with further lengthening of the gap, ignition occurs. Actually, two variables are involved—the temperature and the volume of the heated region.

The effects of temperature and volume are differentiated more effectively if the premixed gases from the burner are passed through a spark gap formed from pointed carbon rods. The quantity of electricity discharged across the gap is used to vary the temperature, and the length of the gap is varied to yield differences in the volume of the heated region. The details of the experimental setup are left to the reader.

FLAME STABILIZATION

Many of the desired results produced by flames require stabilization of flames either within combustion chambers or on the lips of burners. Sometimes the position of a flame is maintained by a pilot light, as in the case of the diffusion gas burners used in many home heating plants. In some ramjet engines being developed for hypersonic aircraft, the position of the flame is regulated by the location of a stationary shock wave that causes ignition of the fuel/air mixture as it passes into the combustion chamber.

A very common method of stabilizing flames is to provide either a heat sink, which lowers the flame temperature sufficiently to quench the flame in its vicinity, or a free-radical sink, which removes intermediate products in the combustion reaction. Actually, any object to which a flame attaches probably acts both as a heat and a free-radical sink. The stabilizing effect of the lip of a bunsen burner was noted in a previous experiment concerning flame ignition. The burner lip, acting as a heat and free-radical sink, quenches the flame in its vicinity; and the flame becomes attached to the burner. This occurs because as the lip is approached, the velocity at which the flame burns toward the burner decreases at a slower rate than the velocity of the gas or gas/air mixture issuing from the mouth of the burner. (The different rates of flow of gas in the burner tube as a function of the distance from the center are similar to the laminar flow present in any slowly moving fluid confined by a duct.)

The relationship between the gas pressure and quenching distance can be noted qualitatively with a bunsen burner. After taping shut the air vents at the base of the burner, the gas is turned on and ignited. The gas flow is then reduced until a small flame about 1 mm high burns at the top of the burner. The gas pressure is further reduced slowly, and the increasing distance (quenching distance) of the flame from the lip is noted. If the surrounding air is sufficiently calm, it is possible to stabilize a flame only a few millimeters in diameter at the mouth of the burner.

The diameter of the mixing tube is also important in stabilizing a flame. This can be observed qualitatively by attempting to establish a flame on the gas jet at the base of a bunsen burner from which the mixing tube has been removed. Even with low gas flows, the flame is easily blown off. If the tube is too large, the flame strikes back. Flames are stabilized on burners with large-diameter tubes by providing a grill, which acts as a heat sink. The grill, such as found on a Meker burner, divides the flame into a number of flamelets, each of which is stabilized by interaction with, and heat loss to, the grill. This method of flame stabilization can be studied with a bunsen burner. With the primary air vents closed, a flame about 3 in. high is established on the burner. The flame is then extinguished, a wire gauze is inserted in the gas stream above the burner, and the gas/air mixture above the screen is ignited. Initially, the flame attaches to the screen, but if the screen becomes sufficiently hot, the flame strikes back and attaches to the lip of the burner. If the flame does not strike back, the gas flow should be increased to raise the temperature of the screen. If the barrel of the burner is removed and this sequence is repeated, the flame blows off when the gauze is relatively close to the jet. This indicates that the flame velocity is less than the gas velocity. When the gauze is moved to greater heights, the flame attaches to the gauze and has the appearance of a premixed bunsen-burner flame because sufficient mixing of air and gas has occurred. As the height of the gauze from the gas jet increases, the flame becomes more turbulent and finally becomes detached. Similar effects with a wire gauze are produced when using the premixed gas/air mixture from a bunsen burner. Heat and free-radical sinks of other geometries such as metal rods can also be used to stabilize flames. Variables in these experiments dealing with flame stabilization include flowrates, fuel/oxidant ratios, and the fuel/oxidant pair.

DIFFUSION AND PREMIXED FLAMES

The appearance of the blue-cone flame formed by burning natural gas and air that have been premixed in a bunsen burner differs greatly from the yellow flame produced by burning natural gas in air. The yellow color is associated with the presence of elemental carbon that, in the burning of some carbonaceous fuels, can aggregate to form soot. The formation of soot can be observed by burning heavy hydrocarbons such as paraffin. To observe the presence or lack of soot formation, various organic liquids can be combusted in an ordinary alcohol lamp and the amount of soot formed can be noted. Secondary and primary alcohols of low molecular weight produce no soot. Increasing soot formation is generally observed with increasing molecular weight, branching, and unsaturation in the fuel molecules. Flame temperature, however, also determines the luminosity caused by elemental carbon and the degree of soot formation; thus one must be conservative in making inferences of molecular structure from the nature of flames.

The premixed flame of a bunsen burner is composed of a blue mantle and a narrow, blue-green, conical zone, called the flame front. The temperature of the fuel/air mixture rises rapidly in the flame front, and the reactant molecules obtain sufficient energy to initiate combustion through bimolecular collisions. Dissociated molecular species, atoms, and free radicals result and are cleaned up in the inherently slower termolecular reactions occurring in the mantle of the flame.

The pale-blue color of the outer mantle of a premixed bunsen-burner flame is associated with the presence of carbon monoxide and atomic oxygen. The intensity of the light is directly proportional to the concentration of each and, thus, to the rate of formation of carbon dioxide. The elementary step in the reaction mechanism for the formation of carbon dioxide is

$$CO\ (g) + O(g) \rightarrow CO_2^*\ (g) \rightarrow CO_2\ (g) + h\nu$$

The asterisk denotes an electronically excited molecule.

The air vents at the base of a bunsen burner are usually of such size as to yield a fuel-rich flame even with the vents open fully. The remainder of the air (secondary air) needed for combustion comes from that surrounding the flame itself. The premixed flame is stabilized and the mantle is formed somewhat by the interdiffusion of secondary air and the reactants that have entered at the base of the burner. The secondary air widens the limits between the flame striking back and blowing off. As the primary air vents are closed, the flame becomes more luminous, indicating an increased amount of elemental carbon. The primary air vents are closed (and even taped over, if necessary) to yield a diffusion flame, one in which the fuel and air are mixed only by interdiffusion.

FLAME VELOCITY

Flame velocities depend on the nature of the gases being combusted, the fuel/oxidant ratio, the presence of other molecular species, the pressure, the temperature, and wall effects. For a stationary, flat flame under given conditions, the rate of propagation of the flame, that is, the velocity of the flame front v_0, is equal to the fuel/air velocity v_g normal to the flame front (Figure 5–7, from Frestrom (14)). Thus, $v_0 = v_g$ for flat flames, including those stabilized on a fine screen. For a cone-shaped flame such as the premixed flame of a bunsen burner, the solution for v_0 is fairly straightforward if the flame front is assumed to be conical and the burning velocity is assumed to be constant over the flame front. As noted in Figure 5–8, $v_0 = v_g \sin \theta$, where θ is one-half the apex angle of the cone (14). One can calculate v_0 by noting that the volume flow of gas from the end of the burner must equal the volume flow of gas across the flame front. Where A_b and A_c are the areas of the mouth of the burner (πr^2) and the

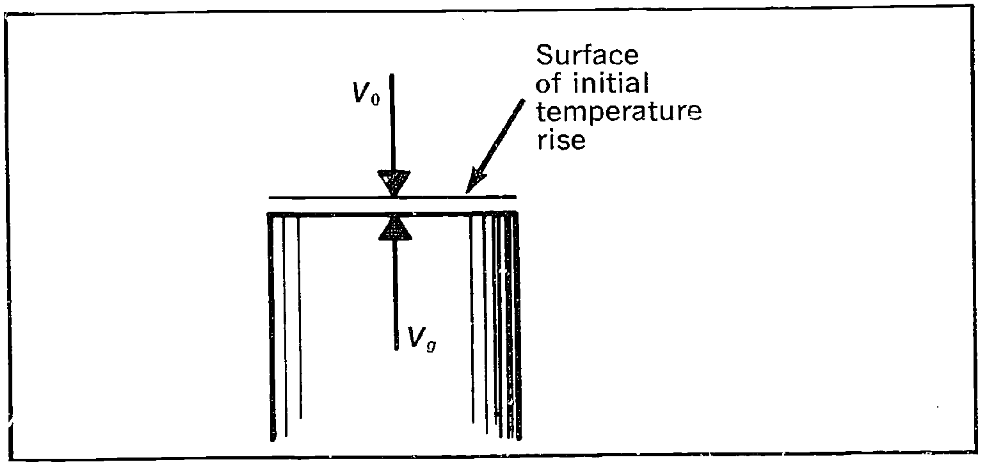


FIGURE 5-7. *Relationship between the flame and gas velocities in a flat flame front (14). The flame and gas velocities are equal for flat flame fronts.*

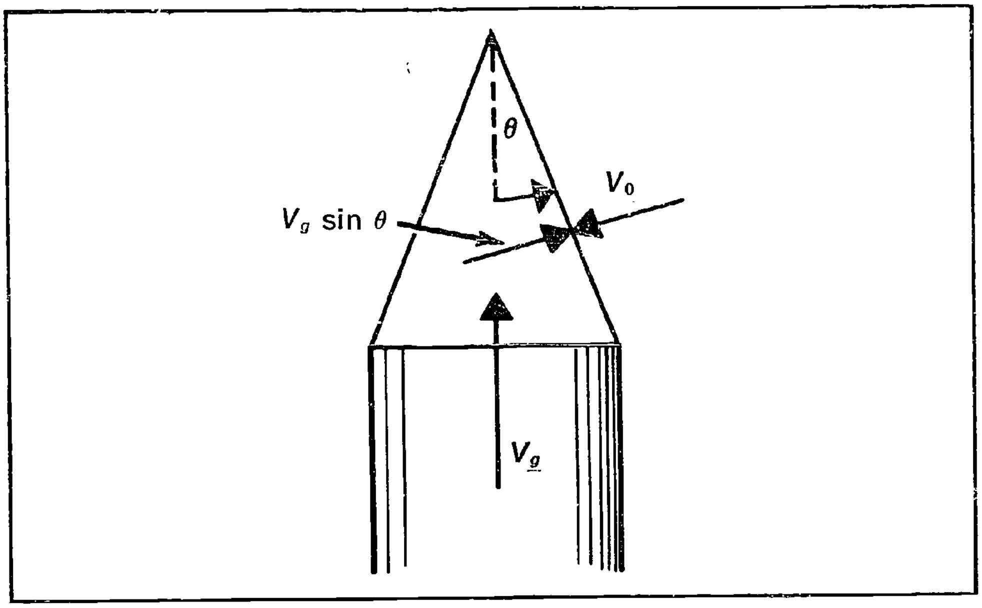


FIGURE 5-8. *Relationship between the flame and gas velocities in a conical flame front. The velocity of the flame front* V_0 *is equal to* $V_g \sin \theta$*, where* V_g *is the gas velocity and* θ *is one-half the apex angle of the cone-shaped flame front (14).*

cone (πrh), respectively, then the equality of the volume flows gives $A_b v_g = A_c v_0$. The area of the cone is estimated through knowledge of the height of the cone of a stationary flame. To find its height, sight the cone across the edge of an opaque ruler or through a clear plastic ruler. Because the apex of the cone is curved, the height is estimated by visually extrapolating the sides of the cone to the point of their intersection. The area A_c is calculated from the measured value of the height of the cone and the radius of the mouth of the burner. Although the value of

A_b can also be calculated from knowledge of the geometry of the burner, the value of v_g is not so easily determined. Instead, the product $A_b v_g$, the volume flow of gas, is measured experimentally. Using a fairly standard method for measuring the volume flow of gases, one observes the rate (cubic centimeter per second) at which a soap bubble is carried through a graduated, open-ended tube. A 50-ml buret, preferably the type used with a pinchcock or one from which the base has been removed, can serve as the tube (Figure 5–9). The measurement is performed

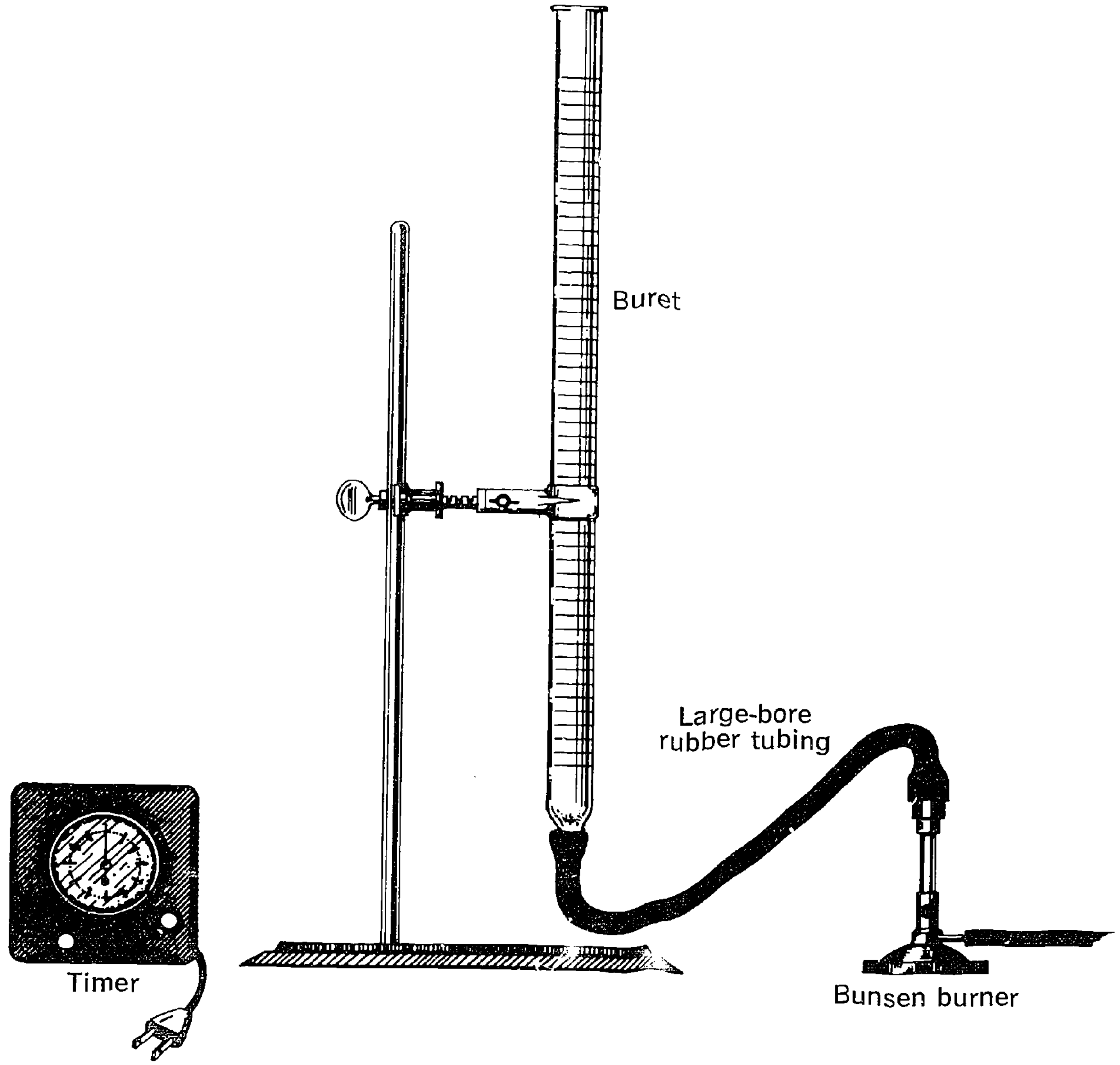


FIGURE 5–9. *Determination of gas flowrates. Volume flowrates of a gas (cubic centimeters per second) are found by timing the movement of soap bubbles through the buret.*

as follows. A bunsen burner is lighted, the air supply is adjusted to yield a conical flame front, and the height of the cone is measured. Without changing the gas or air adjustments of the burner, the flame is blown out and the top of the burner tube is connected to the base of the buret by a piece of large-diameter rubber tubing such as that used to deliver gas to the burner. With the inner walls of the buret previously wetted, a small amount of liquid-soap solution is poured down from the top of the buret. The gas/air flow through the buret will blow bubbles that often rise the full length of the tube. Only enough soap solution to produce several bubbles at any one time should be used. Measurement of the times a particular bubble passes predetermined points in the buret yields the volume flowrate of the gas from the mouth of the burner $A_b v_g$ in cubic centimeters per second. Constrictions in the flow apparatus should be minimized to obtain good values of the volume flowrate, and the results from several determinations should be averaged. With the experimentally determined value of $A_b v_g$ and the calculated value of A_c, find the flame velocity from the expression $v_0 = (A_b v_g / A_c)$.

The rate of combustion in a diffusion flame is controlled by the rate of interdiffusion of the fuel and oxidizer, the reaction rate of the fuel with the oxidizer being much faster. One can roughly estimate the average diffusion coefficient of the oxidant by measuring the height to which a diffusion flame rises (15). The equation for this relationship is $D \approx (vr^2/2h)$, where v is the gas velocity, r is the radius of the burner, and h is the height of the flame. The relationship may be derived from the following argument. The time required for fuel to flow from the burner tube to the tip of the flame is equal to h/v. In the same time, the oxidant transverses the burner radius r by a random walk diffusion process; this time is equal to $r^2/2D$. The gas flow should be at a sufficiently slow rate to prevent a turbulent flame. The value of vr^2 can be determined in a manner similar to that shown in Figure 5–9 where the values for the volume flow are divided by π to give vr^2. The value of the diffusion coefficient which is measured is that for oxygen under the experimental conditions.

TOPICS FOR THE DEVELOPMENT OF ADDITIONAL ACTIVITIES

In most of the following activities, combustion is viewed under a wide variety of conditions, and safety glasses should be worn.

Most of us cannot imagine flames without differential density effects that tend to make them pointed upward in shape. In a zero-gravity environment the nature of flames is considerably different, especially with respect to the rate of transport of oxidant to the fuel and products from the combustion site. In the absence of convection currents caused by differential density effects, these transport processes must occur by diffusion alone. To illustrate the nature of a small flame in a zero-gravity environment, convection currents can be minimized by selecting the fuel/oxidant pair for which densities of the hot gases are nearly those of the ambient gases. This condition occurs when 100 percent HNO_3 burns in hydrogen gas. The shape of a HNO_3/H_2 flame burning at the end of a jet can be contrasted with that of hexane burning in air (Figure 5-10).

Flames have a structure that can be characterized by temperature or the concentration of a particular species. Regions in a flame can be probed with a small metal tube attached indirectly to an aspirator (Figure 5-11). The rate at which gases are withdrawn from the flame can be regulated by the screw compressor on the test bottle. Appropriate test solutions or indicators can be placed in the test bottle and the gases bubbled through them. The temperature profile of a flame can be examined in a similar manner using a small thermocouple.

The variation of the rate of combustion with the state of subdivision of the fuel is well known. This phenomenon can be demonstrated with solids by comparing the rate at which a strongly heated spoonful of lycopodium powder burns with the rate the powder burns when it is blown from a plastic squeeze bottle across a flame. The same effect with liquids can be noted by comparing the rate at which fuel oil burns in an open dish with the rate at which droplets of the oil burn when ignited by a pilot flame. Care should be used if the latter effect is demonstrated with fuels more volatile than fuel oil. Even with fuel oil,

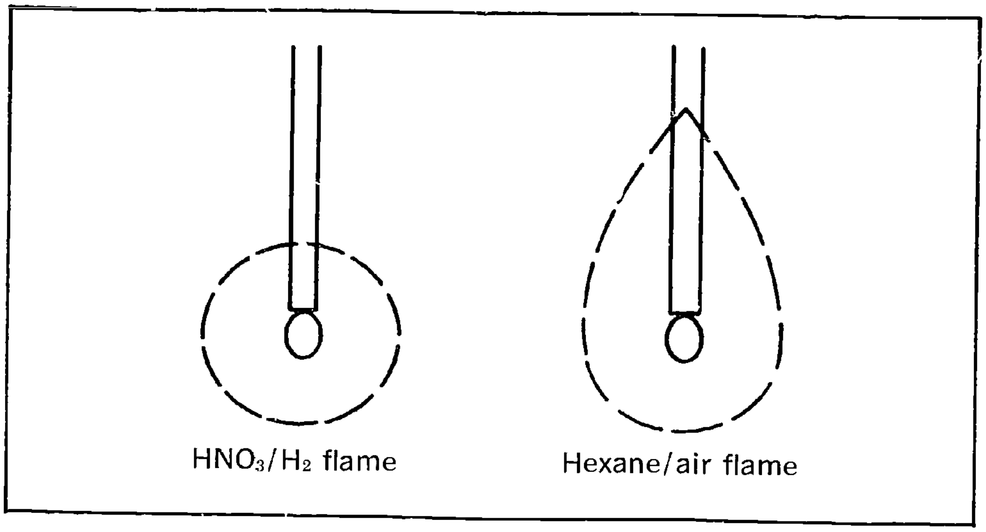


FIGURE 5-10. *Simulation of zero-gravity effects. The differential density effects occurring in the hexane/air flame are absent in the HNO_3/H_2 flame; the shape of the latter is therefore the same as that observed in a zero-gravity environment (14).*

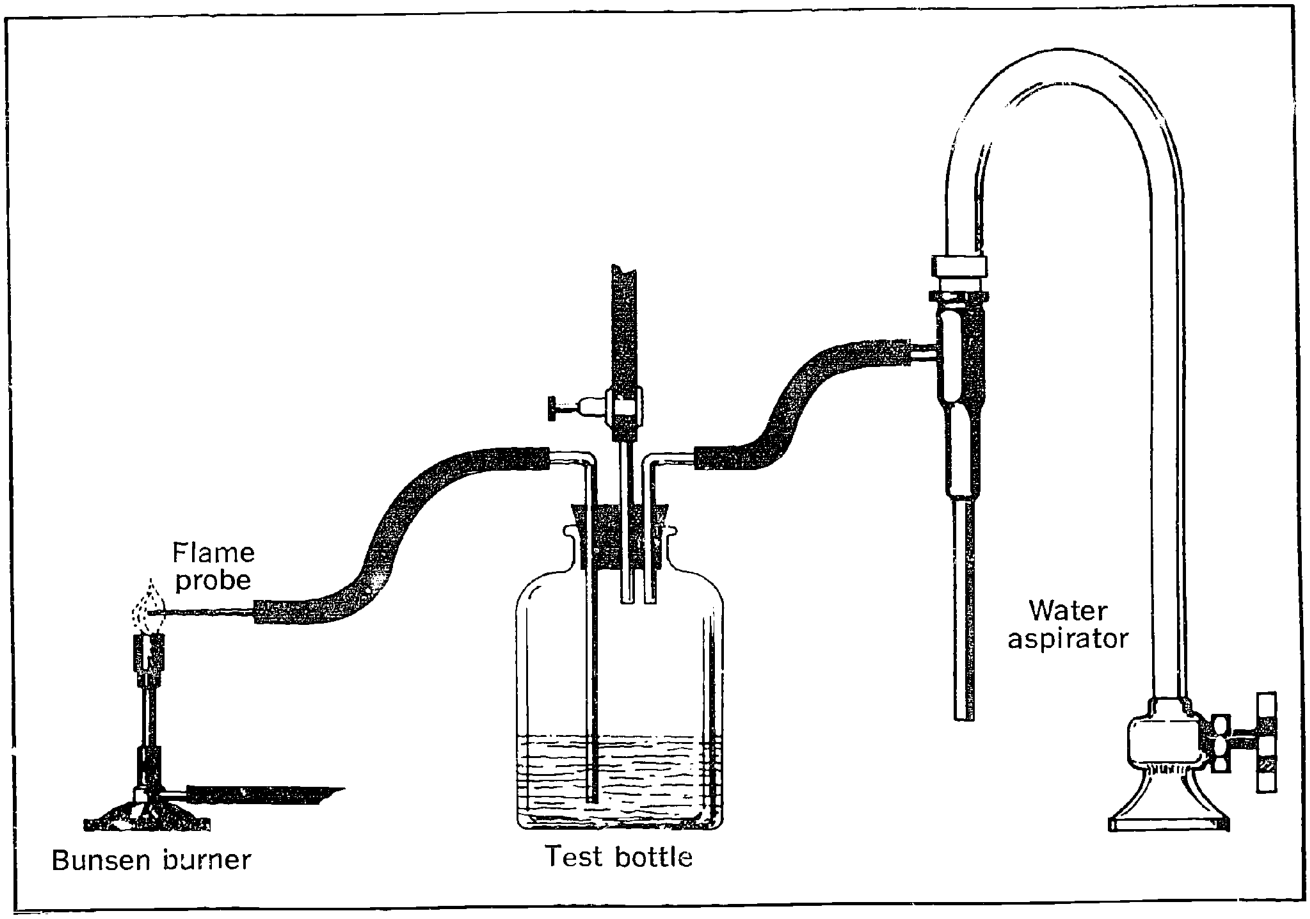


FIGURE 5–11. *Determining the chemical profile of a flame. The chemical or thermal profiles of flames can be probed using appropriate test solutions or instrumentation.*

the demonstration should be performed outdoors. The combustion of atomized fuel oil also can be observed through the opened fire door of an oil-burning furnace.

A glass combustion tube permits the observation of flame fronts that are not stabilized but are free to move. A glass tube 3 to 4 ft long and 1 to 2 in. in diameter can be supported horizontally across buret clamps on two ringstands. A bunsen burner fitted with a stopper on its barrel is supported horizontally by a buret clamp on a third ringstand (Figure 5–12). The gas is turned on, and the burner is inserted lightly into the end of the glass tube. The flame is lighted at the opposite end of the glass tube and the burner is withdrawn. If a satisfactory air/gas mixture is used, the flame front can be observed to pass through the tube. The velocity of the flame front can be noted qualitatively to vary with the air/gas ratio and the temperature of the gases.

Because the rates of some reactions are diffusion controlled, it

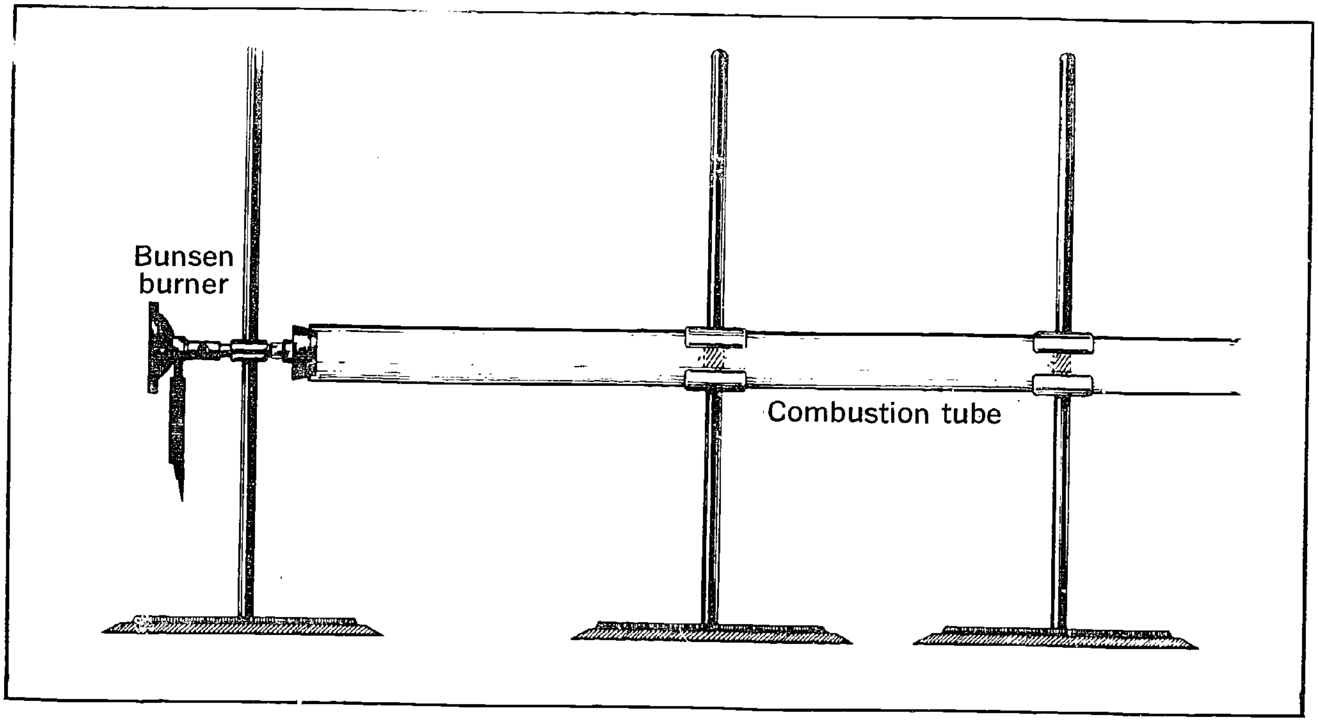


FIGURE 5–12. *Glass combustion tube. A flame initiated at the open end of the combustion tube passes through the tube when the burner is removed.*

becomes important that one know about diffusion rates. Part of the arrangement shown in Figure 5–12 can be used to measure the relative rate of diffusion of gases. The glass tube is clamped across the two ringstands and is leveled with a carpenter's level to minimize differential density effects. The ends of the tube are fitted with two corks, one of which is partially bored at the small end and fitted with a plug of cotton. To measure the rate at which certain gases diffuse through the tube, a long narrow piece of absorbent paper is wetted with an appropriate indicator, dried, and placed lengthwise in the tube. The paper can be easily inserted into the tube if the tube is held in a vertical position. With the tube clamped in the horizontal position, the cotton plug is dampened with an appropriate substance, and the corks are placed on the ends of the tube. The diffusion of gas through the tube can be observed on the paper; and the rate, measured. Relative rates of diffusion can be related to the molecular weights of the gases, and the relationship $\bar{c} \propto (1/\sqrt{m})$ can be determined or illustrated. Phenolphthalein, litmus, or other indicators can be used with aqueous solutions of NH_3, HCl, SO_2, CO_2, NO_2, or volatile organic amines.

Vibrations often occur in flames, sometimes with undesirable effects on combustion chambers. Vibrating flames are studied with singing tubes in Unit 3, "Chemical Rocket Propellants."

LITERATUF CITED

1. Brokaw, R. S. 1964. Analytic solutions to the ignition kinetics of the hydrogen-oxygen reaction, p. 2. NASA TN D–2542. NTIS N65–12305#.

*2. Brokaw, R. S., F. E. Belles, B. J. Clark, and F. J. Zeleznik. 1966. Combustion, pp. 13–20. *In* Conference on selected technology for the petroleum industry. NASA SP–5053. GPO, $1.25.

3. Franciscus, L. C., and E. A. Lezberg. 1963. Effects of exhaust nozzle recombination on hypersonic ramjet performance. AIAA Journal 1: 2071.

4. Raper, O. F., and W. B. Demore. 1964. Reaction of O(^{1}D) with CO. Journal of Chemical Physics 40: 1053.

5. Wong, E. L., and A. E. Potter. 1963. Reaction rates of hydrogen, ammonia, and methane with mixtures of atomic and molecular oxygen. Journal of Chemical Physics 39: 2211.

6. Wong, E. L., and A. E. Potter. 1965. Mass spectrometric investigation of reactions of oxygen atoms with hydrogen and ammonia. NASA TN D–2648. NTIS N65–16585#.

7. Brabbs, T. A., and F. E. Belles. 1966. Recombination of carbon monoxide and atomic oxygen at high temperature. Combustion Institute, 11th International Symposium on Combustion. (Berkeley, Calif., Aug. 14–20, 1966.) AIAA A66–40527.

8. National Aeronautics and Space Administration. Dissipation of energy by drag braking in the atmosphere. Educational Brief 4004. NASA Manned Spacecraft Center.

9. Wegener, P. P. 1966. Gas dynamics. Chemical and Engineering News 44(28): 77.

*10. National Aeronautics and Space Administration. 1962. Gas dynamics in space exploration. NASA SP–24. GPO, $0.40. NTIS N63–11514#.

11. Presley, L. L., C. Chrackenian, Jr., and R. Watson. 1966. The dissociation rate of carbon monoxide between 7,000° and 15,000° K. NASA Ames Research Center. AIAA A66–33660.

**Recommended general sources of information.*

12. Howe, J. T., and Y. S. Sheaffer. 1964. Chemical relaxation behind strong normal shock waves in carbon dioxide including interdependent dissociation and ionization processes. NASA TN D–2131. NTIS N64–15221#.

13. Brabbs, T. A., F. E. Belles, and S. A. Zlatarick. 1963. Shock-tube study of carbon dioxide dissociation rate. Journal of Chemical Physics 38: 1939.

*14. Fristrom, R. M., and A. A. Westenberg. 1965. Flame structure, Chapter 2. McGraw-Hill Book Co., Inc., New York.

15. Gaydon, A. G., and H. G. Wolfhard. 1960. Flames, p. 137. Chapman & Hall, Ltd., London.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70–12345#).

**Recommended general sources of information.*

unit 6

unit 6

SPACE VEHICLE LUBRICATION

Topics that may be enriched by use of this unit:

- Oxides
- Sulfides
- Laminar solids
- Silicones
- Oils
- Soft metals
- Physical properties
- Friction

Our exploration of space has been accompanied by an acute need for a variety of substances that will act as lubricants under extreme conditions of temperature, pressure, load, speed, and duration of use. Scientists and engineers, especially those of NASA and their contractors, are preparing and testing lubricants to meet the wide spectrum of environments encountered in space (1, 2, 3). Before considering specific lubricants and lubricating techniques used in space travel, let us consider some of the aspects of space and space vehicles that are relevant to choosing space lubricants.

CONDITIONS AFFECTING LUBRICANTS

High Vacuum

Space, itself, is characterized by very low pressures in the range of 10^{-11} to 10^{-18} mm Hg. Under such low pressures, conventional oils and the oil components of greases evaporate very rapidly. For instance, under atmospheric pressure, a typical petroleum oil having an average molecular weight of about 1000 amu evaporates at a rate of about 1.0×10^{-12} g/cm^2/min. In the nearly perfect vacuum of space, however, the rate is about 0.25 g/cm^2/min, almost a million-million times faster (4). Even soft metals, such as copper, lead, tin, and cadmium used in bearing materials here on Earth, evaporate at significant rates in space. Vaporization of substances within space vehicles has the added disadvantage that the vapors can condense on other surfaces, such as optical and electrical equipment, thus impairing equipment or causing its complete failure. These vapors may also be toxic or simply annoying to living inhabitants of a vehicle. (See Unit 2, "Life-Support Systems.")

Another consequence of the extremely low pressures in space is that bare metal surfaces weld together when placed in contact. The more similar the metals, the more readily they cold weld. Metal surfaces do not cold weld under usual conditions on Earth because of the presence of protective oxide coatings or adsorbed gases on their surfaces. Under the low pressures in space, however, some oxide coatings decompose and adsorbed gases are desorbed, exposing the bare metal surfaces. In addition, abrasion of an oxide coating in space is not followed by regeneration of the coating as it would be in the oxidizing atmosphere of the Earth. When metal surfaces rub together in space, therefore, there is a great likelihood that they will cold weld, thus greatly increasing the frictional force between them and possibly leading to malfunction of the equipment.

Another consequence of the very low pressures in space is that the physical properties of materials sometimes change as a consequence of being outgassed, a process that removes adsorbed gases from the surfaces as well as gases dissolved in the material. Outgassing some substances, especially plastics and metals, makes them more brittle. These effects of high vacuum must be considered when selecting lubricants and components of bearings.

Extreme Temperatures

Another environmental factor that reaches extreme proportions in space missions is that of temperature. The temperature of space is effectively absolute zero; and exposed, unheated structures such as radio antennas operate at very low temperatures. Bearings and sliding electrical contacts located on the exteriors of space vehicles therefore require lubrication with substances quite different from those used even in the coldest regions on Earth. At the other extreme, very high temperatures occur inside the space vehicles. For instance, bearings of turbines and pumps in nuclear-power generators will require substances that can lubricate the structural metals at temperatures that would vaporize and char ordinary petroleum lubricants.

Corrosive Substances

Another factor that is relevant in choosing a suitable lubricant for use in space is the presence of corrosive substances. These substances include strong oxidizing agents used as liquid rocket propellants and molten alkali metals used as heat-exchanging fluids in nuclear-power generators. The pumps and valves for manipulating such substances cannot be lubricated with most conventional lubricants because of reaction of the lubricant with the corrosive materials. For instance, explosions can occur when petroleum oils are placed under impact in the presence of strongly oxidizing rocket propellants; thus, failure of bearing seals or even normal creepage of petroleum oils could cause failure of a mission. Suitable lubricants must also be resistant to the chemical environment of the rocket during prelaunch storage and testing and during launching.

Other Aspects

The relative speeds of rubbing lubricated surfaces are also extreme in space systems. For instance, some structural surfaces of a space vehicle occasionally slide against each other, whereas other rubbing surfaces are found in mechanisms that operate at speeds up to hundreds of thousands of revolutions per minute. Loads also vary from hundredths of a pound to hundreds of pounds or larger. A complicating feature of space travel is that the load of a bearing may vary considerably in the prelaunch, launch, and space environments. Thus, lubricants and bearings that are suitable for the zero-gravity environment of space must withstand the extreme pressures, loads, and vibrations encountered in moving components to the launch site and launching the assembled vehicle.

Most importantly, the lubricated mechanism must not fail to perform its function. Whether the useful lifetime of a mechanism is measured in seconds or thousands of hours, the reliability of the mechanism is essential. Even if lubricant failure in space did occur at a time when repair of the lubricated mechanism was possible, the weight penalty of stocking spare parts aboard the space vehicle is prohibitive. Therefore, careful specification and extensive testing of components by NASA space scientists are necessary under simulated prelaunch, launch, and space conditions. Parts of space vehicles that are left in a worn condition following testing are replaced by equivalent ones for the actual mission in space.

Reducing the weight of a space vehicle is relevant to lubrication problems in several ways other than that mentioned in the preceding paragraph. One of these is that by lowering the amount of friction in a mechanism, the power requirements of the mechanism are also lowered. This, in turn, lowers the physical size and weight of motors, connecting shafts, bearings, and associated hardware as well as the power requirements of the spacecraft as a whole. Weight and size penalties are also important when considering use of a recirculating lubricating system, which requires a reservoir of lubricant, pumps, flow regulators, ducts, and possibly a heat exchanger. These components not only increase the size and weight of a lubrication system but also increase the possibility of its malfunction. The problem faced by NASA system designers, therefore, is to provide mechanisms of maximum reliability and minimum power requirement, size and weight.

TECHNIQUES OF LUBRICATION

Now that we have considered some of the demands placed on lubricated systems in space vehicles, let us discuss two main techniques of lubrication used in space vehicles: those of thick- and thin-film lubrication.

Thick-Film or Fluid Lubrication

Thick-film lubrication is known more commonly as hydrodynamic or hydrostatic lubrication, depending on whether the fluid pressure is maintained by the lubricated mechanism itself or by external means, respectively. It occurs when bearing surfaces are held sufficiently far apart by the lubricant that irregularities or asperities in the bearing surfaces do not come into contact with each other. In a journal bearing, for instance, the rolling surface moves up onto a layer of lubricant continuously so that there is no metal contact on the bearing surfaces. (An analogy is the beach surfing done on the thin layer of water from a receding ocean wave.) Bearing surfaces also may be held apart by magnetic, electrostatic, or acoustical forces; because no lubricant is used, these bearings will not be discussed.

Thick-film lubricated bearings are machined with great precision so that a lubricant film of proper thickness is maintained between the bearing surfaces during operation of the mechanism (Figure 6-1, from Grassam and Powell (5)). The pressure within the lubricant can be maintained by the lubricated mechanism itself or by some external method. In any event, the lubricant carries the load (Figure 6-2); and, therefore, the properties of the lubricant are of primary importance in thick-film lubrication. These properties include viscosity; liquid range, if the fluid is a liquid; temperature tolerance; and reactivity with the bearing materials.

In thick-film lubrication the lubricant must remain sufficiently viscous during operation that the bearing surfaces do not come into contact with each other. Nevertheless, typical thick-film lubricants have low viscosities and are almost ineffective lubricants under the conditions of thin-film or boundary lubrication (Figure 6-2). Gas lubricants, such as air or nitrogen, and liquid lubricants, such as sodium and mercury, commonly provide little protection for bearing surfaces in contact. This is especially important during startup and shutdown of mechanisms having bearings lubricated hydrodynamically. Hydrostatically lubricated bearings have the advantage of preventing boundary lubrication during these same periods but have the inherent disadvantages of increased weight and complexity. Contact between the bearing surfaces can also occur during periods when

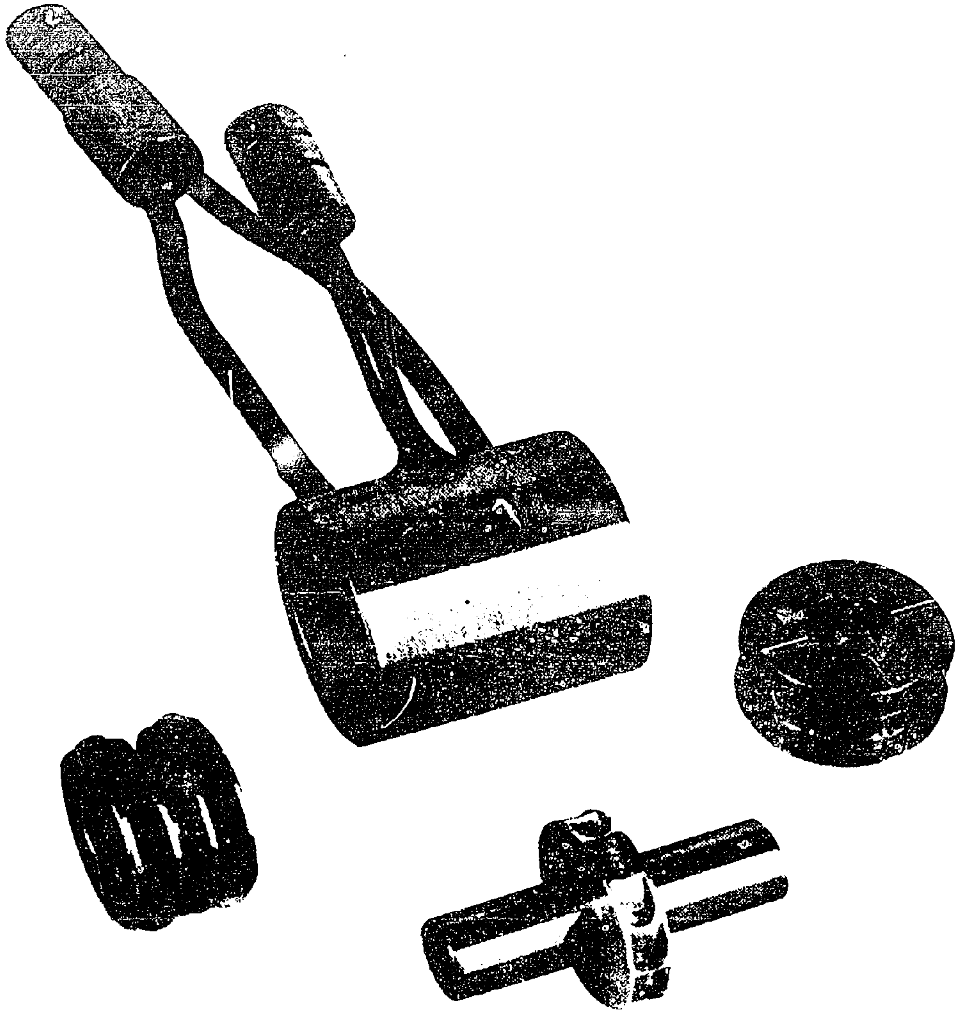
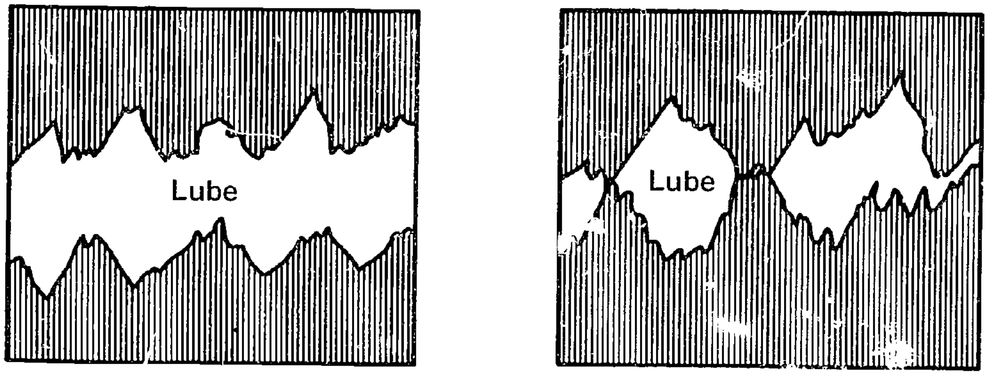


FIGURE 6–1. *A small experimental air turbine having air-lubricated journal and thrust bearings (5). No contact normally occurs between the bearing surfaces when the turbine is rotating.*



Thick-film lubrication

Thin-film lubrication

FIGURE 6–2. *Thick-film and thin-film lubrication. Asperities in the bearing [illegible] do not come into contact with each other during normal operation of a thick-film lubricated bearing.*

a space vehicle experiences high levels of acceleration and vibration or during instabilities in the flow of the lubricant. A partial answer to these problems is to operate the bearing only under conditions where the lubricant has the necessary physical properties and remains stable. In addition, the bearing surfaces can be coated with a thin film of a suitable boundary lubricant to reduce the friction and damage occurring during periods of boundary lubrication.

A second important property of a thick-film lubricant, if it is a liquid, is its liquid range. Long liquid ranges such as those of sodium (m.p. 90° C and b.p. 887° C) and gallium (m.p. 30° C and b.p. 1980° C) allow a thick-film lubricated bearing using one of these substances as a lubricant to operate over a wide temperature range. This can be a great advantage in nuclear-power generator systems where such liquids can serve both as the heat-exchanging fluid and as the lubricant for the bearings of the circulating pumps (6).

As might be expected, the temperature tolerance of a thick-film lubricant is important. The lubricant should not decompose at the working temperature of the lubricated mechanism. This limitation can be circumvented partially if the lubricant is not recirculated but is discarded after it passes through the bearing. In many space applications, however, the "once-through" approach would require prohibitive amounts of lubricants. Nevertheless, the once-through method is well adapted to lubrication of the pumps that force liquid propellants into the combustion chambers of liquid-propellant rocket engines. (See Unit 3, "Chemical Rocket Propellants.")

Another consideration in selecting thick-film lubricants is the reactivity of the lubricant with the bearing surfaces. In general, reactions are of two types: oxidation and reduction. Some potential thick-film lubricants, such as liquid metals and hydrogen, reduce the naturally occurring oxide coatings on bearings, thereby increasing the damage occurring during periods of boundary lubrication. Other potential thick-film lubricants, such as liquid N_2O_4 and O_2, are oxidants that can corrode the surfaces of bearings. This is especially serious in the case of thick-film lubrication because slight changes in the geometry of the bearing increase the likelihood of bearing failure.

In spite of these limitations, thick-film lubricated bearings have several advantages. First, they provide minimum friction. This is because the bearing materials do not come into contact with each other, and therefore the frictional force is caused only by the low shear forces in the lubricant. Typically, coefficients of friction (i.e., the ratio of the frictional force to the load) are on the order of 0.001. This allows operation of these bearings at speeds of several thousand revolutions per minute, making them useful components of gyroscopes in guidance systems. Thick-film lubricated bearings have another important attribute. Because of the fluid nature of the lubricant and the bearing design, the rotating member of the bearing is somewhat protected from vibration and rapid acceleration. That is, the lubricating fluid damps oscillations in the rotor produced by changes in the motion of the space vehicle. This property of thick-film lubricated bearings is especially beneficial during the prelaunch assembly and testing of the vehicle and during the critical conditions of launching.

Thin-Film or Boundary Lubrication

Thin-film lubrication occurs whenever the film of lubricant between surfaces is squeezed out until the two surfaces come into physical contact with each other (Figure 6–2). Actually, the points of contact have a total area much less than the apparent area of contact. This is because, regardless of how smooth the surfaces appear even when examined under an optical microscope, there is considerable roughness. This roughness is shown diagrammatically in Figure 6–2, and profilometer traces of actual bearing surfaces are shown in Figure 6–3 (from Kragelskii

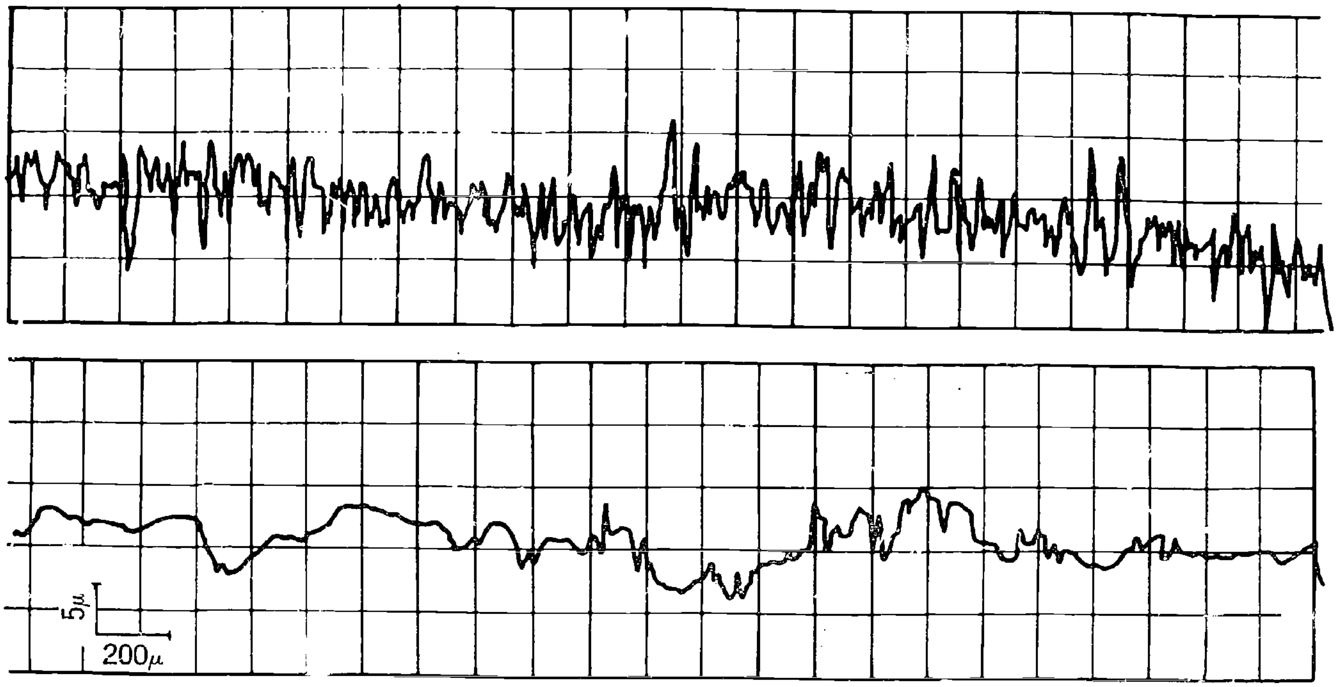


FIGURE 6–3. *Profilometer traces indicating the asperities of a ground steel surface. The two traces were made on the same sample in two directions at right angles to each other (7).*

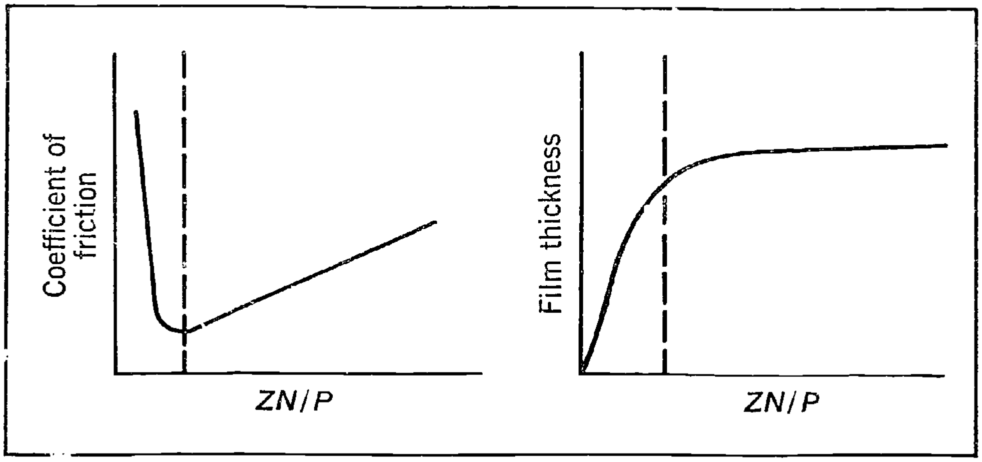


FIGURE 6–4. *Coefficient of friction and film thickness as a function of the parameter* ZN/P (8). *Boundary lubrication occurs to the left and fluid lubrication to the right of the dashed line in each figure. Decreasing* ZN/P *favors boundary conditions.*

(7)). When the asperities on two surfaces moving relative to each other come into contact, increased friction and wear occur. Figure 6–4 (from Bisson and Anderson (8)) indicates how the frictional force increases as the thickness of the lubricant film is decreased. The commonly used parameter ZN/P in Figure 6–4 includes the following variables: The viscosity of the lubricant Z; the relative speed of the two surfaces N; and the load carried by the bearing, or the bearing pressure P. As is noted in the figure, the occurrence of boundary lubrication is favored by low lubricant viscosities, low speeds, and large loads.

The rapid increase in the coefficient of friction with decreasing ZN/P can be considered to result from the shearing of welded junctions at the points of contact and from the plowing out of the softer surface by asperities of the harder surface (8). (Bearing surfaces are often made with one surface softer than the other.) The results of these two effects are shown in Figure 6–5 (from Sliney, Strom, and Allen (6)). Neglecting the fluid drag in regions between two surfaces where thick-film lubrication occurs, the frictional force can be taken as the sum of these two effects:

$$\text{Frictional force } F = \text{shear} + \text{plowing}$$

The shear force is equal to the shear strength of the welded junctions s times the area of these junctions A. The plowing contribution to the frictional force can be written as the product of the compressive yield strength or flow pressure p times the effective area over which plowing is occurring A'.

$$F = \text{shear} + \text{plowing} = As + A'p$$

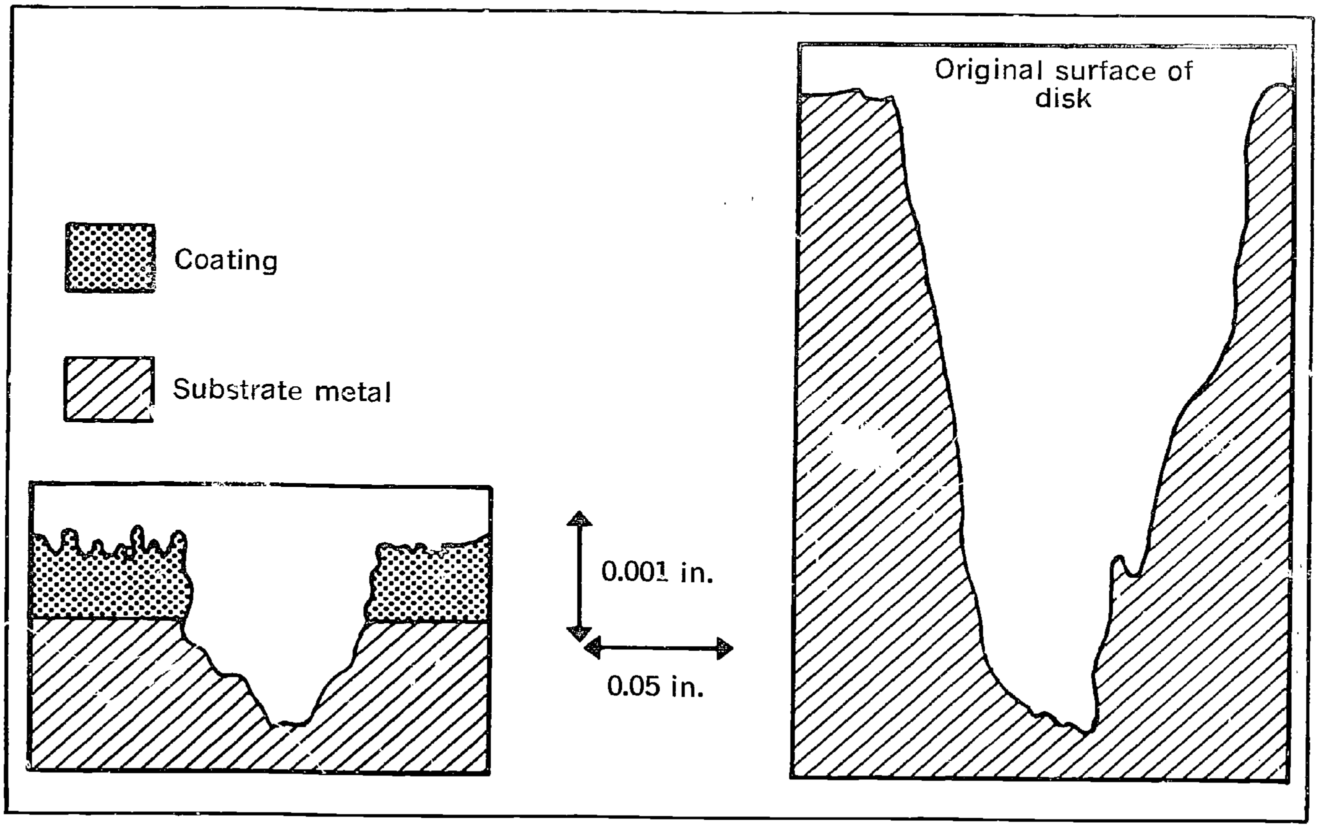


FIGURE 6–5. *Wear profiles in metal surfaces for coated and uncoated samples given similar treatment (6).*

Because the plowing term is much smaller than the shear term we can write

$$F \approx As$$

The area of the welded junctions depends on the load the bearing is carrying W and the flow pressure of the softer material according to the equation

$$A = \frac{W}{p}$$

That is, the area of contact increases with increasing load and increasing softness or decreasing flow pressure of the softer of the two surfaces. For a given load, this phenomenon is illustrated in Figure 6–6. Substituting the expression for A into that for the frictional force gives

$$F \approx As = \frac{Ws}{p}$$

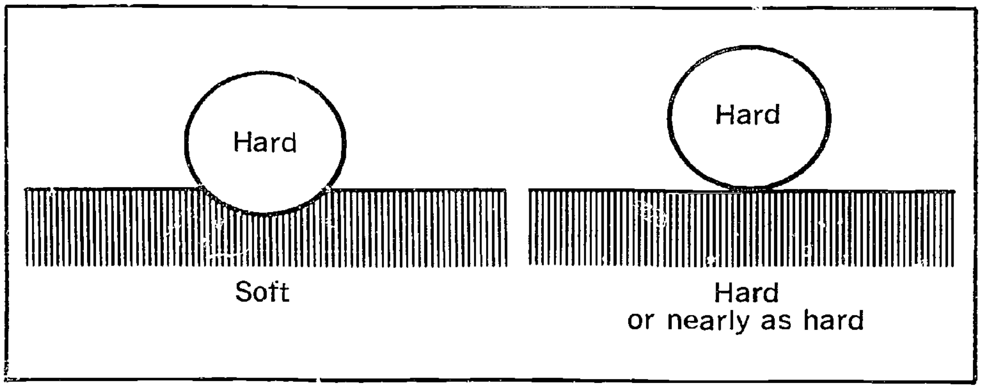


FIGURE 6–6. *Effect of flow pressure on area of contact. The area of contact increases with increasing softness of one or both of the materials.*

or, because the coefficient of friction f is defined as

$$f = \frac{\text{frictional force}}{\text{load}} = \frac{F}{W}$$

then (8)

$$f \simeq \frac{s}{p}$$

This equation has important implications. It tells us that for a particular load we can reduce the coefficient of friction for two surfaces by reducing the sheer strength of the welded junctions and by increasing the flow pressure of the softer material. Because no one material has both of these properties, reduction of the ratio s/p can be achieved in practice by coating one of two hard surfaces with a thin coat of material having low shear strength. Thereby, the load is supported without severe deformation of the coating, and welded junctions occurring between the hard and soft surfaces have low shear strength (Figure 6–7).

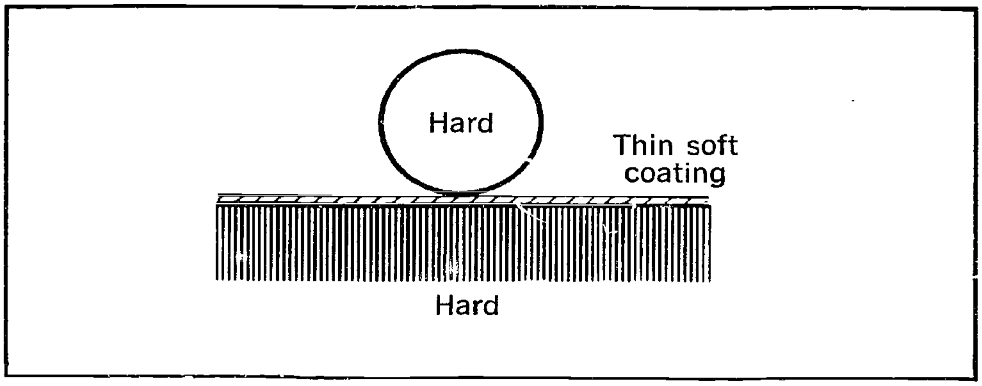


FIGURE 6–7. *Use of thin coatings of soft materials as lubricants. The thin, soft coating is supported by a harder substrate to reduce the area of contact of the surfaces. Use of the soft coating lowers the shear strength of the welded junctions.*

In general, the more dissimilar (less soluble) the rubbing surfaces are, the less tendency there is for them to weld to each other. For instance, metal surfaces can be paired with those of polymers, ceramics, or cermets.

THIN-FILM LUBRICANTS

Thin films acting as lubricants can be composed of oxide coatings and other chemical compounds of the metal substrate; fluid lubricants including oils; laminar solids; soft metals; plastics; and cermets and ceramics.

Oxide Coatings

Oxide coatings are present on metal surfaces even if the surrounding atmosphere contains only small amounts of oxygen. These oxide coatings protect the substrate metals against cold welding but, in general, do not give low coefficients of friction. Nevertheless, oxide coatings that decompose in the nearly perfect vacuum of space or become displaced through wear are not regenerated in space as they are in the presence of the Earth's atmosphere. In addition, other gases that normally would be adsorbed on metal surfaces that are exposed to the Earth's atmosphere also are removed in the vacuum of space. In this degassed condition, metals readily cold weld (9). This is of concern in sliding electrical contacts, hatches, slip joints, docking space vehicles, and other situations where metal surfaces rub together in the high vacuum of space. Because oxygen gas is present in the cabins of manned space vehicles, metal surfaces in the cabins are protected against cold welding. Protective oxide coatings are also present on the metal surfaces of thick-film lubricated bearings using air, liquid oxygen, or other oxygen-containing fluids as lubricants. These coatings are especially important during startup or shutdown of the system when the bearing surfaces may come in contact.

Oxides are not the only compounds of the substrate metals that can be useful in reducing wear. Chlorides and especially sulfides of the substrate metals can serve as thin-film lubricants. An interesting example is provided by the inclusion of elemental sulfur or chlorine in fused salts used as thick-film lubricants. The dissolved sulfur or chlorine reacts with the substrate, giving a more wear-resistant layer than the substrate itself. Should the protective layer be abraded during operation of the mechanism, the dissolved reactants can combine with the bare substrate to regenerate the protective coating (10). Compounds of the substrate that have a laminar structure have especially good lubricating qualities.

Fluid Lubricants

Many thin-film fluid lubricants used in ground systems are based on petroleum products. Conventional petroleum oils and greases find restricted use in space, however, because of the effects of high vacuum, extreme temperatures, and penetrating radiation. The use of hermetically sealed bearings overcomes the evaporation problem caused by the low pressures in space but adds weight to the bearing mechanism and increases its complexity. Labyrinth seals on bearings also can reduce lubricant losses (11). These seals are constructed with intricate paths through which the lubricant must pass in order for it to escape from the bearing. Labyrinth seals allow use of petroleum oils in greases for space missions of up to several months' duration. In spite of the high-temperature degradation of petroleum products, the lubricating and cooling properties of petroleum oils can sometimes still be taken advantage of if the lubricant is discarded after it passes through the lubricated mechanism. For instance, a heat-sensitive oil can be atomized and carried through a bearing with a flow of gases.

In addition to developing improved petroleum-based lubricants and better seals, NASA scientists are studying synthetic oils and greases including those based on silicones. There are silicone-based oils that not only have lower vapor pressures but are more resistant to high temperatures and penetrating radiation than their petroleum-based counterparts. For instance, phenyl methyl silicone oil in grease can lubricate lightly loaded bearings in the wide temperature range of −54° to 500° C and is resistant to damage by radiation.

Other fluid lubricants include molten alkali metals and mercury. These metals are potential lubricants in nuclear-power generators where they serve as the heat-exchanging fluids. Mercury and molten alkali metals do not yield favorable coefficients of friction, but the lubricating qualities of mercury can be improved significantly by inclusion of molybdenum disulfide MoS_2 (10). Molten salts have also been investigated for use as fluid lubricants, but in general they are more corrosive than metals such as rubidium and mercury.

Laminar Solids

Laminar solids such as graphite are used widely as thin-film lubricants. The lubricating properties of these substances result from the [illegible] ear strengths existing between particular planes in their [illegible] al lattices. It is interesting to note, however, that the lubricating properties of graphite are dependent on the presence of small amounts of adsorbed substances such as water or ammonia (2). Use of graphite as a lubricant in space is restricted, therefore, to compartments where a sufficient vapor pressure of one or more of these substances occurs. Exposed to the high vacuum of space, graphite not only loses its lubricating qualities but may become abrasive instead. Fortunately, there are laminar solids that retain their lubricating properties in the extreme environment of space. One of these is molybdenum disulfide, a common additive to commercial petroleum-based lubricants.

Molybdenum disulfide has several properties that make it widely applicable as a lubricant. It has a low coefficient of friction that remains nearly constant in the temperature range − 70° to 340° C, and it is also stable under conditions of high radiation and high vacuum. As is the case for solid lubricants in general, however, molybdenum disulfide does not remove heat from the friction zone. Retention of heat at points where rubbing surfaces are in contact can generate local temperatures beyond that required to decompose this lubricant. Laminar solids that have a higher temperature tolerance than MoS_2 include PbO and PbS. For instance, PbO has good lubricating properties in the range 390° to 540° C.

A film of MoS_2 can be established on a surface by brushing, burnishing, spraying, and other similar methods. If the MoS_2 does not adhere well to the substrate, it can be mixed with bonding agents such as Na_2O, Ag, Mo, SiO_2, or various silicates before application. Addition of the bonding agent generally increases the coefficient of friction of the film, but more importantly it increases its resistance to wear.

A film of MoS_2 can be maintained on bearing surfaces in several interesting ways. For instance, if one of a pair of rubbing surfaces is a plastic material, MoS_2 can be mixed with the monomer before it is polymerized and shaped. As the plastic component wears, freshly exposed MoS_2 is added to the bearing surfaces. Molybdenum disulfide also can be included in the matrices of some metals. For metals fabricated at temperatures high enough to decompose the lubricant, the MoS_2 can be placed in pits or grooves in the bearing surface. In mechanical systems in which there is a flow of gases such as a gas turbine, appropriate amounts of MoS_2 can be bled into the gas stream and carried to any bearings that are bathed by the gas flow. Still another method involves chemically regenerating the lubricant on the bearing surfaces. In cases where the substrate metal is molybdenum, sulfur-containing compounds such as hydrogen sulfide or carbon disulfide can be introduced periodically into the bearing mechanism where they react with the substrate to give MoS_2. Thus, the MoS_2 is restored on surfaces from which it was removed previously by wear. Within the limitations imposed by the properties of the materials, these methods also can be used in supplying other types of lubricants to bearing surfaces.

Soft Metals

Another group of materials that have good lubricating qualities are soft metals. For thin-film applications, soft metals such as gold, silver, cadmium, zinc, lead, and tin are supported by hard substrates (12). The soft metals provide low shear strengths and the hard substrates keep the area of contact between the rubbing surfaces small. Of the metals listed, however, only gold and silver do not evaporate significantly under the low pressures in space. As lubricants, gold and silver have the added advantages of being temperature tolerant to about 540° C and stable to penetrating radiation.

Thin films of soft metals can be established on substrate metals in several ways, including burnishing, vacuum deposition (13), and electrochemical plating either by immersion or electrolysis. In any case, good adhesion of the film to the substrate is essential for obtaining long-wearing coatings. This need places extreme requirements on the preparation of the substrate surface. In general, the more soluble the substrate and soft metal are in each other, the stronger is the adhesive bond formed between them. If the soft metal does not adhere sufficiently to the substrate, several other methods can be used to supply the soft-metal lubricant to the bearing surfaces. The soft metal can be placed in indentations in the surface of the bearing or mixed with the substrate material before the bearing is fabricated. In either case, a thin film of the soft metal is maintained on the bearing surfaces as they wear. If the substrate is a plastic material, inclusion of a metal in the plastic matrix has the added advantage that its presence improves the heat-conducting properties of the plastic. This reduces the localized high temperatures caused by friction that are typical of plastic bearings even when used under moderate speed and load conditions.

Plastics

Plastics have several properties that make them useful components of bearings. Most importantly, many plastics have low coefficients of friction when paired with metals. In addition, plastics have relatively low densities compared to metals; this is of particular importance for space missions where weight is an important consideration. Nevertheless, plastics are poor conductors of heat, and frictional heat can cause their degradation. This danger can be lessened by inclusion of soft metals or by backing thin layers of plastics with metal to conduct away the heat. Because many plastics having good lubricating properties do not form a strong bond to metals, use of plastics as lubricants sometimes involves other methods. For instance, the lubricant, often Teflon (polytetrafluoroethene or nylon, can be powdered and supplied dry to gears and bearings. Plastic materials also may be included in cavities in metal bearing surfaces or in the matrices of substrates. The latter method is often difficult in practice because of the characteristically high fabrication temperatures of metals as opposed to the low-temperature resistance (often 90° to 140° C) of plastics. Plastics also have the disadvantages of higher thermal expansion and poorer radiation stability than many other types of lubricants. Nevertheless, the self-lubricating properties of plastics such as Teflon and nylon make them very desirable lubricants or structural materials for bearings used under low-load and low-speed conditions. In general, oils, laminar solids, and soft metals can improve the coefficients of friction of plastics, but Teflon has such a low coefficient of friction that it often is used alone.

Cermets, Ceramics, and Other High-Temperature Lubricants

Certain carbides, intermetallics, cermets, and ceramics are potential lubricants for use at very high temperatures in the range 540° C to in excess of 1100° C. Carbides of tungsten, titanium, and chromium can be used for temperatures to 800° C; and silicate-based ceramics are being studied for use to 1100° C. Coatings of cermets, such as a mixture of chromium and alumina, can be used as lubricants at temperatures in excess of 1100° C. All of these materials and the substrate metals must be resistant to high-temperature deformation to allow for proper functioning of bearings under extreme temperatures. In theory, some high-temperature alloys such as the Ni and Co superalloys can be used for lubricative coatings as well as for substrate metals. However, it has been found difficult to prepare alloys that are resistant to oxidation and embrittlement at such high temperatures. The lubricating properties of intermetallics, graphite, and some ceramics in the temperature range 1100° to 1600° C are being studied (14).

LUBRICANT TESTING

Potential space lubricants are synthesized and screened in various NASA laboratories. After a potential lubricant has passed tests under simulated space conditions, it is tested in space itself. One of the purposes of Rangers 1 and 2 was to test a variety of space lubricants. It was found that the lubricating qualities of some substances in space differed considerably from those observed even under simulated space conditions here on Earth (15). Considerable care is necessary in selecting and testing potential space lubricants in order that the weight and size of lubricated mechanisms are minimized and the reliability optimized.

ACTIVITIES

Space scientists pay considerable attention to reducing friction and protecting materials in space vehicles from abrasion. This requires a continuing search for lubricants that function properly under extreme ranges in temperature and pressure. Although testing lubricants under extreme conditions requires special apparatus, several experiments follow that illustrate lubrication testing procedures.

Even though the nature of friction is not understood completely, we can examine ways to reduce friction through lubrication. Some aspects of lubrication can be investigated using simple equipment for finding the magnitude of starting and sliding frictional forces. Then one can attempt to relate the reduction of frictional forces to the properties of particular lubricants such as viscosity, molecular structure, and adhesion.

COMPARISON OF FRICTIONAL FORCES AND COEFFICIENTS OF STATIC FRICTION

Place two similar rectangular blocks side by side on a smooth metal or wooden slab 2 to 3 ft in length and wide enough to have about 2 in. between the blocks. With the blocks at one end, the slab is tilted as shown in Figure 6–8 until the blocks begin to

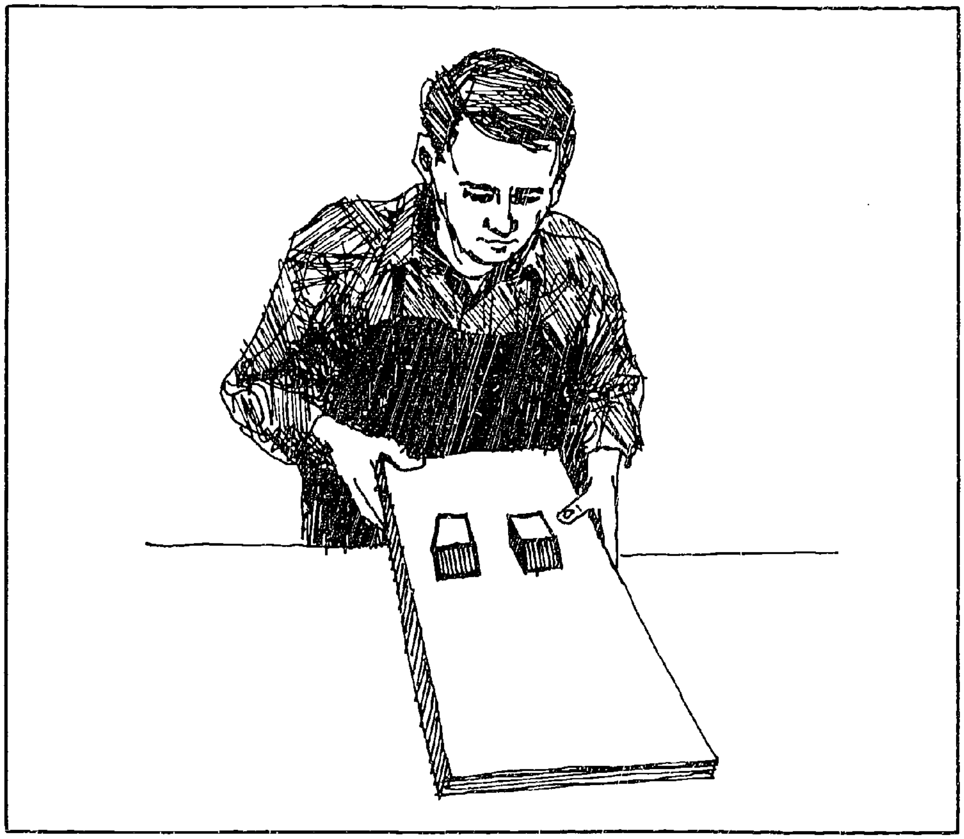


FIGURE 6–8. *Inclined-plane method for testing lubricants. One of a pair of similar blocks is coated with a potential lubricant. The order in which the blocks begin to slide is noted as the angle of the inclined plane is increased.*

slide. The frictional force on one block can then be replaced by that within a potential lubricant by coating one side of the block and one side of the slab with the lubricant. The slab is tilted and, by observing the order in which the blocks begin to slide, one can qualitatively compare the frictional forces. Pairs of lubricants can be compared in a similar manner. Care should be used in cleaning the rubbing surfaces when changing lubricants.

The maximum frictional force, the force just before a block begins to slide, is equal to the product of the coefficient of static friction and the force normal to the slab that is caused by the weight of the block. Knowing the weight of a block and the angle of the slab from a horizontal line when the block just begins to slide, one can calculate the frictional force and the coefficient of static or starting friction.

$$\text{Coefficient of static friction} = \frac{\text{frictional force}}{\text{load (normal to plane)}}$$

$$= \text{tangent of the angle the inclined plane makes with the tabletop}$$

For a particular block, lubricants can then be compared more quantitatively.

Lubricants that are particularly suitable to these experimental methods are liquids, suspensions of solids in liquids, or solids that easily adhere to the surfaces to be lubricated. One can use alcohols, water, or benzene in pure form; mineral oil or glycerin in pure forms or as carriers for lamellar solids such as MoS_2 and graphite; or solids such as powdered plastics.

DETERMINATION OF FRICTIONAL FORCES AND COEFFICIENTS OF SLIDING FRICTION

An experimental setup that is especially suitable for determining sliding frictional forces is depicted in Figure 6–9. A metal block or weighted wooden block fitted with a screw eye is connected to a weight hanger by a string passing over a pulley. (A metal can suspended from the string can replace the weight hanger; sand or water can be added to the can to vary its weight.) Sufficient weight is added to the hanger so that the block continues to move at a uniform speed once it is given a push to overcome the static frictional force. Again, potential lubricants are compared by contrasting the values obtained for frictional forces or coefficients of sliding friction. This setup can also be used to determine starting frictional forces.

The lubricating qualities of a particular substance such as mineral oil can be studied. Interestingly, mineral oil has better lubri-

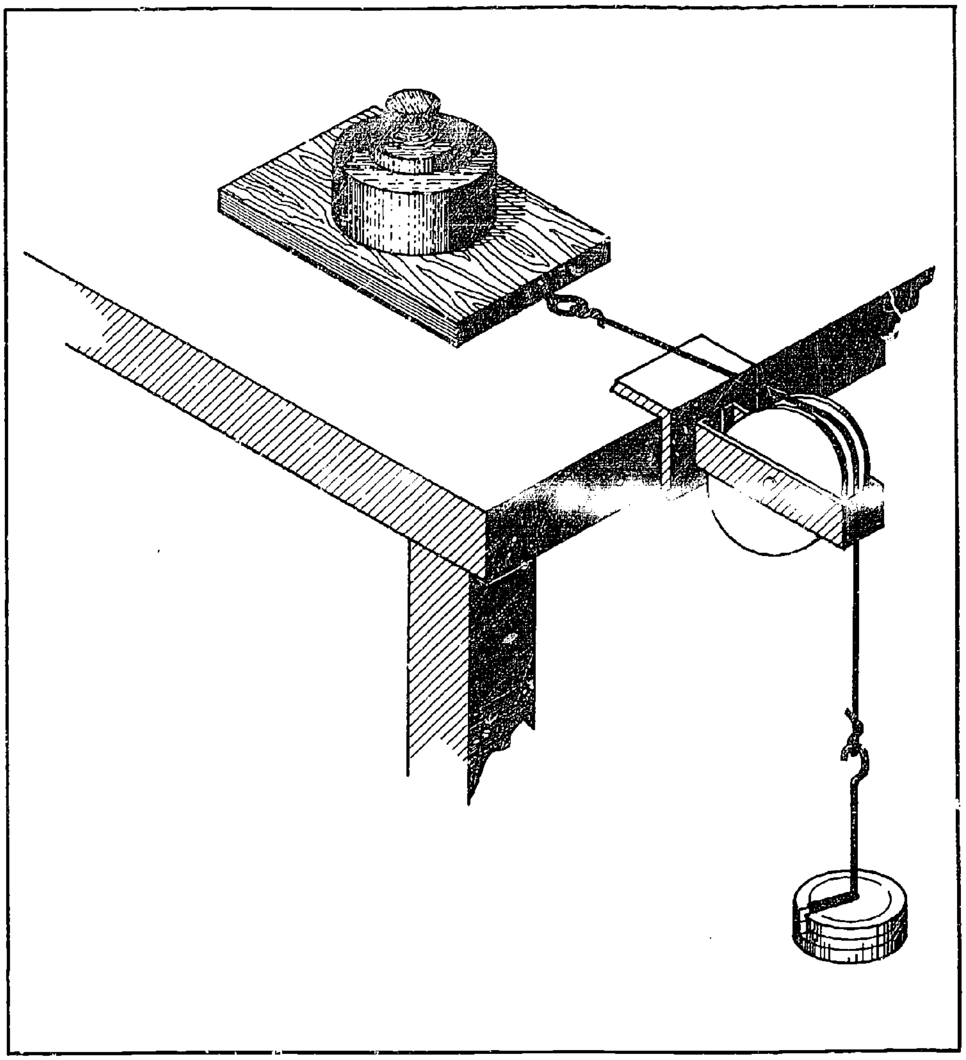


FIGURE 6–9. *Determination of coefficient of friction in the presence of various lubricants. The test block is lubricated, loaded, and caused to slide at a uniform rate by adding an appropriate amount of weight to the weight hanger.*

cating qualities when it has had considerable contact with air. The acids that are formed in contact with air and that enhance its lubricating qualities can be removed by passing the oil through fuller's earth and filtering.

In using the apparatus, solid lubricants such as graphite or liquid lubricants such as silicones can be simply spread on cleaned sliding surfaces, while metals such as lead and gold can be deposited electrolytically. A rather interesting technique, a Langmuir trough, for adding monomolecular layers of lubricants to a substrate can be illustrated with stearic acid. Stearic acid is allowed to spread over the surface of distilled water in a tray. When the acid has its maximum spread as controlled by a movable barrier, a layer of the acid is transferred to the friction block by bringing the block in contact with the acid. The cycle can be repeated several times, and the effectiveness of lubrication can also be studied as a function of the thickness of the lubricant.

TOPICS FOR THE DEVELOPMENT OF ADDITIONAL ACTIVITIES

If machine-shop tools are available, a variety of other lubrication tests are possible. For instance, a single ball bearing resting in a pocket formed from three other balls in mutual contact can be turned by a drill press. The load can be varied, and even measured with a spring scale or weights on the press handle. The ball bearing should be of the common specification SAE 52100. Qualitative results including variation of temperature and pressure can be made by using an optical microscope to study the striations produced on the balls. In addition, the turning shaft of a small electric motor can be slowed by a clamp operated like a nutcracker. Bearing surfaces and lubricants can be tested by measuring the force required on the clamp to stop the motor.

LITERATURE CITED

*1. Bisson, E. E., and W. J. Anderson. 1964. Advanced bearing technology, Chapter 1. NASA SP-38. GPO, $1.75.

*2. Johnson, J. H., and A. S. Irwin. 1962. Survey of frictional problems in spacecraft. NASA CR-58704. NTIS N64-29508#.

*3. Clauss, F. J., and W. C. Young. 1965. Materials for lubricated systems, Chapter 12. *In* C. G. Goetzel, J. B. Rittenhouse, and J. B. Singletary, Space materials handbook. Addison-Wesley Publishing Co., Inc., Reading, Mass.

4. Salmon, W. A., and H. Scammell. 1962. Proceedings of a symposium on lubrication in space, Section 1. Baird-Atomic, Inc., and Arthur D. Little, Inc., Cambridge, Mass. NTIS N64-19952#.

5. Grassam, N. S., and J. W. Powell. 1964. Gas lubricated bearings, p. 154. Butterworths Science Publishers, London.

6. Sliney, H. E., T. N. Strom, and G. P. Allen. 1964. Fused fluoride coatings as solid lubricants in liquid sodium, hydrogen, vacuum, and air. NASA TN D-2348. NTIS N64-26414#.

**Recommended general sources of information.*

7. Kragelskii, I. V. 1965. Friction and wear, p. 35. Butterworths Science Publishers, London.

8. Bisson, E. E., and W. J. Anderson. 1964. Advanced bearing technology, pp. 16–19. NASA SP–38. GPO, $1.75.

9. Moeller, C. E., J. Bossert, and M. Noland. 1966. Cold molecular welding study in ultra-high vacuum. NASA CR–65390. NTIS N66–28544#.

10. Tynnyy, A. N., M. I. Chayevskiy, and V. A. Telerskiy. 1962. The feasibility of the use of liquid-metal fusions as lubricants (trans.). Foreign Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. NTIS N64–16427#.

11. Salmon, W. A., and C. M. Apt. 1962. A lubrication system for space vehicles, p. 97. *In* W. A. Salmon and H. Scammell, Proceedings of a symposium on lubrication in space. Baird-Atomic, Inc., and Arthur D. Little, Inc., Cambridge, Mass. NTIS N64–81875#. [Reprint]

12. Rabinowicz, E., M. Imai, and V. Santos. 1963. Friction and wear at elevated temperatures. RTD–TDR–63–4272, Part 5. Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base. NTIS N64–17513#.

13. Spalvins, T., and D. H. Buckley. 1965. Vapor-deposited thin gold films as lubricants in vacuum (10^{-11} mm Hg). NASA TN D–3040. NTIS N65–34221#.

14. Abbott, H. M. 1963. Gears, bearings, and lubricants for aerospace applications: an annotated bibliography, entry 5. Lockheed Missiles & Space Co., Palo Alto, Calif. NTIS N64–24921#.

15. Rittenhouse, J. B., J. B. Singletary, and H. M. Abbott. 1965. Spacecraft materials experience, pp. 498–500. *In* C. G. Goetzel, J. B. Rittenhouse, and J. B. Singletary, Space materials handbook. Addison-Wesley Publishing Co., Inc., Reading, Mass.

OTHER REFERENCES

Adams, J. L. 1965. Space technology: Vol. II, Spacecraft mechanical engineering, Chapter 9. NASA SP–66. GPO, $0.60.

Campbell, M. E., J. B. Loser, and E. Gneegas. 1966. Solid lubricants. NASA SP-5059. GPO, $0.50.

Johnson, R. L., D. H. Buckley, and M. A. Swikert. 1964. Studies of lubricating materials in vacuum. NASA TM X-52009. NTIS N65-35475.

Plunkett, J. D. NASA contributions to the technology of inorganic coatings, Chapter 3. NASA SP-5014. GPO, $1.00.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70-12345#).

unit 7

unit 7

OPTICAL COATINGS FOR TEMPERATURE CONTROL OF SPACE VEHICLES

Topics that may be enriched by use of this unit:

- Absorption and emission of electromagnetic radiation
- Temperature
- Heat energy
- Energy transfer
- Aluminum
- Ceramics
- Paints
- Corrosion

Regulation of the temperature of a space vehicle is a complex problem because extreme temperatures are encountered during a typical mission in space. Although gas particles in space are found in excited states and thus are not at a temperature of absolute zero, they are so sparse as to cause an object in space to behave as if it were in an absolute zero environment. Nevertheless, local temperatures in and about space vehicles can be quite high. The problem of temperature control is made more complex by the fact that a space vehicle may be in drastically different temperature environments during various portions of a mission. Consequently, space scientists are developing methods for maintaining the entire spacecraft and the components of spacecraft within suitable ranges of temperature (Figure 7-1).

Maintaining temperatures in any multifunctional structure requires regulating the gross intake and output of energy, plus creating local temperature environments within the structure. This problem is solved in an ordinary dwelling in the winter by balancing the gross release of energy within the structure with the energy losses to the surroundings. By combining heat energy sources, such as the combustion of fossil fuels, with radiative, conductive, and convective methods of heat transfer, the rate of heat loss is balanced so that temperatures in the range of 20° to 25° C are achieved. Of course, higher or lower temperatures are desirable in small regions such as a freezer or oven. These are achieved by heat pumps or conversion of other forms of energy into heat. Heat shielding protects the remaining

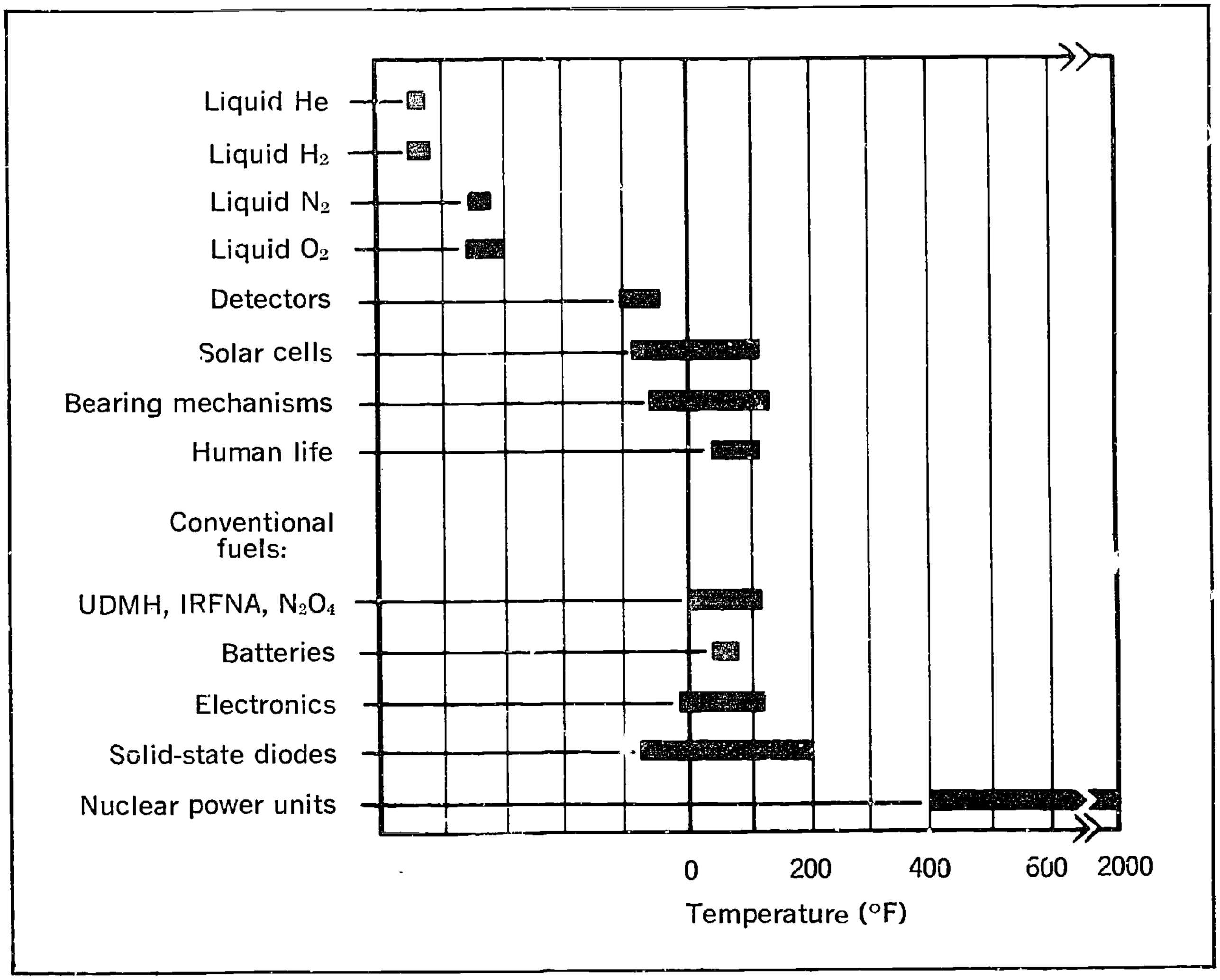


FIGURE 7–1. *Temperature tolerances of typical spacecraft components (1).*

living quarters from these temperature extremes and increases the efficiency of maintaining high- and low-temperature regions.

The basic problem of maintaining the temperature of spacecraft is much like that illustrated with the dwelling but with at least two major differences. First, any major sources of heat energy in the spacecraft at launching provide a considerable weight disadvantage for the mission. Second, space is characterized by extremely low gas pressures and, consequently, the transfer of heat between a spacecraft and its surroundings is essentially by radiation. In this unit we shall consider how surface treatments are used to help determine spacecraft temperatures.

Within the solar system a spacecraft receives electromagnetic radiation directly from bright stars, predominately from the Sun, and in the form of reflected sunlight (albedo) and infrared emission from large nearby bodies, such as planets and moons (Figure 7–2). The fraction of incident radiation absorbed by the spacecraft depends on the nature of its surface and the quality or wavelength distribution of the incident radiation. The energy received by a spacecraft from its surroundings in addition to that liberated from nuclear, chemical, mechanical, and electrical processes occurring within the spacecraft itself is dissipated into space in the form of infrared radiation. The quantity and quality of this emission are determined by the natures of the surfaces of the spacecraft and by their temperatures.

Within limits, the balance between the amounts of energy absorbed and emitted by an object in space often can be regulated by selection of its surfaces. Because a variety of temperature environments must be provided in a typical spacecraft, optical requirements of the surfaces are often determined for each

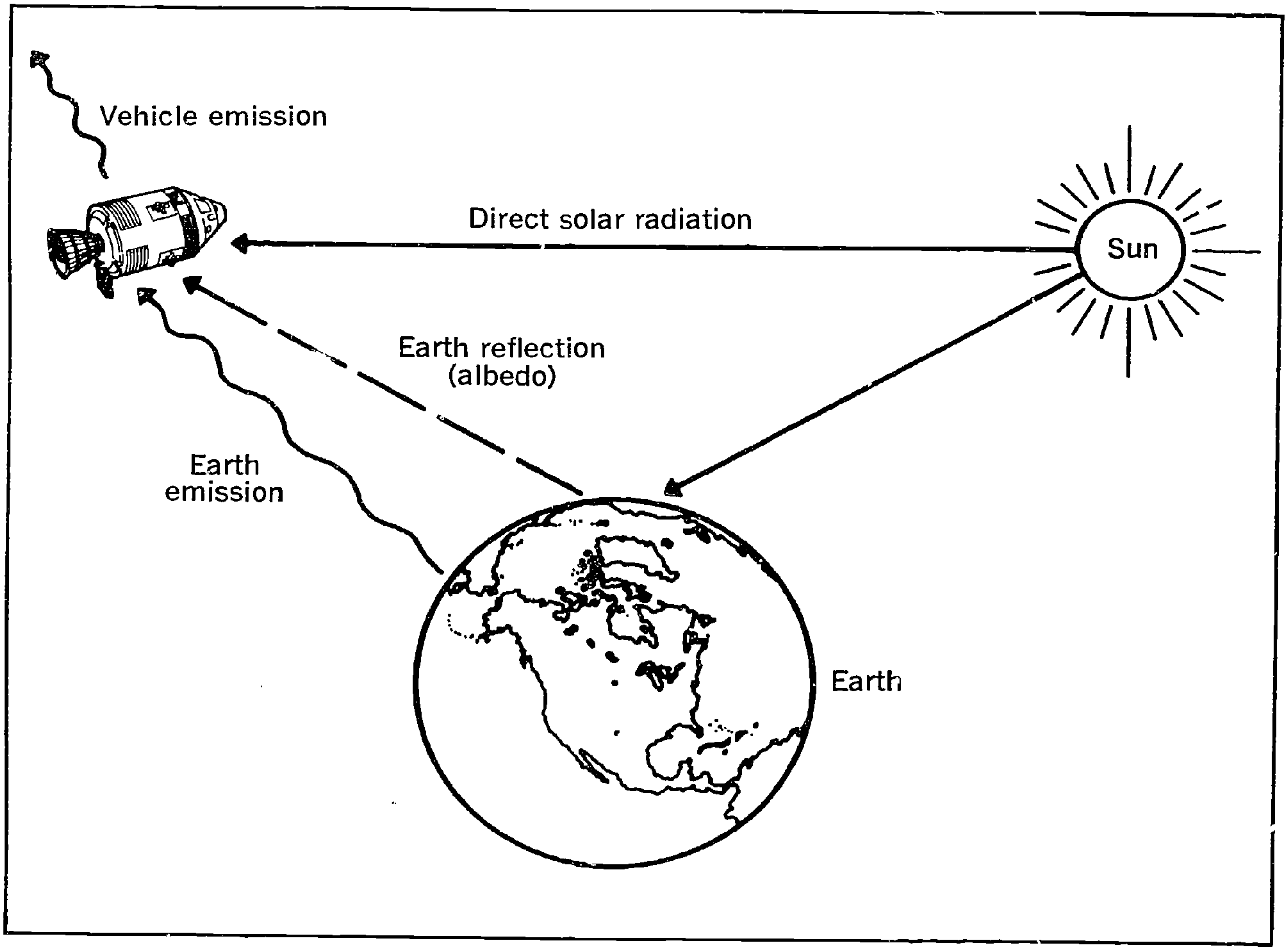


FIGURE 7–2. *Heat balance in spacecraft. A spacecraft orbiting the Earth receives electromagnetic radiation from several important sources and dissipates heat in the form of infrared radiation.*

compartment. Furthermore, if the position of a compartment is maintained with respect to an important source of radiation, then the sides of the compartment may be given individual surface treatments. For instance, the portion of the main compartment of the Mariner 4 spacecraft that was maintained in the direction of the Sun was covered with black Dacron, whereas the shaded side had an outer coating of aluminized Teflon.

Once NASA space scientists determine the approximate compartmental temperature requirements, calculations are performed yielding a temperature history for each component in the compartment. Heating or cooling devices, conductive heat paths, and heat shielding are used to maintain particular components at temperatures different from that of the compartment itself. The workability of the finished product is then tested in a space simulator. This involves placing the spacecraft into a vacuum tank with cold walls and using heat lamps to simulate solar radiation.

Temperature regulation is made more difficult by changes that commonly occur in the radiation environment of a spacecraft. The prelaunch environment of a vehicle is drastically different from that encountered in space. For instance, maintaining cryogenic fuels under prelaunch conditions requires more insulation and cooling capacity than is necessary at the effectively low temperatures encountered in space. In addition, the radiation environment can change when a spacecraft changes its position with respect to important heat sources such as the Sun or the Earth. For instance, a mission to Venus or Mars involves a considerable range in the intensity of light from the Sun. Periods when spacecraft are eclipsed from the Sun by planets or moons also introduce problems. For example, the Ranger was warmed slightly before launch because of the time it would spe Earth's shadow before entering the sunlight. Temperature control must also be maintained during high-temperature pulses that occur as a spacecraft moves through a planetary atmosphere. (See Unit 8, "Ablative Materials for High-Temperature Thermal Protection.") Not only must the components be maintained in their operable temperature ranges during these periods, but the optical properties of the temperature-controlling surfaces should not be altered significantly by the high temperatures.

Temperature-controlling devices are classified either as active or passive depending on whether they respond to different temperature environments. In both active and passive methods, an important approach to achieving compartmental temperatures in the proper ranges is by the use of external surfaces that have appropriate light-absorbing and -emitting characteristics. The

TABLE 7–1 CHARACTERISTICS OF THERMAL CONTROL COATINGS

Type	Range			Example
	Solar Absorptivity, α_s	Emissivity, ϵ	Ratio, α_s/ϵ	
Solar reflector	0.1–0.3	0.8–0.9	0.1–0.4	White paint
Flat reflector	0.1–0.3	0.1–0.3	1	Aluminum paint
Flat absorber	0.8–0.9	0.8–0.9	1	Black paint
Solar absorber	0.2–0.5	0.03–0.3	2–15	Polished metal

From Gilligan, Sibert, and Greening (2).

absorbing qualities of a surface are described in terms of its solar absorptivity α_s, the fraction of solar radiation that is absorbed. An ideal blackbody would have an α_s value of unity. The reflected light from planets and moons has nearly the same wavelength distribution (quality) as solar radiation, and thus the solar absorptivity also gives the total fraction of light absorbed from these sources. The infrared emittance of a particular surface is given in terms of its emissivity ϵ. Emissivity is the ratio of the energy emitted by a surface to that which would be emitted by an ideal blackbody at the same temperature. Surfaces and surface coatings are grouped on the basis of their relative values of α_s and ϵ as shown in Table 7–1 (2).

SOLAR REFLECTORS

Solar reflectors are characterized by small values of the ratio α_s/ϵ. They are substances that reflect most incident radiation and readily radiate energy in the form of infrared photons. Such surfaces are useful for coating compartments that require low temperatures, such as storage tanks for cryogenic fuels. Two types of materials have been tested that have these properties: white paints and secondary mirrors. The nature of the emissivity of these solar reflectors is compared with that of the limiting case or ideal solar reflector in Figure 7–3.

Solar reflectors of white paints can be made by the addition of stable white pigments to organic vehicles. However, the optical properties of paints made with organic vehicles are especially susceptible to alteration in space where the intensities of ultraviolet and soft X-ray radiation are relatively high. These components of the solar spectrum have sufficient energy to rupture chemical bonds in organic vehicles; such changes usually cause an increase in the value of α_s/ϵ. Paints containing organic vehicles are also more readily degraded by high-temperature pulses that occur during ascent or descent of spacecraft through planetary atmospheres. Silicone paints, with white pigments such as TiO_2 and ZnO, are more stable [illegible] high temperatures and

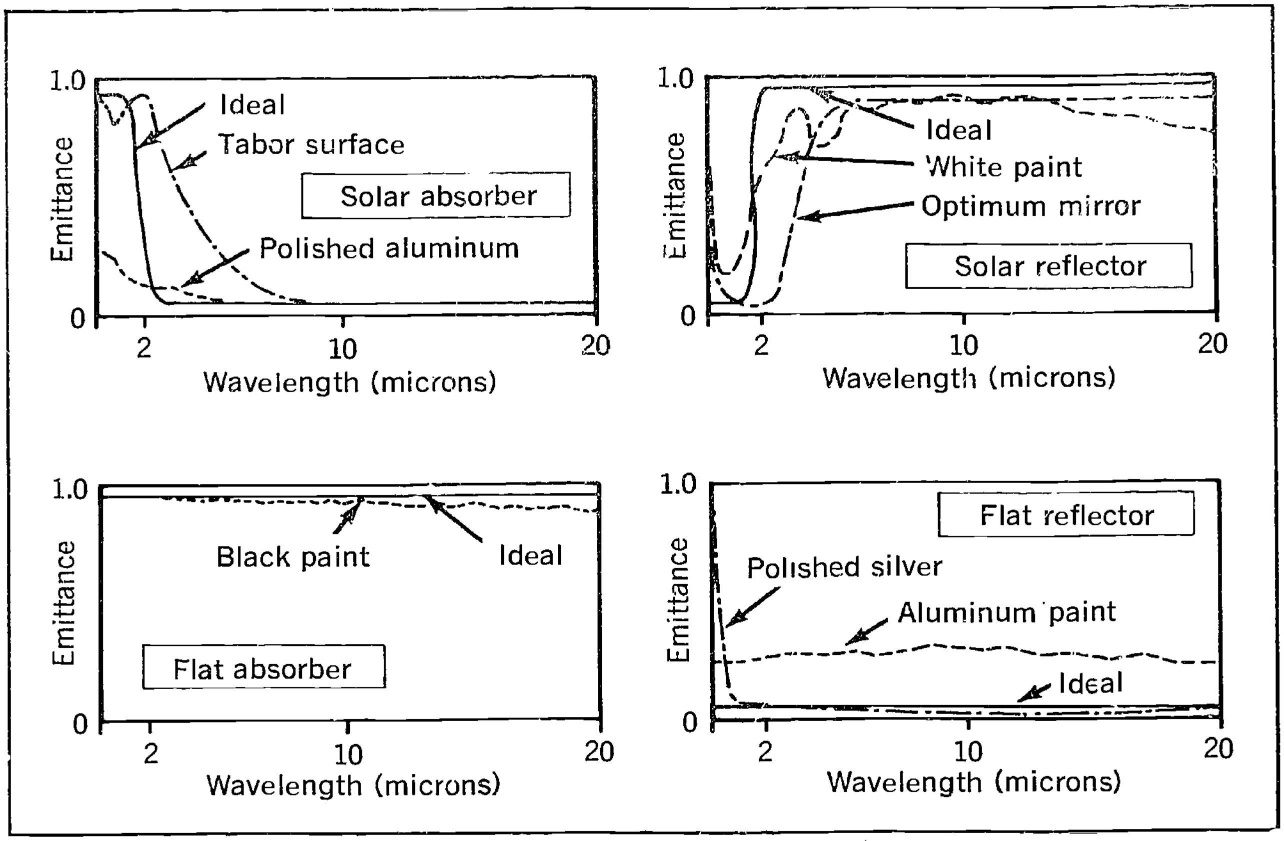


FIGURE 7–3. *Representative spectral emittance curves. The wavelength distributions of light emitted by substances and ideal materials are given for four types of optical surfaces (1).*

the short-wavelength radiation from the Sun, but in some cases, are difficult to bond to a spacecraft. On the other hand, ceramics have good adhesion for common structural materials, such as aluminum, in addition to superior temperature and radiation stability. Ceramic optical coatings, however, are difficult to apply. Ceramics are formed from white pigments mixed with vehicles such as water or aqueous alkali metal silicates or phosphates. Suitable pigments are finely powdered lithium aluminum silicates, silica, alumina, and zinc oxide. The pigment-vehicle mixture can be applied to substrate materials by ordinary techniques such as spraying, brushing, or dipping. The substrate is uniformly coated several times, and each coating is cured at temperatures of several hundred degrees Celsius before the next coating is applied. The total thickness of the ceramic coating is kept small, 2 to 3 mils, to discourage the formation of cracks. After selecting a coating with appropriate optical properties, there is still the question of how stable the physical and optical properties of the coating will be during the construction and testing of the vehicle and in the prelaunch, launch, and space environments (3, pp. S–88 to S–102; 4; 5). Not only must care be exercised in the selection of a coating, but also in the protection of the optical properties of the coating after it is applied to the substrate material.

Another type of solar reflector that has found application in controlling the temperatures of space vehicles is called a secondary mirror. A secondary mirror is formed by coating a shiny metal surface with a material that has a high infrared emittance and is also transparent to solar radiation. The solar absorbance of the mirror is close to that of the metal backing, and the infrared emittance is a function of the transparent substance. For instance, the Vanguard satellite was coated with a secondary mirror formed by evaporating a film of aluminum on the base metal and covering the film with a 0.65-μ-thick film of silicon monoxide SiO. The thickness of the SiO was chosen to yield an α_s/ϵ ratio of 1.3, to maintain the internal temperature of the satellite in the workable range of the electronic components. A uniform thickness was possible because of the regular shape of this satellite; the Vanguard satellite was spherical. For more irregularly shaped objects, coatings of uniform thickness are more difficult to apply.

FLAT REFLECTORS

Surfaces that reflect solar radiation but emit only a small amount of infrared radiation are called flat reflectors (Table 7–1). Materials having these optical properties are not common, and surfaces that are flat reflectors are presently obtained with highly polished metals or paints pigmented with metal flakes. The emissivities of polished silver and aluminum paint are shown in Figure 7–3. As before, the optical [illegible] these coatings can be altered either as a result of corrosion of the polished metal or through chemical changes in the vehicle of the paint.

FLAT ABSORBERS

Flat absorbers, a third class of optical surfaces, differ from flat reflectors in that they have high solar absorbances and high infrared emittances (Table 7–1). Because these qualities are easily obtained from any rough black matte surface (Figure 7–3), the choice of a particular coating material is usually dominated by other characteristics of the coating. These considerations include temperature resistance, mechanical strength, abrasion resistance, adhesive strength, flexibility, cost, and ease of application. Paints that are flat absorbers can be made from black pigments. These pigments include oxides or mixed oxides such as Cr_3O_4, $Fe_2O_3 \cdot NiO$, Fe_3O_4, or $Mn_2O_3 \cdot NiO$. The pigments are ground and dispersed in silicone elastomers or alkali metal silicate vehicles and applied to the base structure.

There are several other approaches that can be used to obtain dark oxide coatings on surfaces. The substrate material can be plated with metals, such as copper or nickel, followed by oxidation of the coating. Because the base materials for space applications are often alloys of aluminum or magnesium, experimental work is also being done with anodizing. Through anodizing one might produce a coating that would provide protection from corrosion and the desired optical properties. For instance, by controlling solution concentration, current density, and anodizing time, the surface of anodized magnesium has values of absorptivity in the range of 0.53 to 0.72 and values of emissivity in the range of 0.50 to 0.82 (1, p. 129).

SOLAR ABSORBERS

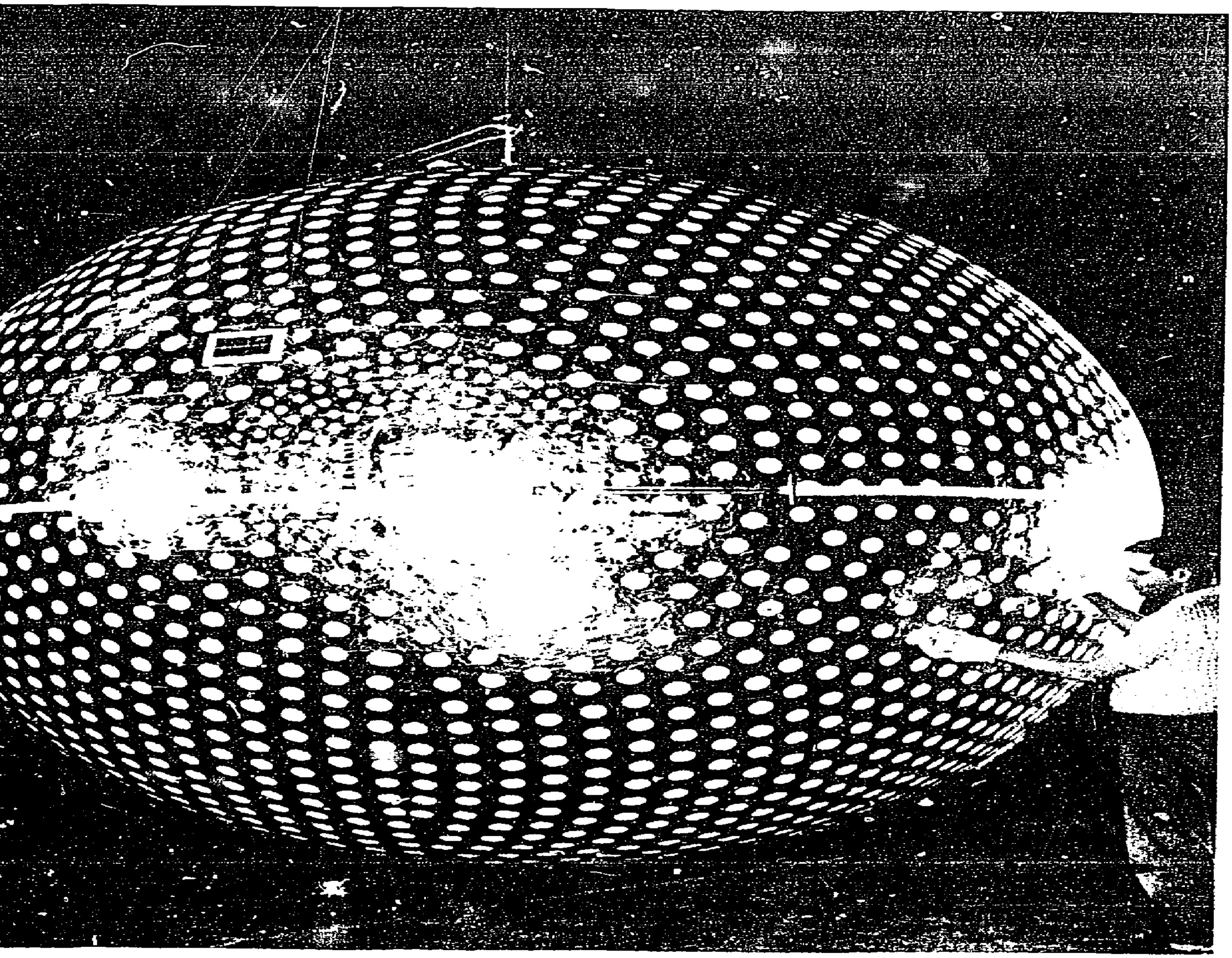
The final class of thermal coatings, characterized by the highest values of α_s/ϵ, are called solar absorbers (Table 7–1). Such materials absorb moderate amounts of solar energy striking their surfaces but emit very small amounts of infrared radiation (Figure 7–3). High values of α_s/ϵ can be achieved from polished metal surfaces, metal films, or thin films of metal oxides. These surfaces appear black yet have the infrared emittance of the substrate. Such coatings lead to high surface temperatures and have potential application in solar-energy converters. Polished metal surfaces have been utilized on several spacecraft, including those of the Ranger and Mariner series (6, 7).

In actual practice, a variety of surface treatments may be used in the control of temperatures of spacecraft (3, pp. S–18 to S–33; 8). For instance, the outer surface of Explorer 1, the first U.S. spacecraft, was stainless steel that was both oxidized to a straw color and striped with aluminum oxide. The aluminum surfaces of some later Explorer satellites were dotted with white paint (Figure 7–4). More sophisticated temperature control for the Mariner spacecraft (Figure 7–5) was achieved by a large number of surface treatments (9). Heat shielding on the Mariner 4 was provided on the sunny side or upper deck of the spacecraft by 30 layers of crinkled, aluminum-coated Mylar covered by black Dacron. Aluminized Teflon was used on the lower deck, which was directed away from the Sun. Exposed cable harnesses and wiring were wrapped with aluminized polyvinylfluoride or Teflon. The panels of solar cells were backed with black paint to dissipate most of the solar energy as it was absorbed, thus keeping the temperature of the solar cells in a workable range of −17° to 55° C. The antenna disk was painted green. Instruments were plated with gold. In addition to these passive methods, the

FIGURE 7-4. *Tw*
co
wa

Ma
co
ge
pos
coi
ish
rac
fle

Fr
im



-ft-diameter Explorer 9 satellite with 3600 white dots for temperature
. The shell was constructed of Mylar polyester film and aluminum foil and
tted with white epoxy.

er 2 and 4 spacecraft used an active temperature-
olling device involving optical surfaces. The electronic
was maintained between 13° and 30° C by regulating the
on of six sets of louvers (Figures 7–5 and 7–6) by means of
bimetallic strips. The louvers had outer surfaces of pol-
aluminum (solar absorber), but when opened exposed a
ing surface of TiO_2-silicone base white paint (solar re-
) beneath.

these examples it is apparent that optical surfaces play an
tant role in achieving desired temperature levels of com-

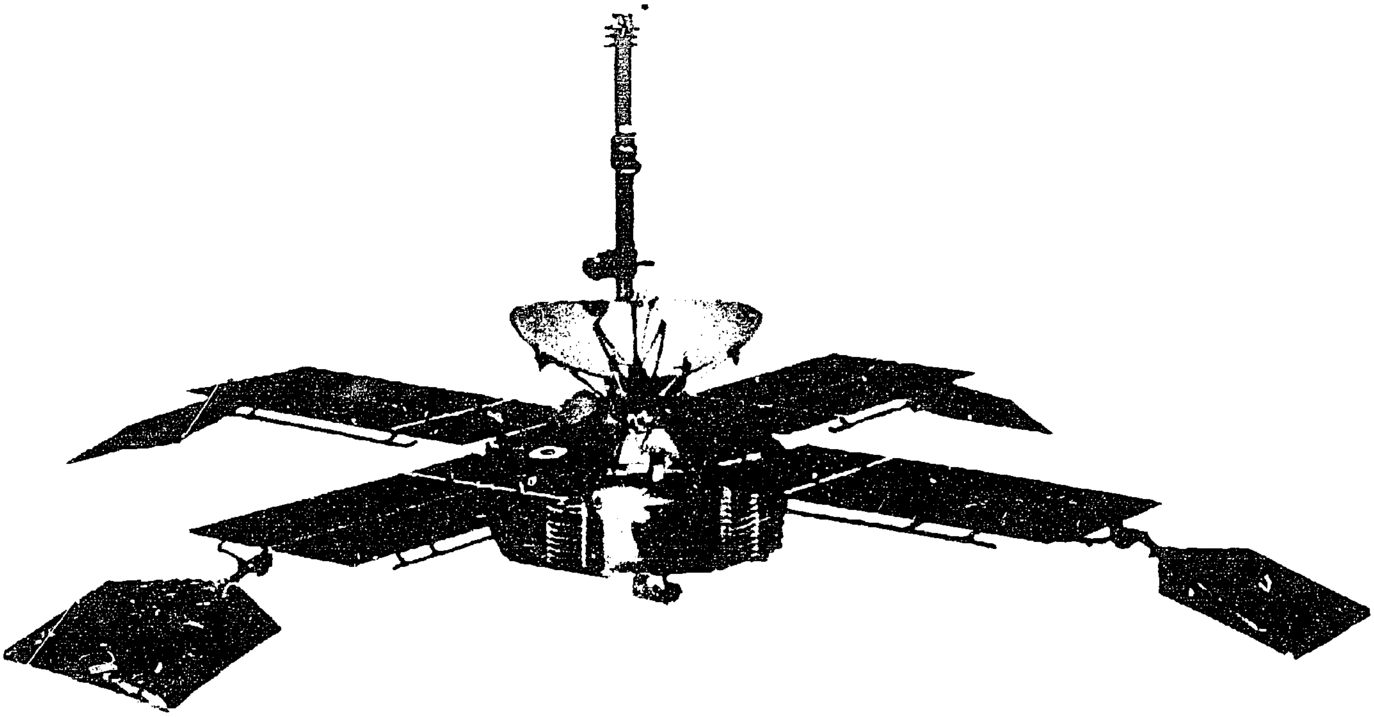


FIGURE 7–5. *Mariner 4 spacecraft with passive and active methods of temperature regulation.*

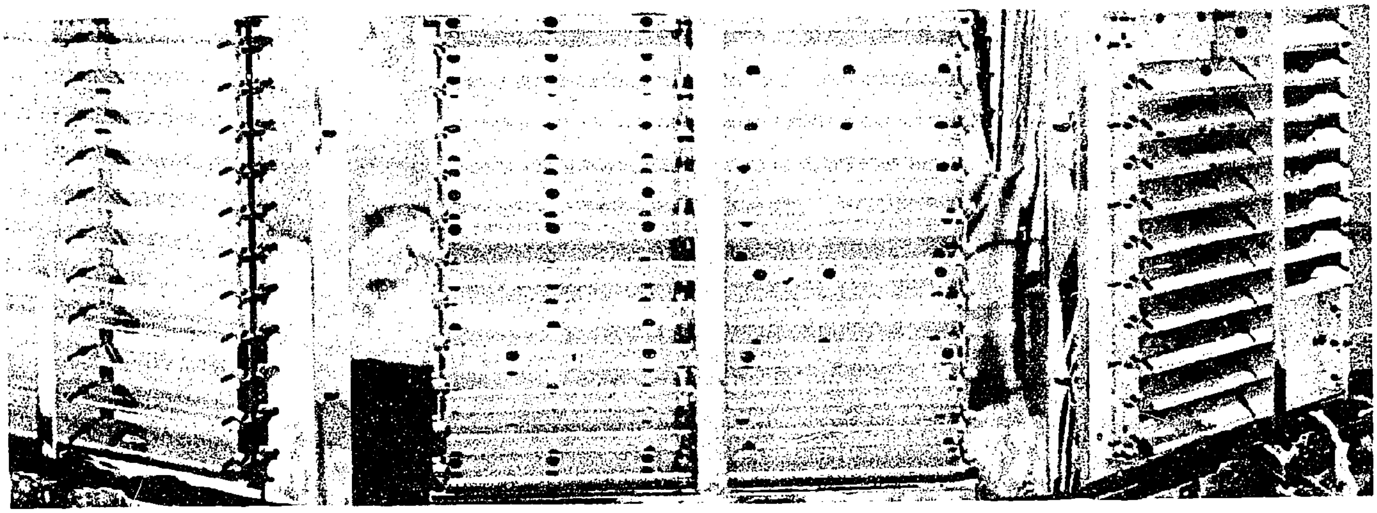


FIGURE 7–6. *Thermal-control louvers of the Mariner 4 spacecraft. The amount of heat dissipated from the electronic compartment of the spacecraft was regulated by the position of the louvers.*

ponents and compartments of spacecraft. Each mission in space requires a completely new set of data that NASA scientists must consider in selecting appropriate thermal-controlling optical surfaces. In actual practice, thermal-controlling surfaces are combined with conductive heat paths, heat shields, heat pumps, and heat sources to maintain the numerous temperature environments necessary for successful completion of a mission.

ACTIVITIES

Optical coatings can be used to help maintain the bulk temperature of a compartment in a space vehicle just as the internal temperatures of gasoline storage tanks, buildings, or automobiles are controlled or influenced by various surface coatings. The optical properties of surfaces are examined in the first four activities. The actual use that can be made of a particular optical surface depends not only on its optical properties but also on its resistance to corrosion, heat, radiation, and mechanical damage. Experiences with these aspects of coatings are found in the other two activities.

INTRODUCTORY EXPERIENCES WITH OPTICAL SURFACES

A number of qualitative experiments or demonstrations can show the differing ability of materials to absorb and emit electromagnetic radiation. One can simply cover the bulbs of several thermometers with sheets of material having various optical properties. These materials may include black or white cloth, paper, plastic, aluminum foil, glass, or even a mirror. Light from sources such as incandescent lamps or the Sun is allowed to shine on the sheets; however, the light source should be sufficiently broad to give a rather uniform intensity of light on all samples. After temperature equilibrium has been established, the bulk effectiveness of the materials in reflecting, absorbing, emitting, and transmitting radiation can be compared by noting the readings of the thermometers.

If a good absorbing material is selected, one can illustrate with the same setup how the temperature of an object changes with distance from a radiant energy source. This illustration of the inverse-square law can then be associated with the problem of maintaining the temperature of a spacecraft that is changing its distance from one or more of its important sources of radiant energy. The problems associated with an intermittent source, as in the case of a satellite that is periodically eclipsed by the object about which it is orbiting, can also be demonstrated. A nearly shadowed body could quickly lose heat in the effective absolute-zero environment of space. This can be illustrated by placing one side of the bulb of a thermometer in contact with a covered glass petri dish containing ice and covering the bulb with an absorbing material such as black cloth. A cycling of temperature can be noted as a light source such as a heat lamp or high-wattage bulb is turned on and off. For demonstration purposes, thermocouples may be used to make the reading from these experiments visible to larger groups.

QUALITATIVE COMPARISON OF OPTICAL COATINGS

A second experimental setup for qualitatively determining the optical properties of materials can be constructed by inserting an incandescent bulb into a metal food can that has had the top and bottom removed. The two optical surfaces to be compared are previously coated on one-half of the outside and/or inside of the can as shown in Figure 7–7. Two thermometers suspended

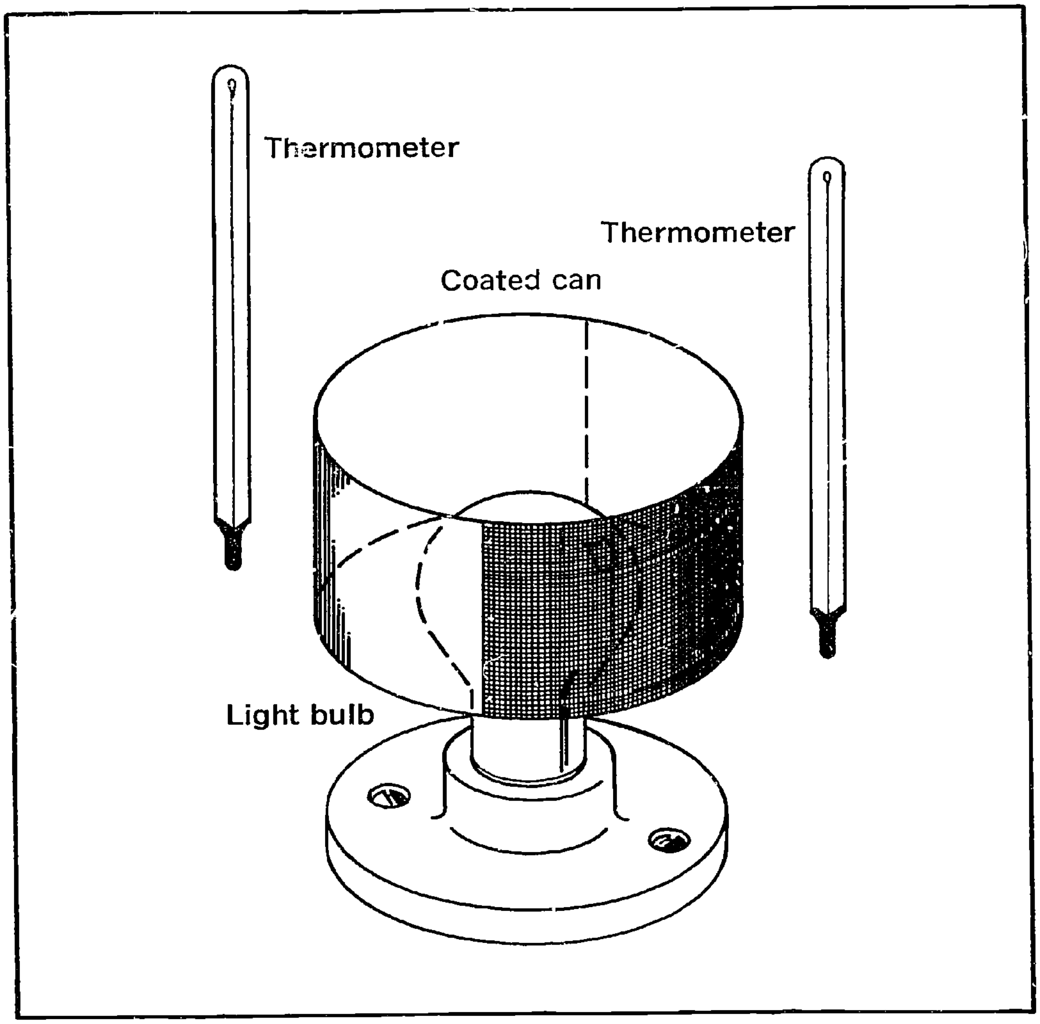


FIGURE 7–7. *Apparatus for examining the optical properties of coatings. Thermometers are hung at equal distances from a food can having two optical surfaces. Differences in the emitting properties of the two surfaces are noted by comparing the readings of the thermometers.*

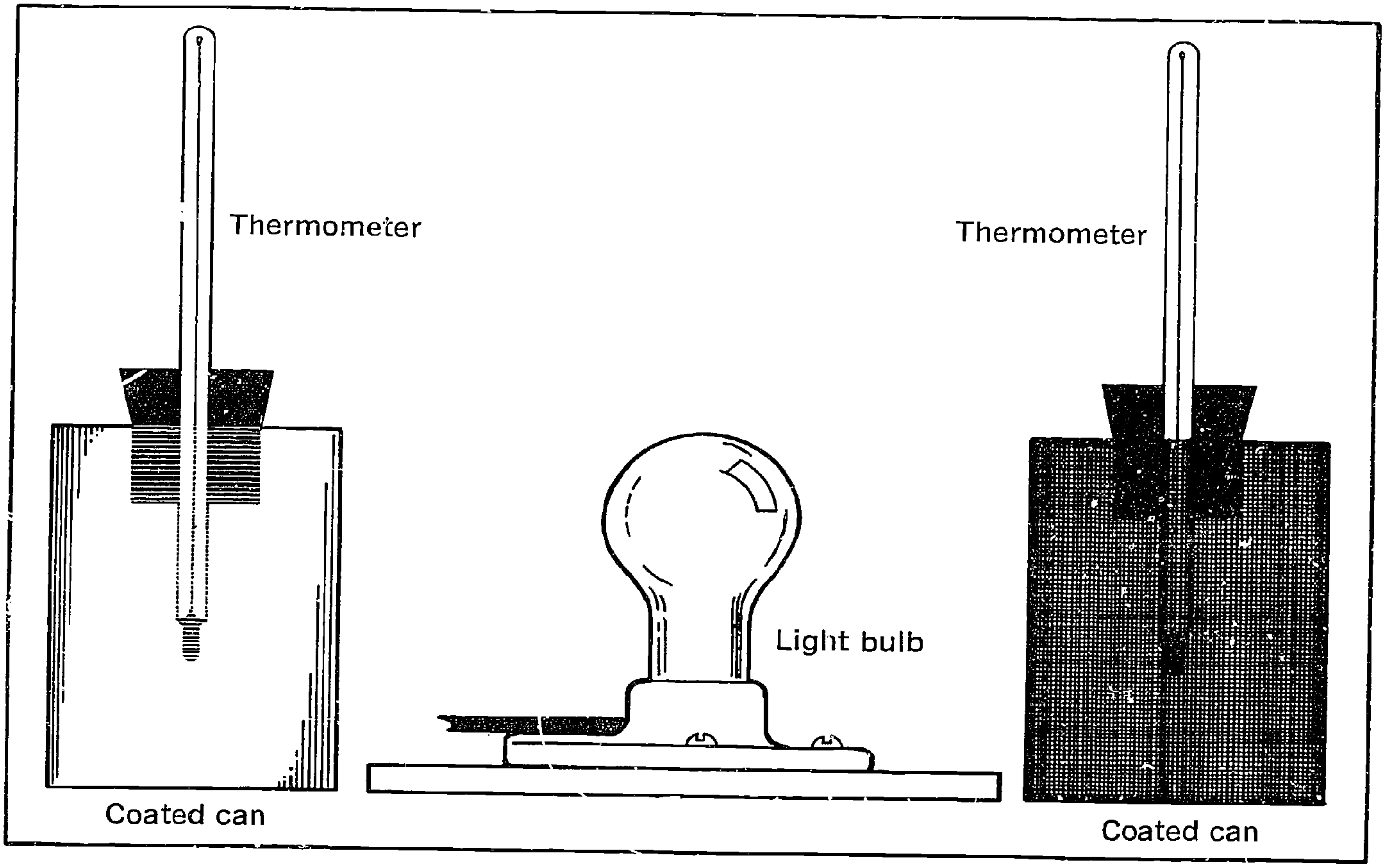


FIGURE 7–8. *A variation of the apparatus shown in Figure 7–7 for examining the optical properties of coatings. Two optical surfaces are coated on food cans that are then fitted with thermometers and placed equidistant from a light bulb.*

on opposite sides of the can indicate differences in the optical properties of the surfaces. Gross differences in the radiative properties of two coatings can even be felt with one's hands. A variation of this apparatus is shown in Figure 7–8. Two thermometers are placed in closed cans that have received different surface treatments. An incandescent bulb is placed equidistant from the cans.

QUANTITATIVE COMPARISON OF OPTICAL COATINGS

A more quantitative comparison of the optical properties of coatings can be made with the apparatus shown in Figure 7–9. An insulated container with one open side can be constructed from portions of metal food cans, one inserted into the other and separated by loose asbestos fibers or crushed paper. The cans are cut or drilled to permit the firm positioning of a thermometer with its bulb near the center of the inner chamber. (A thermocouple attached directly to the underside of the cover by epoxy,

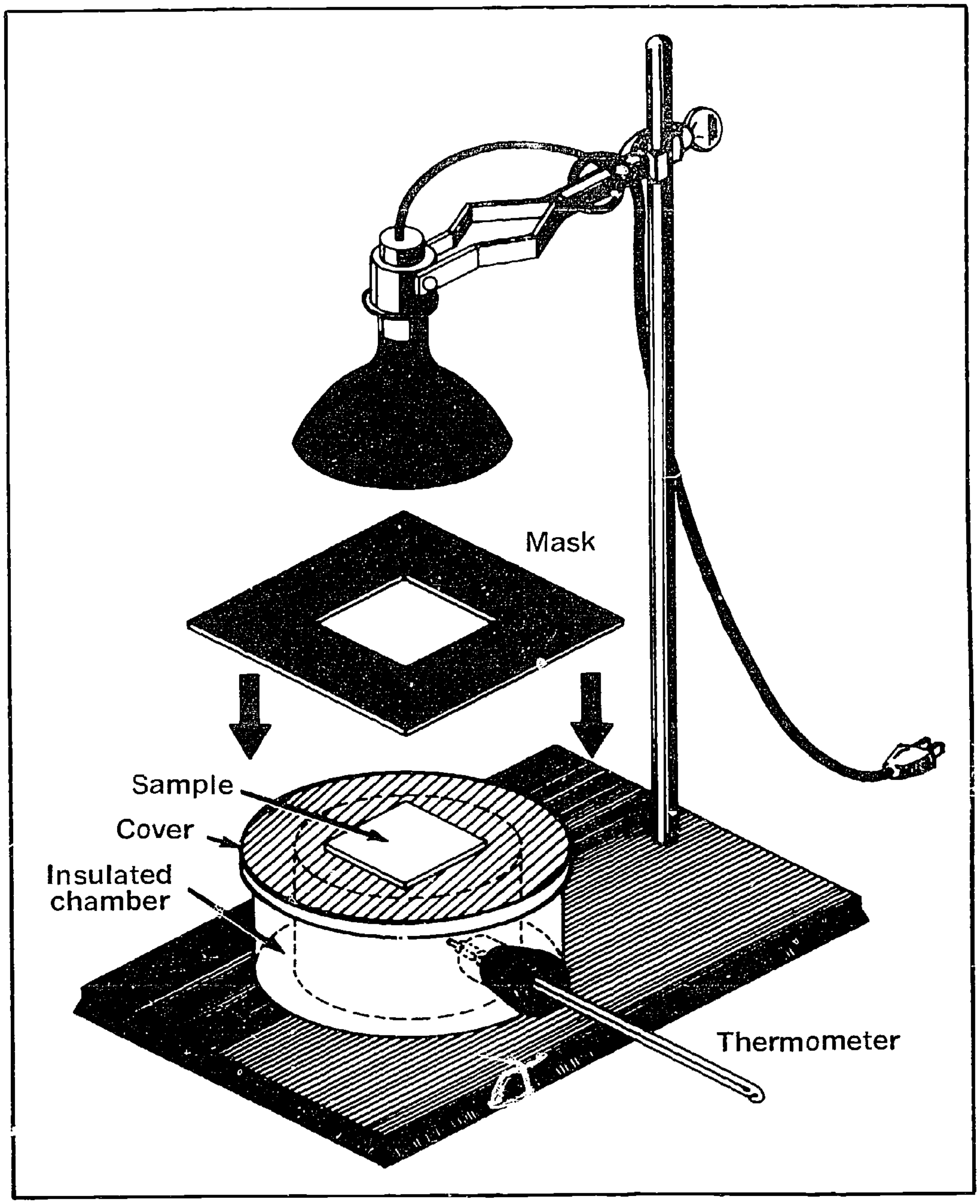


FIGURE 7–9. *Thermal-test chamber apparatus for investigating the optical properties of materials. The sample optical surface is placed on the cover of the chamber and covered with the mask. The mask exposes a reproducible area to a radiant heat source placed at a known distance above the sample.*

cement can be substituted for the thermometer.) The chamber is closed by covering the open side with a circular sheet of a good heat-conducting material such as copper or aluminum and is made airtight by fastening the cover to the outer can with plastic electrical tape. The optical material to be tested is placed directly on the cover or is coated on squares of copper or aluminum that are in turn placed on the cover. In either case, the specimen is covered with a mask made by cutting approximately a 2- by 2-in. square from the center of a sheet of asbestos. The mask yields a uniform area of lighted surface when the source of light is placed over the thermal-test chamber. The source of light is placed at a known and reproducible distance from the specimen. The source is turned on and the maximum temperature of the chamber or, to be more accurate, the difference between the temperature of the room and the chamber—that is, the temperature rise—is recorded. Differences in thickness of coatings, pigment-vehicle combinations and ratios, and pigment particle size can be investigated. Artist paints and glazes along with ordinary house paints, mirrors, and anodized and polished metals can serve as specimens. Pigments such as TiO_2, Fe_2O_3, and NiO can be mixed with organic vehicles or glazes in various proportions in forming the test coatings.

SPECTROPHOTOMETERS AND OPTICAL PROPERTIES OF COATINGS

The above experiments have used light sources with very broad spectra. More detailed information about coatings can be obtained by measuring their optical properties as function of wavelength. The ability of thin coatings to absorb or transmit radiation can be examined in any conventional infrared or ultraviolet spectrophotometer. Coatings can be applied to appropriate crystals such as CsBr or NaCl for infrared, glass for visible, and quartz for ultraviolet analysis. The coatings must be applied in sufficiently thin layers so as not to appear opaque to the instrument in question. The absorbance or transmittance can be plotted against wavelength, yielding plots similar in form to those of Figure 7–3. The quality of the reflected light can be viewed if a reflectance attachment is available for a spectrophotometer.

HEAT RESISTANCE OF OPTICAL COATINGS

The heat resistance of a coating can be examined by suspending a specimen in the path of a flame from a bunsen burner or acetylene torch (Figure 7–10). The heat test can be made more quantitative by using flames that are comparable in size, color, and distance from the optical surface. One can also compare the results produced by the oxidizing and reducing regions in a flame. High-temperature ovens or kilns are especially useful in examining the effect of high temperatures on optical coatings and for studying the effects of temperature cycling. The apparatus described in the preceding two activities can be used to characterize changes in the optical properties of surfaces as a result of heat.

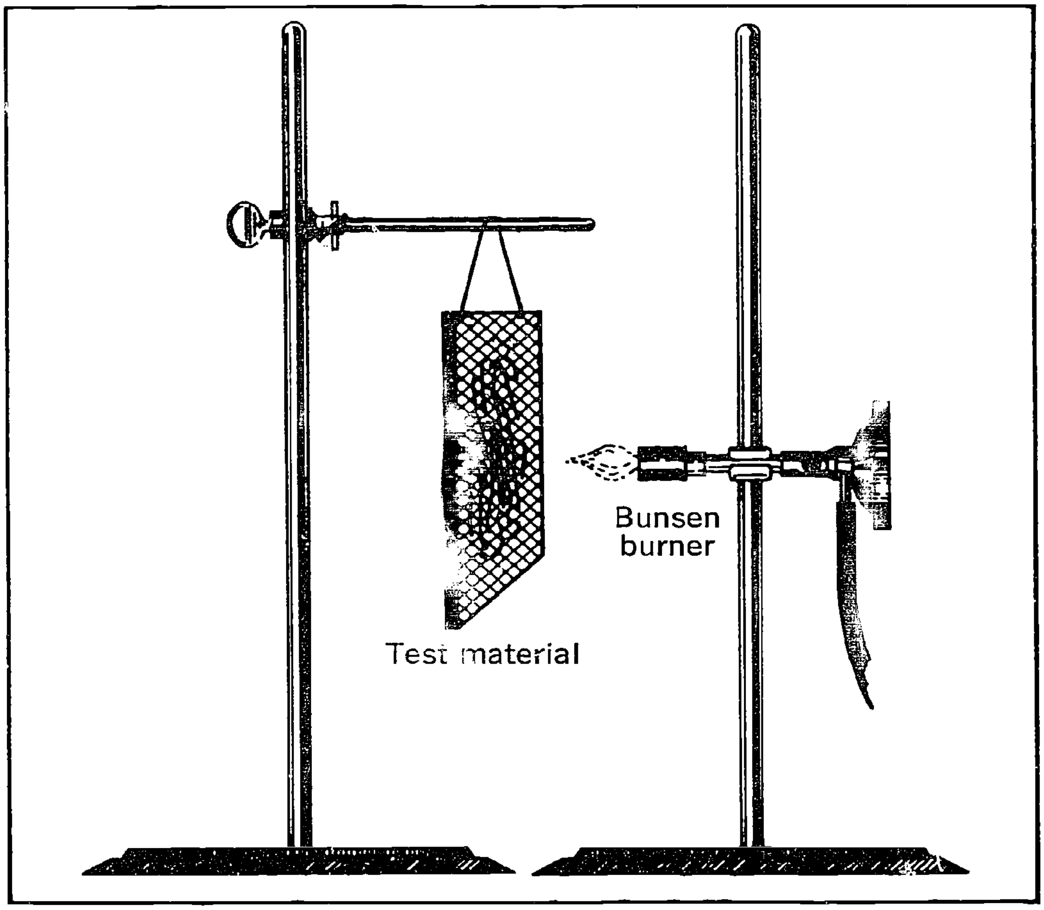


FIGURE 7–10. *Determination of the heat resistance of optical coatings. The flame of a burner is directed on the test surface and the effects studied.*

CORROSION RESISTANCE OF OPTICAL COATINGS

The resistance of a coating to chemical attack (corrosion) can be examined in an apparatus such as is shown in Figure 7–11. A bottle is fitted with a rubber stopper or cork that is bored or cut to accept the ends of several rods or strips of metal. The metal rods or strips are coated with test materials and suspended in various potentially corrosive fluids. The fluids can be ordinary fuels and oxidants such as kerosene, NO_2 (N_2O_4 is actually the rocket fuel), and oxygen. In addition, one can include the gases CH_4, NH_3, and CO_2 to simulate planetary atmospheres. Another potentially corrosive agent is water, either in the liquid or gaseous form. Comparison of the effects of liquid and gaseous water can be made simultaneously by only partially filling the test bottle with water. Seawater can be simulated by 3 percent solution of NaCl. A solution containing products of microbial activity can be simulated by a solution that is 3 percent NaCl and 5 percent acetic acid. Supporting media for the growth of organisms also can be included in the test cell and micro-

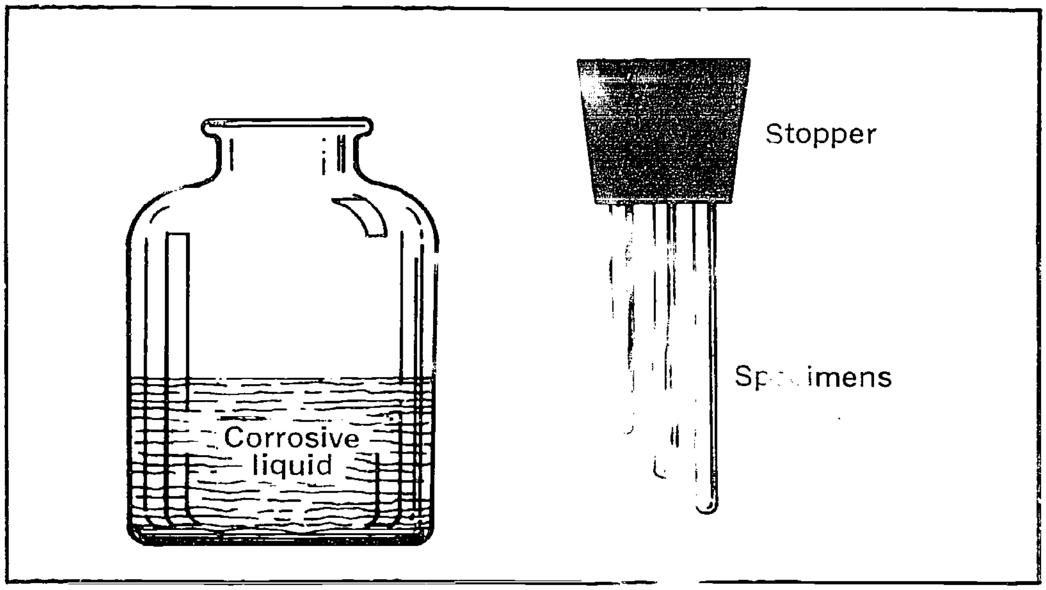


FIGURE 7–11. *Corrosion test chamber. Specimens are suspended from the stopper in contact with corrosive liquids or gases in the test chamber.*

organisms can be grown in the bottle itself. The corrosion bottle can be stored at temperatures higher or lower than room temperature to qualitatively observe temperature effects. (The bottle should be vented when used at temperatures higher than room temperature.) The stoppered corrosion test bottle can be vented so that corrosion is observed in the continued presence of O_2 or air. Venting the test chamber also removes the possibility that the bottle will explode because of the accumulation of gaseous products of corrosion. Using the corrosion bottle, one can also observe the nature of corrosion when test samples are alternately submerged in a corrosive liquid and then placed in contact with gases. This is accomplished by periodically removing the stopper holding the specimens or by inverting a partially filled test bottle.

TOPICS FOR THE DEVELOPMENT OF ADDITIONAL ACTIVITIES

To test the resistance of optical coatings to the high levels of ultraviolet radiation found in space, coatings can be exposed to the radiation from a mercury vapor lamp or black light. The effects can be observed visually, with the thermal test chamber, and in some cases by use of spectrophotometers. The stability of organic-based paints can be contrasted with ceramics.

The above procedures can be used to test corrosion and radiation stability of coatings whose primary function is other than that of control of temperature. These experiments can also be combined with those of anodizing. In addition, the corrosion bottle can be used to study cathodic protection by attaching a wire between appropriate samples such as iron and magnesium. Still other experiments can be developed to examine the resistance of coatings to additional effects such as vibration, vacuum, and human and mechanical handling.

LITERATURE CITED

*1. Vajta, T. F. 1965. Thermal control materials, Chapter 10. *In* C. G. Goetzel, J. B. Rittenhouse, and J. B. Singletary, Space materials handbook, Addison-Wesley Publishing Co., Inc., Reading, Mass.

2. Gilligan, J. E., M. E. Sibert, and T. A. Greening. 1963. Passive thermal control coatings, p. 3. Lockheed Missiles & Space Co., Palo Alto, Calif. NTIS N64–30474#.

3. Rittenhouse, J. B., and J. B. Singletary. 1966. Space materials handbook: supplement 1 to the second edition. NASA SP–3025. NTIS N66–18439#.

4. Pezdirtz, G. F. 1962. Nonmetallic materials for spacecraft, p. 16. *In* Materials for space operations. NASA SP–27. GPO, $0.35.

5. Neiger, J. B. 1965. Physical impact phenomena, Chapter 8. *In* C. G. Goetzel, J. B. Rittenhouse, and J. B. Singletary, Space materials handbook. Addison-Wesley Publishing Co., Inc., Reading, Mass.

6. Mariner: Mission to Venus, p. 33. 1963. McGraw-Hill Book Co., Inc., New York.

7. National Aeronautics and Space Administration. 1966. The view from Ranger, p. 30. NASA EP–38. GPO, $0.40.

8. Brooks, G. W. 1962. Research, design considerations, and technological problems of structures for spacecraft, p. 42. *In* Structures for space operations. NASA SP–28. GPO, $0.35.

9. NASA Jet Propulsion Laboratory. 1966. Report from Mars: Mariner IV 1964–1965, pp. 15 to 16. NASA EP–39. GPO, $0.50.

**Recommended general sources of information.*

OTHER REFERENCES

Gardner, M. H. 1965. Chemistry in the space age, Chapter 7. Holt, Rinehart & Winston, Inc., New York.

*Plunkett, J. D. 1964. NASA contributions to the technology of inorganic coatings, Chapter 2. NASA SP–5014. GPO, $1.00.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70–12345#).

Recommended general sources of information.

unit 8

unit 8

ABLATIVE MATERIALS FOR HIGH-TEMPERATURE THERMAL PROTECTION

Topics that may be enriched by use of this unit:

- Organic polymers
- Pyrolysis
- Heat conduction
- Insulation
- Heat capacity
- Polymerization

The problem of guarding space vehicles from the temperature extremes encountered during a mission has resulted in the development of several types of thermal protection systems. Protection against the effectively very low temperatures encountered in interplanetary space is discussed in Unit 7, "Optical Coatings for Temperature Control of Space Vehicles." Protection against the high temperatures in chemical rocket engines and on the surfaces of space vehicles entering planetary atmospheres provides another demanding problem facing space scientists. For example, the flame temperature in the combustion chamber of a liquid propellant rocket may range from about 3000° C for a fuel/oxidant pair such as hydrogen and oxygen to about 4000° C for some of the more exotic propellants such as fluorine and oxygen. These temperatures are well above the melting point of metals commonly used as structural materials (1). Therefore, the walls of combustion chambers as well as exhaust nozzles must be protected. Although regenerative cooling techniques (Unit 3, "Chemical Rocket Propellants") provide at least a partial answer to this problem, the continued development of higher performance rocket engines will require the concomitant development of more efficient high-temperature thermal protection systems.

Spacecraft must also be protected from high-temperature pulses produced by aerodynamic heating, especially during the reentry phase of a mission. For instance, a space vehicle entering the Earth's atmosphere must dissipate a large amount of kinetic energy. By making the shape of the reentry vehicle very blunt, a large portion (about 99 percent) of this energy can be transferred to the atmosphere. (See Unit 5, "Rates of High-Temperature Reactions Associated With Space Vehicles.") The remainder of the heat is absorbed by the vehicle and even this amount is sufficient to produce severe increases in temperature. Protection of the reentry vehicle and its contents thus represents another application for high-temperature thermal protection systems.

THERMAL INSULATION AND ABLATION

To be suitable as a thermal insulator, a substance should possess the following characteristics (2): a high capacity for heat absorption or rejection, a low thermal conductivity, and a low density. In addition, space-vehicle applications require that the substance be able to withstand the mechanical stresses associated with high-velocity, turbulent gas flows. The latter requirement is considerably more critical in the case of insulators for rocket engines, for example, than in the case of a heat shield for a reentry vehicle. This is because the shear forces that tend to erode the insulator are much greater in the rocket-engine application where the high-velocity discharge of combustion gases provides the thrust necessary to launch the vehicle. Erosion of the insulator from these walls, particularly in the region of the throat, can seriously alter the geometry and thus the performance of the engine (Figure 8–1).

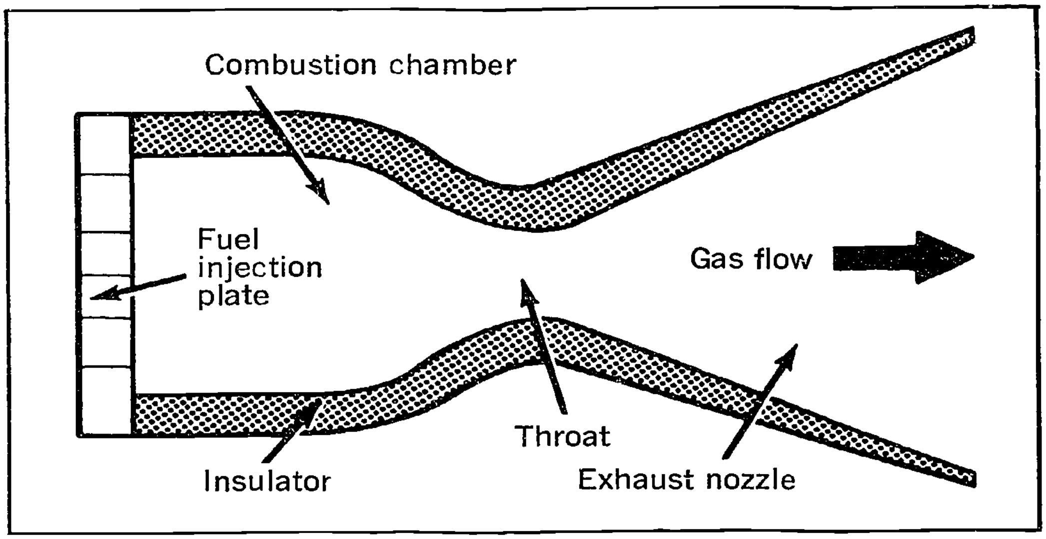


FIGURE 8–1. *Sketch of the heat insulator lining of a liquid rocket engine. The insulator protects the walls of the engine from high-temperature degradation and must itself be resistant to erosion.*

As a class, ablative materials presently find the widest application as thermal insulators for rocket engines and for heat shields of reentry vehicles. Ablation (3, 4) is the systematic sacrifice of surface material through endothermic processes to protect inner structures from a high heat flux. Materials ablate in one of three basic manners (3):

1. They may sublime as, for example, does a material like Teflon.

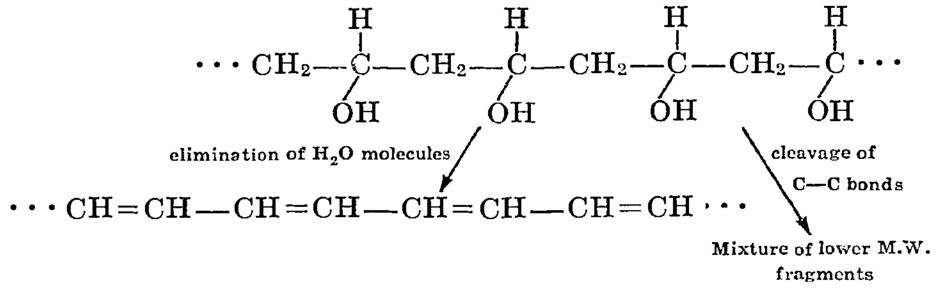
2. They may melt and then vaporize as, for example, does a material like quartz.
3. They may char and then either sublime or melt and vaporize as do many of the composite organic plastics.

The success of ablative materials as thermal insulators depends on their ability to dispose of large amounts of heat with only a small amount of material loss (5). In an admittedly oversimplified form, the sequence of events accompanying the absorption of heat by an ablator is as follows:

> The surface temperature of the ablator starts to increase at a rate determined by such parameters as the magnitude of the incident heat flux and the specific heat of the ablative material. The low thermal conductivity of the ablative material effectively concentrates the absorbed heat in the surface region, thereby protecting subsurface regions from significant temperature increases. As the surface material reaches a sufficiently high temperature, the endothermic processes of decomposition and phase transition remove the surface layer and expose fresh ablative material. Repetition of this sequence may occur until no more ablative material remains.

Some materials, particularly the composite organic plastics, form a char layer during ablation. Although the mechanism of char formation has not yet been established (6), the process may be visualized as occurring in two steps (3). As the heated material in the pyrolysis zone undergoes decomposition, liberated gases cause the formation of foam in the surface layer (primary char). As the gases undergo further decomposition and ultimately escape, the foam hardens, leaving a porous, carbonaceous char layer (secondary char). This is illustrated in Figure 8–2. As a result of these endothermic physical and chemical changes, a large portion of the incident thermal energy is dissipated.

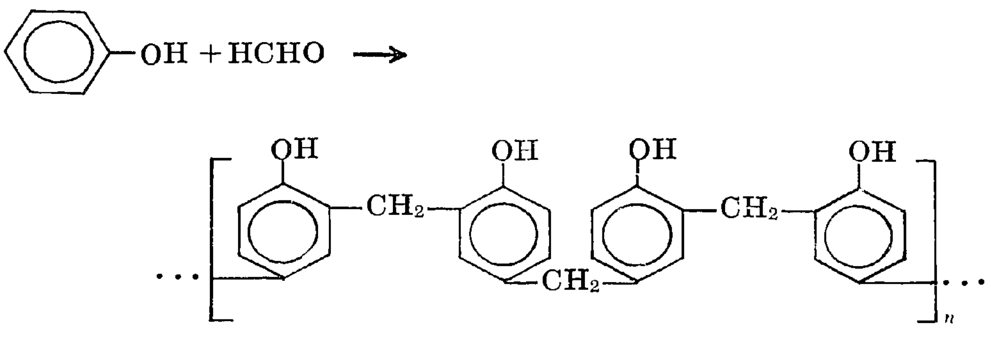
Ablators provide heat protection through several mechanisms. In addition to retarding the flow of heat into subsurface structures by absorption processes, ablative materials have the advantage of being able to dispose of incident heat by rejection processes (7). For example, the countercurrent flow set up by the escaping gaseous decomposition products effectively blocks out a portion of the incident heat and prevents it from reaching the surface material. The magnitude of this convective blockage (4) is determined at least in part by the heat capacity of the escaping gases. Ablative materials that generate gases of high specific heat, such as hydrogen, are preferred. It might be polymers. To facilitate char formation, the polymer should have a high degree of crosslinking; that is, it should be of the thermosetting rather than the thermoplastic type (6). Pyrolysis of a polymer involves a competition between chain-elimination reactions and chain-cleavage reactions. For example, loss of water molecules (elimination) from a linear polymer such as polyvinyl alcohol leaves the carbon skeleton intact, producing a carbonaceous char. Rupture of the carbon-carbon bonds, on the other hand, produces low molecular weight species that tend to be more volatile.



Char formation requires, therefore, that the rate of chain-elimination reactions be greater than that of chain-cleavage reactions. While this condition must be met both for linear and crosslinked polymers, theoretical calculations (6) indicate that the ratio of elimination to cleavage necessary for char formation is considerably greater for a linear polymer than for a crosslinked polymer of similar size and composition.

A typical composite ablative material consists of a char-forming resinous matrix containing a gas-generating component such as nylon and a reinforcing material such as silica, carbon, or graphite in the form of fibers or cloth (4, 5). For example, the ablative heat shield used on the Mercury capsules was a composite of a phenolic resin with reinforcing fiber glass (5).

Thermosetting resins of the phenolic novolac type have found wide application as the char-forming matrix. Novolac is the linear condensation product of phenol and formaldehyde, the structure (9) of which may be represented as:



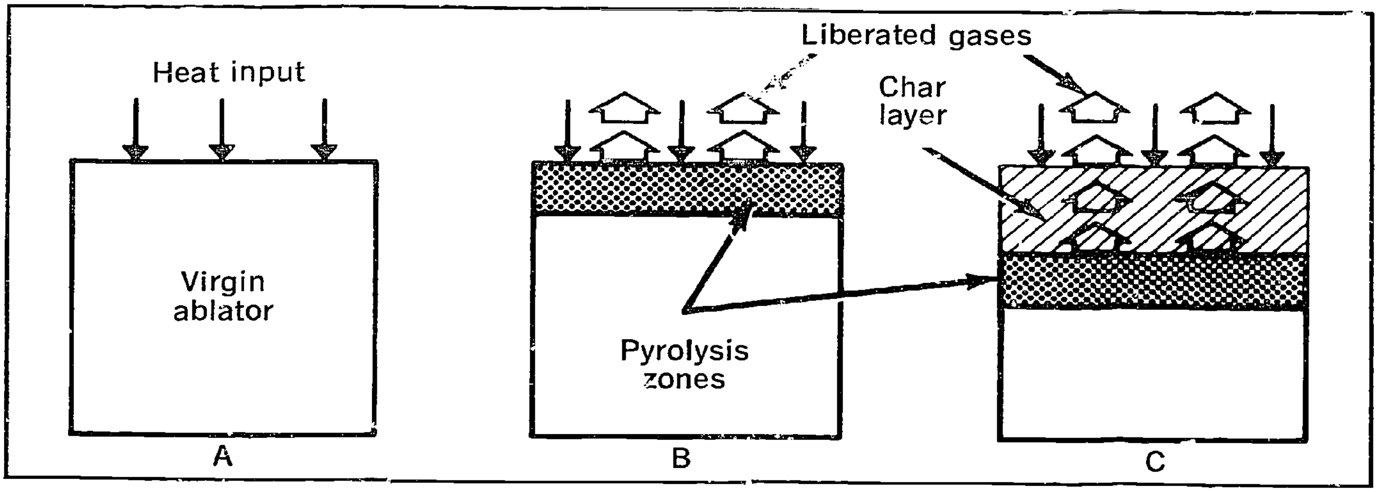


FIGURE 8–2. *Schematic representation of char formation during ablation. Heat incident on the ablator* (A) *causes decomposition of the surface material, liberation of gases, and the formation of foam* (B). *Additional heat hardens the foam and decomposes deeper layers in the ablator* (C).

mentioned that formation of a char layer during ablation is an advantage in this respect. The gaseous decomposition products formed in the pyrolysis zone undergo further breakdown to carbon and hydrogen and absorb additional heat as they percolate through the high-temperature char layer (6).

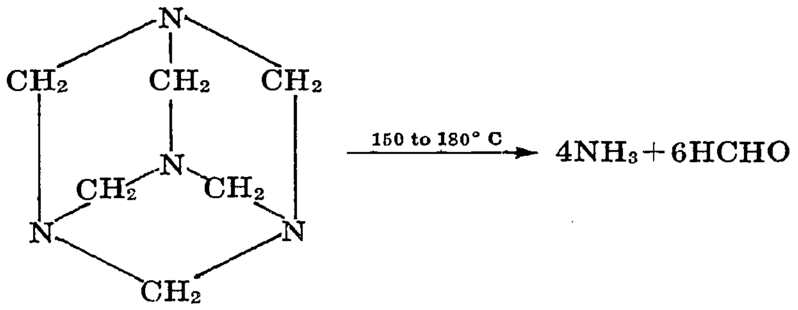
Radiation of heat from the high-temperature surface of the ablative material also provides a means for dissipating some of the incident heat load. The char layer formed by some ablative materials is very effective in this respect (7). Because of its porous nature, the char layer behaves as an insulator; consequently, its surface reaches very high temperatures and reradiates a substantial fraction of the imposed heat load (8).

To summarize, then, an "ideal" ablative material (4, 5, 6) should (*a*) have a high heat of ablation (a measure of the effective heat capacity of an ablating material defined numerically as the ratio of the heating rate input to the mass loss rate), (*b*) have a low density and thermal conductivity so that heat penetrates slowly, (*c*) be capable of radiating at high surface temperatures to take advantage of radiative cooling, (*d*) generate gases of high specific heat to obtain the greatest benefit from convective blockage of incident heat, and (*e*) have good mechanical properties to resist erosion.

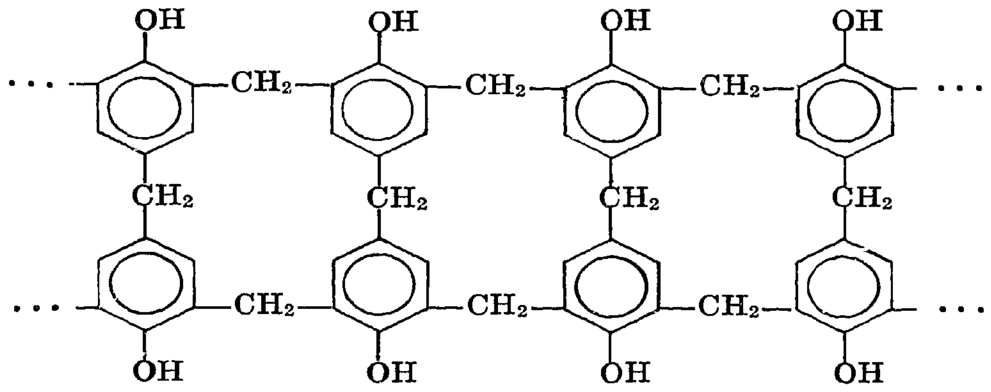
CHEMICAL COMPOSITION OF ABLATORS

Presently, substances that best approximate the qualities of an "ideal" ablator are composite, reinforced char-forming organic

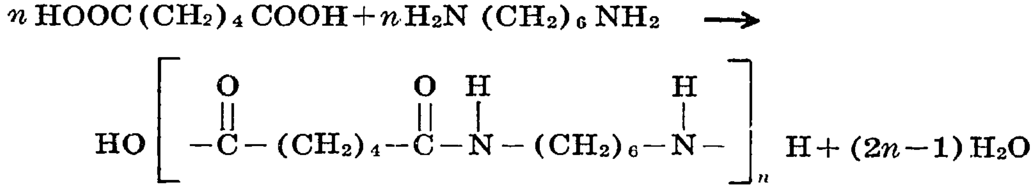
The reaction is generally carried out in aqueous solution with an acid catalyst (e.g., oxalic acid) and an excess of phenol. The linear product, a thermoplastic material, is then converted to an infusible crosslinked polymer by addition of a source of methylene ($-CH_2-$) groups. A commonly employed procedure is to mix the solid novolac resin with hexamethylenetetramine and cure at 150° to 180° C. The hexamethylene compound decomposes (10) in this temperature range:



The ammonia produced in the reaction acts as a catalyst and the formaldehyde provides methylene groups to give a crosslinked structure that may be represented as



Nylon, a linear condensation polymer based on the reaction of adipic acid and hexamethylenediamine:



$$n\,HOOC(CH_2)_4COOH + n\,H_2N\,(CH_2)_6\,NH_2 \longrightarrow HO\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\right]_n H + (2n-1)\,H_2O$$

may be added to the novolac as a gas-generating component.

The product has a melting point of about 260° C, and during pyrolysis undergoes extensive chain cleavage with consequent formation of large quantities of gaseous decomposition products. Little or no carbonaceous char is produced from the nylon.

The reinforcing material of an ablator serves the primary function of helping to anchor the char layer to the uncharred ablative material. In addition, it may serve to provide sites for the deposition of pyrolytic graphite and thereby enhance the radiative efficiency of the char layer, or it may undergo endothermic reactions with decomposition products of the resinous matrix. For example, it has been suggested (6) that silica may react with the deposited graphite to form silicon carbide:

$$SiO_2(s) + 3C(\text{graphite}) \rightarrow SiC(s) + 2CO(g) \qquad \Delta H^\circ_{298} = +151 \text{ kcal/mole}$$

Both the amount and type of reinforcing material may affect ablative performance (6). For example, charring resin ablators containing up to 35 percent by weight of silica fiber behave similarly to nonreinforced systems. When the silica content reaches 50 percent or more by weight, however, a fused silica skin forms over the surface during ablation. The ablative behavior of such a system is less efficient than the nonreinforced system and appears to be controlled primarily by surface vaporization or melting of the reinforcing material. Similarly, when low melting reinforcements such as fiber glass are employed, rapid melting of the surface may also cause poor ablative performance.

ACTIVITIES

PREPARATION OF A CHAR-FORMING ABLATIVE MATERIAL

Many of the char-forming ablative materials used as rocket liners and heat shields are based on the reaction product of phenol (CARE)[1] and formaldehyde (phenolic novolac). This is a thermoplastic material that must be further cured to form an infusible thermosetting resin suitable for use in the char-forming matrix of the ablator.

The phenolic novolac is cured by reaction with a crosslinking agent (e.g., hexamethylenetetramine). The curing process is often carried out in a compression mold at a temperature in the

[1] *Teacher should exercise care in this experiment.*

range 150° to 180° C. The result of this process is that the relatively low-melting (~ 110° C) phenolic novolac is converted to a highly infusible product. Additives, such as nylon, may be incorporated during this curing process.

In this experiment a phenolic novolac resin is prepared and then cured with hexamethylenetetramine.

Procedure for preparation of phenolic novolac.—In a 250-ml round-bottom flask (an Erlenmeyer flask may be used if round-bottom flasks are unavailable), 27.6 g of reagent grade phenol, 20.0 g of formaldehyde (37 percent aqueous solution), and 0.3 g of oxalic acid are thoroughly blended.

A water-cooled reflux condenser is attached to the flask and, with continuous gentle stirring, the reaction mixture is cautiously heated to a temperature of about 100° C. Occasional cooling may be required if a rapid temperature rise occurs in the reaction vessel. The reaction is maintained at this temperature for approximately 2 hr. The reflux condenser is then replaced with a distillation head and condenser, and the water is distilled from the system, with continuous stirring, until the reaction temperature reaches 140° to 150° C. The clear, nearly colorless novolac is then quickly poured into a clean can and allowed to cool. A brittle, glassy solid that is easily powdered and has a melting point of 105° to 110° C is obtained. (This material is soluble in acetone.)

Procedure for curing the novolac.—The novolac material is ground to a fine powder in a mortar. Sufficient hexamethylenetetramine is added to the ground material so that the amine represents about 10 percent by weight of the final mixture. These ingredients should be thoroughly blended. A clean *metal* can having a diameter of about 2 in. (e.g., a frozen-juice can) is wrapped with a sleeve of asbestos. Approximately 3 g of the novolac hexamethylenetetramine mixture is placed into the well at the closed end of the can (Figure 8–3). The can is then placed into an oven at 150° to 180° C for about 2 hr. At the end of this time the can is removed from the oven and is allowed to cool to room temperature. The brownish-yellow resin should remain fused to the base of the can.

INSULATIVE PROPERTIES OF A CHAR-FORMING ABLATOR

In this experiment the effectiveness of a char-forming ablative material in retarding the transfer of heat is examined.

A thermometer is inserted through a cork of sufficient size to plug the open end of the can to which the ablative material has

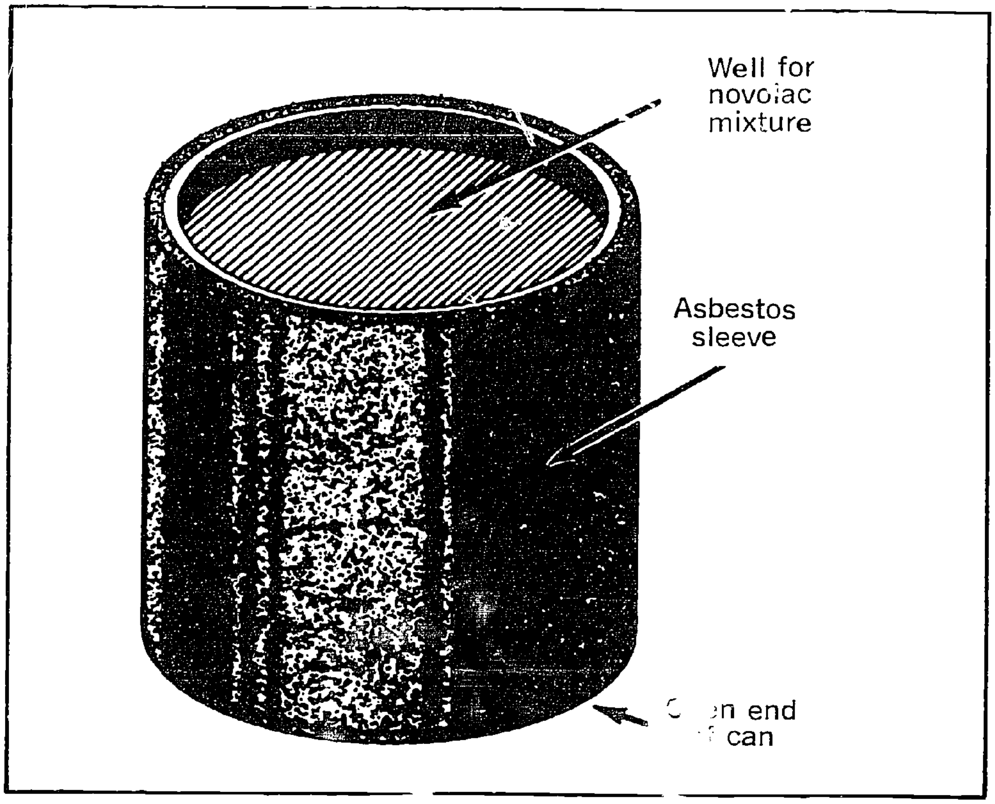


FIGURE 8–3. *Container for curing the novolac resin. A metal can with one open end is wrapped with sheet asbestos and the material to be cured is placed on the closed end.*

been fused. A V-shaped notch should be cut in the side of the cork to allow expanding air to escape during the heating process. With the thermometer in place, the can is clamped in a horizontal position. A bunsen burner is clamped in a horizontal position (Figure 8–4) so that, when lighted, the tip of the inner cone of the flame is nearly in contact with the ablative material. The temperature is recorded at intervals of approximately 30 sec until a temperature of about 200° C is reached. A plot of temperature versus time is made and compared with a plot obtained by similarly heating a duplicate can not having an ablative heat shield.

TOPIC FOR THE DEVELOPMENT OF ADDITIONAL ACTIVITIES

Ablative materials containing additives such as nylon, silica, or fiber glass may be prepared and tested for their effectiveness as ablators. The additives should be in powdered form and mixed with the novolac-hexamethylenetetramine mixture prior to curing. In general, the additives should constitute 30 to 40 percent by weight of the final mixture.

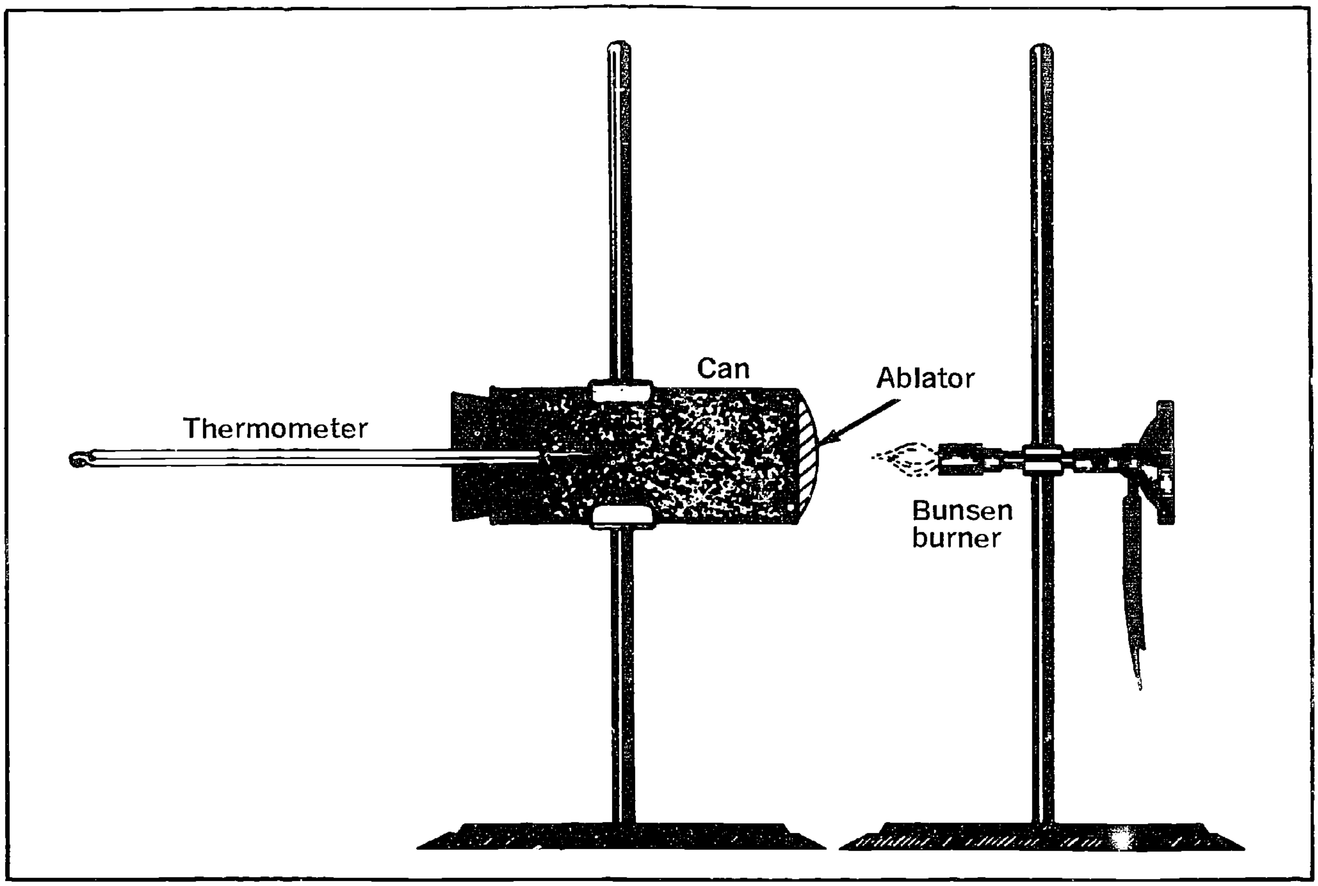


FIGURE 8-4. *Apparatus for ablation tests. The burner flame is directed at the ablator and the effectiveness of the ablator is determined by observing the nature of the temperature rise.*

LITERATURE CITED

1. Yodzis, C. W. 1964. Liquid rockets, p. 277. *In* P. E. Purser, M. A. Faget, and N. F. Smith, Manned spacecraft: engineering design and operation. Fairchild Publications, Inc., New York.

2. Fisher, A., M. A. Kinna, F. J. Kubek, and F. R. Barnet. 1962. The performance of selected plastic materials in a high temperature environment, pp. 1 to 3. U.S. Naval Ordnance Laboratory, White Oak, Md. NTIS N63-10110#.

3. Hanna, P. A. C. 1964. A survey and evaluation of ablation phenomena, pp. 4 to 8. General Dynamics Corp., Pomona, Calif. NTIS N65-21393#.

4. Erb, R. B. 1964. Thermal balance and heat protection, pp. 92 to 96. *In* P. E. Purser, M. A. Faget, and N. F. Smith, Manned spacecraft: engineering design and operation. Fairchild Publications, Inc., New York.

*5. Roberts, L. 1962. Ablation materials for atmospheric entry, pp. 23–30. *In* Materials for space operations. NASA SP–27. GPO, $0.35.

*6. McAllister, L., J. Bolger, H. McCaffery, P. Roy, F. Ward, and A. C. Walker, Jr. 1963. Behavior of pure and reinforced charring polymers during ablation under hypervelocity re-entry conditions, pp. 1 to 14. AVCO Corp., Wilmington, Mass. AIAA A63–15550.

7. Richards, T. E., and J. R. Baxter. 1963. Ablative coatings for short term thermal protection, p. 1. TN CPD–57, Department of Supply, Australian Defence Scientific Service. Weapons Research Establishment Salisbury, South Australia.

8. Anderson, R. A. 1962. Research, design considerations, and technological problems of structures for planetary entry vehicles, pp. 25 to 35. *In* Structures for space operations. NASA SP–28. GPO, $0.35.

9. Keller, L. B. 1965. Development of characterized and reproducible syntactic foam of phenolic nylon for heat shields, p. 7. Hughes Aircraft Co., Culver City, Calif. NTIS N67–11986#.

10. Noller, C. R. 1966. Textbook of organic chemistry, pp. 213 and 443. W. B. Saunders Co., Philadelphia.

OTHER REFERENCE

Glaser, P. E., I. A. Black, R. S. Lindstrom, F. E. Ruccia, and A. E. Wechsler. 1967. High-temperature thermal protection systems. *In* Thermal insulation systems. NASA SP–5027. GPO, $0.60.

FILM

The chemistry of meteor vaporization. 1960. 29 min, sound, color. NASA.

**Recommended general sources of information.*

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70-12345#).

unit 9

unit 9

CHEMICAL EVOLUTION

Topics that may be enriched by use of this unit:

Amino acids
Proteins
Nucleic acids

For centuries men have asked the questions: How did life originate on Earth? Does life exist on other planets? For most of us these questions have represented honest but speculative thinking. Acquiring more definitive answers to these and related questions is one of the major objectives of our Nation's space program.

Before discussing NASA's interest in these questions, perhaps we should define what is meant by the word "life." What characteristics are associated with, and can be used to recognize, a living system? The term "life" as used in this discussion will refer to "any self-replicating, metabolizing system capable of mutation" (1).

Most students are familiar with Darwin's theory of biological evolution which states, in effect, that the diverse forms of life present on the Earth today have evolved from common origins by the processes of mutation and natural selection. This theory begins with the first living system and attempts to account for the elaboration and diversification of that "simple" system into the many and "complex" systems present today. The theory does not, however, attempt to account for the origin of the first living system. It is with this latter point that the theory of chemical evolution is concerned.

THEORY OF CHEMICAL EVOLUTION

The theory of chemical evolution states that life originated spontaneously on the Earth as the culmination of an evolutionary process in which the "molecules of living systems" were elaborated by chemical reactions. Although it is quite obvious that many diverse forms of life exist today, ranging from simple single-celled bacteria to complex multicelled plants and animals, it is equally true that at the molecular level living systems are quite similar. They contain the same types of molecules – water, proteins, nucleic acids, carbohydrates, and lipids. The relative proportions of these molecules and their organization serve to distinguish the different forms of life. The function of the theory of chemical evolution is to account for the formation of these biological molecules and for their organization into living systems.

FORMATION OF BIOLOGICAL MOLECULES

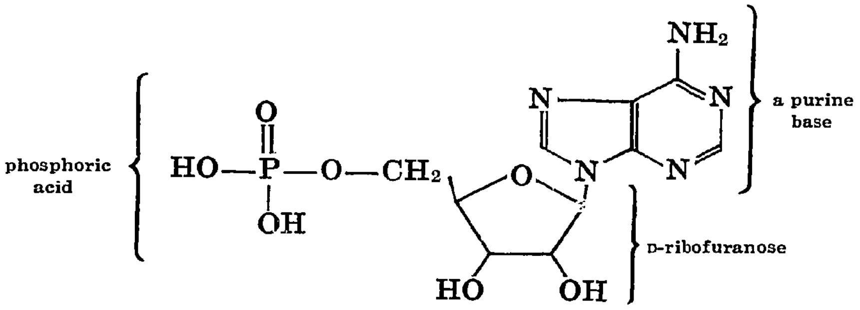
Experiments in chemical evolution have been based on the premise that the origin of life on Earth is primarily a detailed problem in organic chemistry (2). The molecules of which living systems are composed were most likely formed in the absence of any living system by chemical reactions among compounds existing on the primitive Earth. The problem then becomes one of defining two things: (*a*) what substances were available on the primitive Earth, and (*b*) the ways in which these substances could have interacted to produce the biological molecules and macromolecules.

Although there is some disagreement concerning the physical processes involved in the formation of the Earth, it is generally agreed that the nature of the primitive atmosphere was highly reducing (3). Under these conditions the elements of major importance in biological molecules – carbon, hydrogen, nitrogen, and oxygen – would be present most likely as methane, ammonia, water, and hydrogen. Therefore, it is probably through interactions of these substances that biological molecules were formed.

Mixtures of methane, ammonia, hydrogen, and water vapor are quite unreactive in the absence of an external source of energy. Probable sources of energy on the primitive Earth that could have initiated a reaction among these substances include ultraviolet radiation, electrical discharge, radioactivity, and heat. Of these, ultraviolet radiation and electrical discharge would likely have been the most important (3). The relative absence of oxygen and ozone – good absorbers of ultraviolet radiation – from the primitive atmosphere would have permitted much larger quantities of ultraviolet radiation to reach the surface of the Earth than at the present time. Likewise, there is no reason to doubt that electrical discharges (lightning) occurred in the primitive atmosphere in much the same way as today.

Less agreement exists on the role of heat as a source of energy on the primitive Earth. It has been suggested (3) that the temperature of the Earth's crust probably never exceeded 100° C and was, in fact, probably close to present terrestrial temperatures. Others (2, 4) believe that volcanic activity may have been quite extensive during this time and that surface temperatures could have reached 150° to 200° C or higher.

There is then the question of whether these conditions of chemical composition and energy sources were sufficient to form biological molecules. Testing of the hypothesis is confined to laboratory experiments in which a reasonable approximation of the primitive atmosphere is reproduced. As a result of the impetus provided by NASA, such experiments have become quite numerous. Much of this laboratory work has been directed toward elucidating the ways in which proteins and nucleic acids may have originated. Proteins are polymers of amino acids and represent the major structural (tissues) and/or catalytic (enzymes) macromolecules of all living systems on Earth. Nucleic acids are polymers of units known as nucleotides and are the informational macromolecules of living systems. A nucleotide consists of a purine or pyrimidine base in N-glycosidic linkage with either D-ribofuranose or D-2-deoxyribofuranose and phosphoric acid in ester linkage with one of the alcohol groups of the sugar moiety. For example, adenosine monophosphate has the following structure:



In view of the criteria that we have established for a living system—"a self-replicating, metabolizing system capable of mutation"—it is logical that interest should center on these two macromolecules. The reactions of metabolism are catalyzed by a group of proteins known as enzymes. Self-replication requires the ability to transfer information from one generation to the next, and mutation occurs as a result of changes in the nucleic acid molecules. Hence both of these macromolecules may be considered indispensable to living systems.

EXPERIMENTS IN CHEMICAL EVOLUTION

One of the earliest laboratory experiments (1953) was that of S. L. Miller (5) in which an electric discharge (to simulate lightning) was passed through an atmosphere of methane,

ammonia, water vapor, and hydrogen (Figure 9–1).
the reaction products revealed the presence of a
compounds, including formaldehyde, hydrogen cya
least four different amino acids commonly found in
Strecker-type synthesis (illustrated as follows for t
amino acid, glycine) has been proposed as the rout
the amino acids were formed.

Gas phase:

$$CH_4 + NH_3 + H_2O + H_2 \rightarrow HCHO + HCN + \text{other pr}$$

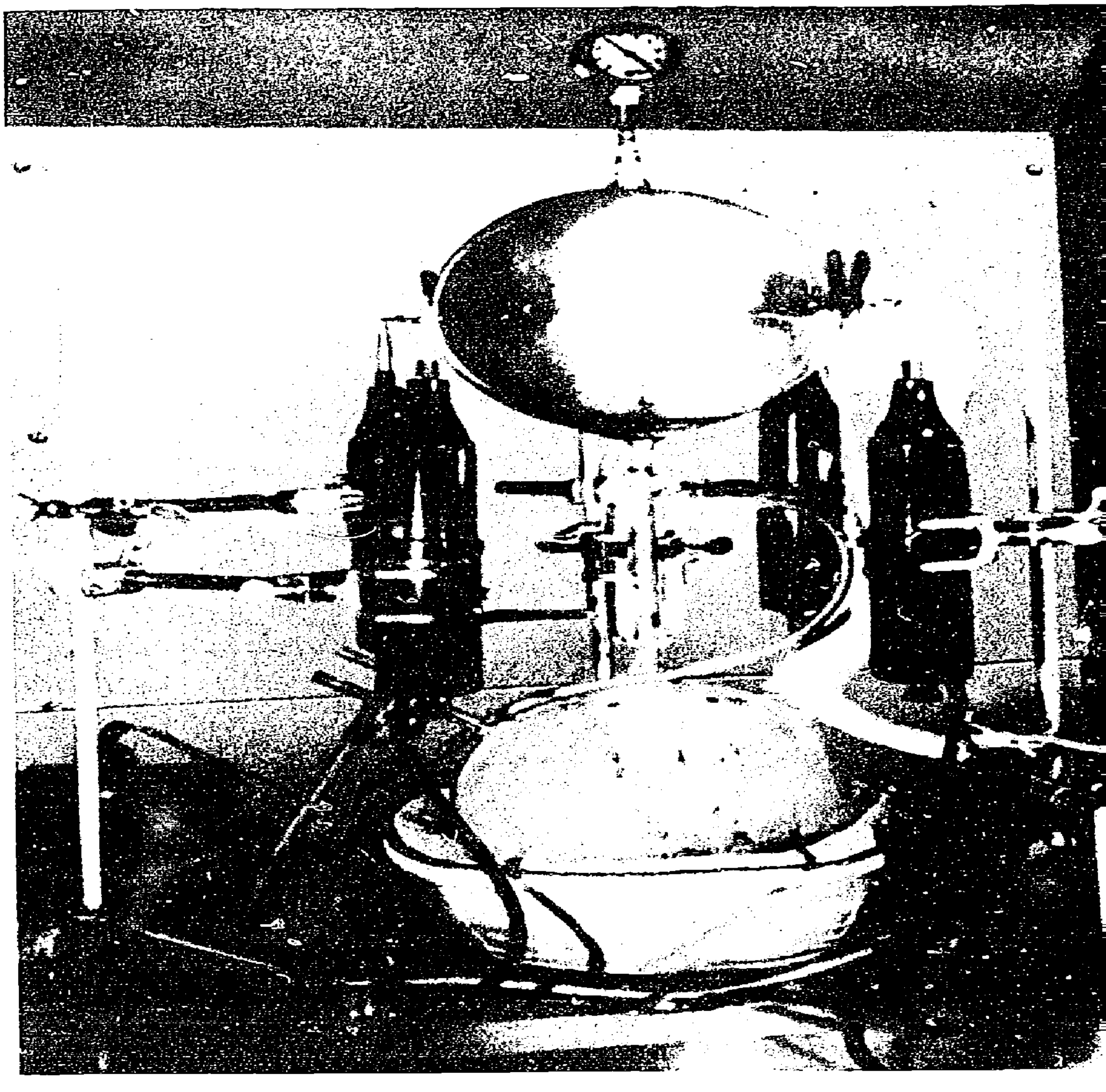


FIGURE 9–1. *Electric discharge apparatus. Simulated lightning is passed thro*
primitive Earth atmosphere composed of CH_4, NH_3, H_2O, and H
pounds, including some amino acids, result.

nical Evolution

Analysis of
a variety of
nide, and at
n proteins. A
the simplest
ate by which

roducts

rough a synthetic
$_2$. Different com-

Aqueous phase:

$$HCHO + HCN + NH_3 \rightarrow NH_2CH_2CN + H_2O$$

$$NH_2CH_2CN + 2H_2O \rightarrow \underset{\text{glycine}}{NH_2CH_2COOH} + NH_3$$

This mechanism is consistent with the observed time sequence of product formation (Figure 9–2). These results have been confirmed and extended by Miller and numerous other workers using various starting materials and energy sources. In all successful experiments, reducing conditions prevailed in the reaction mixture.

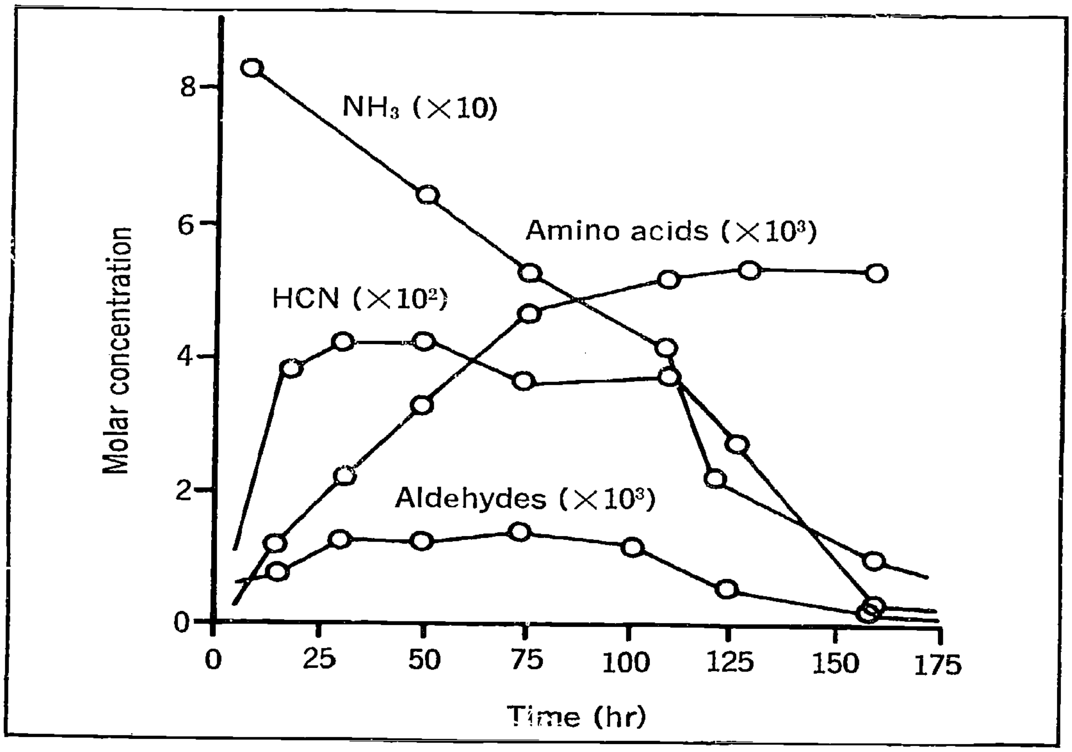
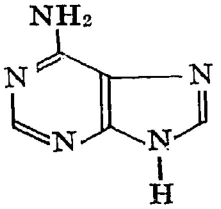


FIGURE 9–2. *Change in concentration of NH_3, HCN, aldehydes, and amino acids during sparking experiment (5). The concentrations of HCN and aldehydes first increase and then decrease as these reaction intermediates combine with ammonia to form amino acids.*

Synthesis of many of the amino acids commonly found in proteins preceded by several years the first demonstrated synthesis of a nucleic acid component under possible primitive Earth conditions. In 1960, J. Oró reported that upon heating an aqueous solution of ammonia and hydrogen cyanide (a product observed in Miller's reaction system), the compound adenine is formed. The reaction probably proceeds with ammonium cyanide as an intermediate:

$$NH_3\,(aq) + HCN\,(aq) \rightarrow NH_4CN\,(aq) \xrightarrow[24\ \text{hr}]{90^\circ\ \text{C}}$$



Since his initial report, Oró has proposed a more detailed mechanism (6). Of all the nitrogen bases commonly found in nucleic acids, adenine is very likely the most important. It is not only a constituent of nucleic acids but also of numerous other biologically important molecules, including the energy-transfer compound adenosine triphosphate (ATP).

Confirmation of the synthesis of adenine from hydrogen cyanide as well as evidence for the synthesis of guanine was established by workers at NASA Ames Research Center (7) who used ultraviolet light as the energy source. Additional experiments by this group have established the synthesis of ribose and deoxyribose, the sugar moieties of the nucleic acids, by the action of ultraviolet radiation on formaldehyde. This reaction, though similar in effect to the polymerization of formaldehyde in alkaline media (Unit 2, "Life-Support Systems"), is not base catalyzed. The pH remains nearly constant at 4.5 throughout the course of reaction.

The first report of a pyrimidine base being synthesized under possible primitive Earth conditions was that of Fox and Harada (8) who, using heat as the energy source, observed the formation of uracil. Oró (6) has proposed mechanisms by which each of the common pyrimidine bases (cytosine, uracil, and thymine) as well as the purine bases (adenine, guanine, xanthine, and hypoxanthine) could have been formed on the primitive Earth. These mechanisms are based upon interaction of compounds observed as products of the reaction of methane, ammonia, water vapor, and hydrogen.

ORGANIZATION PROCESSES

Formation of the necessary biological molecules is only the first step, however, in the development of a living system. The processes by which these molecules were modified and organized into a living system is not only more difficult to postulate, but also more difficult to investigate in the laboratory. Whereas the formation of biological molecules can occur in a relatively short period of time, the modification and organization processes may require intervals of time not amenable to laboratory investigation. For example, it has been estimated that some 2 million years were required for the first one-celled organism to evolve on the primitive Earth (9).

Indicative of the efforts being made to gain some insight into these organizational processes is the work of Ponnamperuma (7) on the synthesis of nucleotides and of Fox (2) on the formation of proteins. Ponnamperuma and his coworkers have shown that adenine and ribose, when exposed to ultraviolet light in the presence of a suitable source of phosphate, can combine to

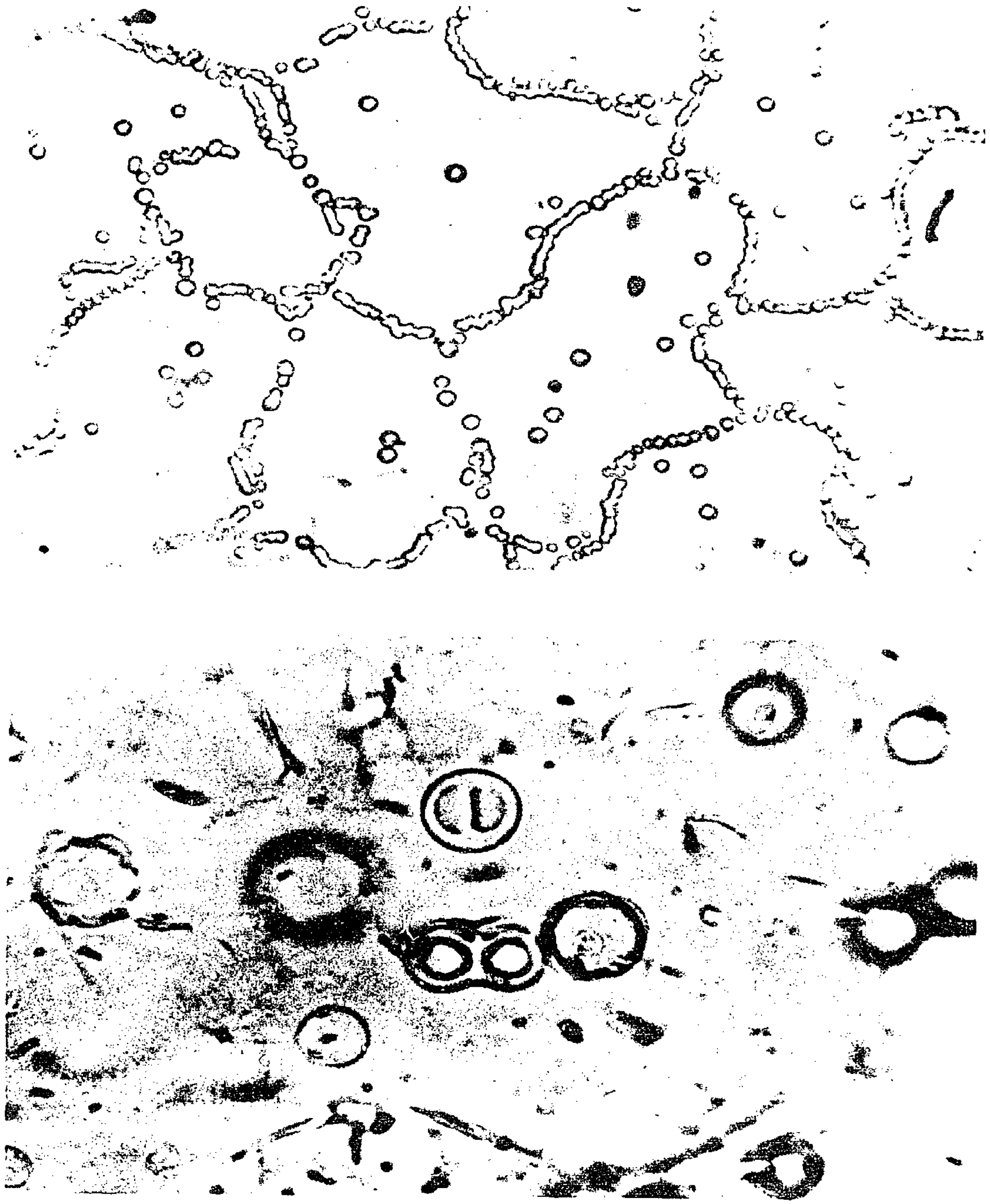


FIGURE 9–3. *Simple cell-like microspheres formed by heating proteinoid.*

form the nucleotide adenosine monophosphate. The energy-storage compound adenosine triphosphate is also produced.

Fox and his associates (10, 11, 12) have shown that moderate heating (170° C) of free α-amino acids, which could have occurred as a result of volcanic activity on the primitive Earth, yields a proteinlike material that they have termed "proteinoid." Among the protein-like properties of this material is a minimal catalytic activity—an ability to promote simple metabolic reactions. In addition, this proteinoid can, through contact with water, organize itself into spherical particles (microspheres) that *resemble* simple cellular structures (Figure 9–3). The emphasis here must be placed on the word *resemble*; they are not living cells. This resemblance suggests a possible route by which the first cell(s) could have originated on Earth.

In summary, such experiments demonstrate the feasibility of the synthesis of biological molecules and their self-organization into structures resembling primitive cells. It may also be logically inferred that similar syntheses could have occurred or could be occurring on other planets having conditions analogous to those postulated for the primitive Earth. A widely held theory of the origin of the solar system suggests that in their early stages the atmospheres of all the planets may have been essentially the same (13). If so, one logically might expect to find biological molecules on all planets; the degree of organization attained by these molecules would have been determined by the environmental changes that occurred on the various planets. (See Unit 10, "Detection of Extraterrestrial Life.") Such findings would do much to substantiate the theory of chemical evolution.

ACTIVITIES

Proteins are the major structural and/or catalytic components of living systems. Their synthesis under possible prebiological conditions on Earth represents an important aspect of the theory of chemical evolution. Similarly, the ability of proteins to organize into structures resembling primitive cells lends credence to the theory of the spontaneous generation of living systems. Beginning with the simple compounds methane, ammonia, water, and hydrogen, the essential steps in the theory of chemical evolution—formation of simple biological molecules, elaboration to more complex molecules and macromolecules, organization into rudimentary cell-like structures—have been demonstrated in the laboratory to a greater or lesser degree.

In the two experiments described here, the simple biological molecules known as amino acids will be polymerized (thermal copolymerization) to protein-like material (proteinoid) in a manner analogous to that of Fox and Harada (10, 11). The proteinoid will then be treated in a manner that causes it to form spherules (microspheres) resembling primitive cells (12).

CHEMICAL SYNTHESIS OF PROTEINACEOUS MATERIAL

A mixture of 0.01 mole of DL-glutamic acid and 0.02 mole of glycine is prepared. (DL-Aspartic acid may be substituted for glutamic acid. Similarly, any of the following may be substituted for glycine: alanine, valine, leucine, or phenylalanine.) The mixture should be ground in a mortar to form a fine powder. This ground mixture is placed into a test tube, and the tube is immersed in an oil bath maintained at 175° to 180° C. The tube is heated for 1 to 2 hr during which time the mixture will melt slowly. Because small quantities of gas are evolved during the heating, do not stopper the test tube. The test tube is removed from the oil bath; the liquid solidifies as the tube cools to room temperature. Upon addition of 10 ml of H_2O, a white-to-gray precipitate separates and is removed by filtration. This precipitate is washed with 10 ml of H_2O and then with 10 ml of ethanol. Its structure can then be confirmed as having protein-like characteristics by the biuret test.

The biuret test is based on the fact that compounds containing two or more peptide bonds produce a pink-to-violet color when treated with alkaline copper sulfate solution. The peptide bond is the characteristic linkage joining amino acid units in a protein molecule. Because free amino acids do not give this reaction, a positive test is indicative of the formation of peptide bonds.

A sample of the protein material previously prepared is dissolved in 2 ml of 0.1 *N* NaOH solution. After addition of three drops of 0.5 percent $CuSO_4$ solution, the formation of a pink to violet color constitutes a positive biuret test. For best results the color should be compared to a blank containing only 2 ml of 0.1 *N* NaOH solution.

PRODUCTION OF MICROSPHERES

A mixture is prepared containing equimolar amounts of as many of the amino acids listed in Table 9-1 as are available. The mixture is ground to form a fine powder.

Into a large test tube is placed 2.0 g of L-glutamic acid. The test tube is immersed in an oil bath maintained at 170° C until the glutamic acid melts (30 to 60 min). To this melt, a mixture of 2.0 g of DL-aspartic acid with 1.0 g of the prepared amino acid mix-

TABLE 9-1 THE AMINO ACIDS USED IN FORMING PROTEINS

Amino Acid	M.W.	Amino Acid	M.W.
DL-Alanine	89	DL-Leucine	131
L-Arginine monohydrochloride	211	DL-Isoleucine	131
L-Cystine	240	DL-Methionine	149
Glycine	75	DL-Phenylalanine	165
L-Histidine monohydrochloride		L-Proline	115
(monohydrate)	210	DL-Serine	105
L-Lysine monohydrochloride	183	DL-Threonine	119
DL-Tryptophan	214	DL-Valine	117
DL-Tyrosine	181		

ture is added with stirring. The resulting mixture is heated at 170° C under an atmosphere of nitrogen or carbon dioxide until the color of the liquid changes to amber (1 to 2 hr). A slow, continuous flush of N_2 or CO_2 from a nozzle lowered partway into the test tube provides the necessary atmosphere. Large amounts of gas are evolved as the reaction proceeds, and the test tube should not be stoppered.

At the end of the heating period the reaction mixture is allowed to cool to room temperature. Twenty ml of water are added to the resultant glass, and the latter is rubbed vigorously with a stirring rod until the glassy material is converted to a yellow-brown granular precipitate. This mixture should be allowed to stand overnight at room temperature.

The precipitate is removed by filtration and washed successively with 10 ml of H_2O and 10 ml of ethanol. About 15 mg of the washed proteinoid material is placed into a test tube and 3.0 ml of 1.25 percent NaCl solution is added. The test tube should be agitated to promote solution.

To prepare a microscope slide, a drop of the test solution is placed near the center of a clean glass slide and allowed to air dry (do not force dry). The slide (smear side up) should be passed through the tip of a flame several times to make the smear adhere to the slide. A drop of immersion oil is placed on the slide, and the tip of the objective lens is immersed in the oil in the usual manner.

The remaining solution is heated to boiling for 1 min and then is allowed to cool to room temperature. One drop of this solution is used to prepare a second microscope slide. Both slides are examined under the oil-immersion objective lens of a light microscope. The larger number of spherical particles on the second slide can be noted.

LITERATURE CITED

1. Young, R. S. 1962. Exobiology, p. 29. *In* Bioastronautics. NASA SP-18. GPO, $0.30.

2. Fox, S. W. 1965. The terrestrial origins of macromolecules and of cells, pp. 1–34. *In* Colloquium on elementary biological systems and abiogenesis. NASA CR-74819. NTIS N66-24842#.

3. Miller, S. L., and H. G. Urey. 1959. Organic compound synthesis on the primitive earth. Science 130: 245.

*4. Young, R. S. 1966. Extraterrestrial biology, pp. 22–35. Holt, Rinehart & Winston, Inc., New York.

5. Miller, S. L. 1957. The mechanism of synthesis of amino acids by electric discharges. Biochimica et Biophysica Acta 23: 484.

6. Oró, J. 1965. Stages and mechanisms of prebiological organic synthesis, pp. 137–161. *In* S. W. Fox, The origin of prebiological systems and of their molecular matrices. Academic Press, Inc., New York.

7. Ponnamperuma, C. 1965. Abiological synthesis of some nucleic acid constituents, pp. 221–235. *In* S. W. Fox, The origin of prebiological systems and of their molecular matrices. Academic Press, Inc., New York.

8. Fox, S. W., and K. Harada. 1961. Synthesis of uracil under conditions of a thermal model of prebiological chemistry. Science 133: 1923.

9. Gardner, M. H. 1965. Chemistry in the space age, p. 167. Holt, Rinehart, & Winston, Inc., New York.

10. Fox, S. W., and K. Harada. 1958. Thermal copolymerization of amino acids to a product resembling protein. Science 128: 214.

11. Fox, S. W., and K. Harada. 1960. The thermal copolymerization of amino acids common to protein. Journal of the American Chemical Society 82: 3745.

12. Fox, S. W., K. Harada, and J. Kendrick. 1959. Production of spherules from synthetic proteinoid and hot water. Science 129: 1221.

**Recommended general sources of information.*

13. National Aeronautics and Space Administration. 1966. Significant achievements in space bioscience 1958 to 1964, p. 8. NASA SP-92. GPO, $0.55.

OTHER REFERENCES

*Fox, S. W., K. Harada, G. Krampitz, and G. Mueller. 1970. Chemical origins of cells. Chemical and Engineering News 48 (26): 80.

*Glasstone, S. 1968. The book of Mars, pp. 153–207. NASA SP–179. GPO, $5.75.

*Kenyon, D. H., and G. Steinman. 1969. Biochemical predestination, pp. 80–259. McGraw-Hill Book Co., Inc., New York.

*Keosian, J. 1964. Origin of life. Reinhold Publishing Corp., New York.

Shinsheimer, R. L. 1967. What is life? California Institute of Technology Quarterly. Offprints available from: Manager, Public Educational Services, NASA Jet Propulsion Laboratory, 4800 Oak Grove Dr., Pasadena, Calif. 91103.

Vogel, H. J., and R. H. Vogel. 1967. Some chemical glimpses of evolution. Chemical and Engineering News 45(52): 90.

FILMS

The chemistry of life. 1961. 19 min, sound, color. NASA.

How did life begin? 1961. 20 min, sound, color. NASA.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70–12345#).

**Recommended general sources of information.*

unit 10

unit 10

DETECTION OF EXTRATERRESTRIAL LIFE

Topics that may be enriched by use of this unit:

- Instrumentation
- Spectroscopy
- Radioactivity
- Mass spectrometry
- Gas chromatography
- Beer-Lambert law

Does life exist elsewhere in the universe? If so, is it similar to life on Earth? If extraterrestrial life does exist, how can it be detected? These are some of the questions underlying the NASA program of extraterrestrial biology. One of the major objectives of this program is to obtain information concerning the universality of life. Physicists and astronomers, through observations of stars and other planets in our universe, have demonstrated the universal nature of various laws of physics. Chemists, through the use of such instruments as an optical telescope equipped with a spectroscope, have demonstrated the presence on other stars and planets of the same elements and simple compounds found here on Earth. Hence, the principles of chemistry also appear to be universal in nature. But biologists have thus far been unsuccessful in their attempts to demonstrate conclusively the presence of living forms on other planets.

A second major objective of NASA's program of extraterrestrial biology is to obtain evidence relative to the theory of the origin of life on Earth. If life arose on Earth by a process of chemical evolution (Unit 9, "Chemical Evolution"), and if many of the planets of the universe at the time of their origin had environments similar to that of the primitive Earth, then the possibility exists that on these planets a similar evolutionary process could have occurred. At least three possible stages can be visualized (1) for such an evolutionary process on another planet:

1. *A prebiota characterized by the absence of living forms.*—The presence of biological molecules might, however, be observed in this stage.

2. *An active biota characterized by the presence of living forms.*—

The complexity of these forms may range from simple, single-celled systems to intricate, multicelled systems.

3. *An extinct biota characterized by the absence of living forms but evidence of former life.* — Such a stage could result if the living forms were unable to adjust to changing conditions on the planet.

Evidence for any of these stages would have important implications regarding the theory of chemical evolution.

One question arises: How can it be determined which, if any, of these stages exist on another planet? Sending astronauts to a nearby planet to make observations and collect samples is one approach. This approach has been realized for the Moon, despite the great difficulties, but most planets are either at such great distances or have such hostile environments that manned space flight to them is not presently feasible, and may never be practical. For such planets the prospect for seeking evidence of life lies, at present, with the use of unmanned spacecraft equipped with life-detection devices.

Facing these problems, space scientists are preparing several unmanned exploratory vehicles equipped with a variety of instruments and other devices designed to detect the chemical, morphological, or functional attributes of life (2). Chemical attributes refer to life-related compounds, proteins and nucleic acids in particular. Morphological attributes refer to structural features, such as organized cells. Functional attributes are metabolic activities.

An assumption inherent in the development of all these life-detection devices is the similarity of the attributes of life in extraterrestrial forms to those of Earth forms. While such an assumption may or may not be totally valid, it is nevertheless necessary. Because we know of no life forms other than those found on Earth, it is logical to develop the initial experiments on the basis of our concrete knowledge rather than on the basis of speculation about the nature of life on other planets. Consequently, the instruments being considered for use aboard these exploratory vehicles are, in many cases, the same types as those currently being used in research laboratories throughout the world. They must, however, be modified in size, weight, and durability to meet the requirements of space travel.

DETECTION OF THE CHEMICAL ATTRIBUTES OF LIFE

Instruments for detecting the life-related molecules may be classified as remote analysis or sample processor types (3). The remote analysis instruments are designed to make observations from a distance—during flyby missions—whereas sample processor types are landed on the surface of a planet and analyze samples of planetary material. It is this latter type that will be discussed.

A search for the chemical attributes of life constitutes the most general approach to the detection of extraterrestrial life. The techniques for detecting biological molecules make no distinction among molecules present as part of a prebiotic stage, as part of active biotic forms, or as remnants of a former biota. Thus, while these techniques will not provide a definite answer to the existence of living systems on another planet, they will provide information regarding the feasibility of such systems.

Among the techniques being considered for the detection of biological molecules are mass spectrometry, gas chromatography, and absorption spectroscopy.

Mass Spectrometry

Mass spectrometry can be used for determining precise atomic weights as well as the masses and abundance of isotopes of elements. Mass spectrometry is based on the principle that positive ions, produced by the bombardment of gaseous atoms or molecules with high-energy electrons, travel in a circular path when accelerated through a magnetic field. The radius of the circular path is related to the charge-to-mass ratio of the ionic particle. Application of this technique to the identification of biological molecules is based upon the fact that a given molecule, when subjected to pyrolysis and ionization under controlled conditions, exhibits a characteristic fragmentation pattern. The mass spectrum produced by these ion fragments is thus characteristic of the molecule and may be used for its identification. For example, the mass spectrum of a sample of water vapor shows the presence of the positive ions H_2O^+, OH^+, O^+, and H^+. The presence of these same ions in the mass spectrum of a sample of planetary material would constitute evidence for the presence of water.

As presently conceived, a primary role of mass spectrometry in life-detection probes will be the identification of amino acids (the monomeric units of proteins) through knowledge of the masses of their pyrolysis products. Laboratory tests are currently being carried out under the auspices of NASA (2, 4, 5) to determine the feasibility of this approach (Figure 10–1).

Gas Chromatography

In gas chromatography, a mixture of substances in the gaseous state is transported through a packed column by an inert carrier gas, usually nitrogen or helium (Figure 10–2). The length of time required for each substance to move through the column is determined in part by the affinity of the substance for the packing material.

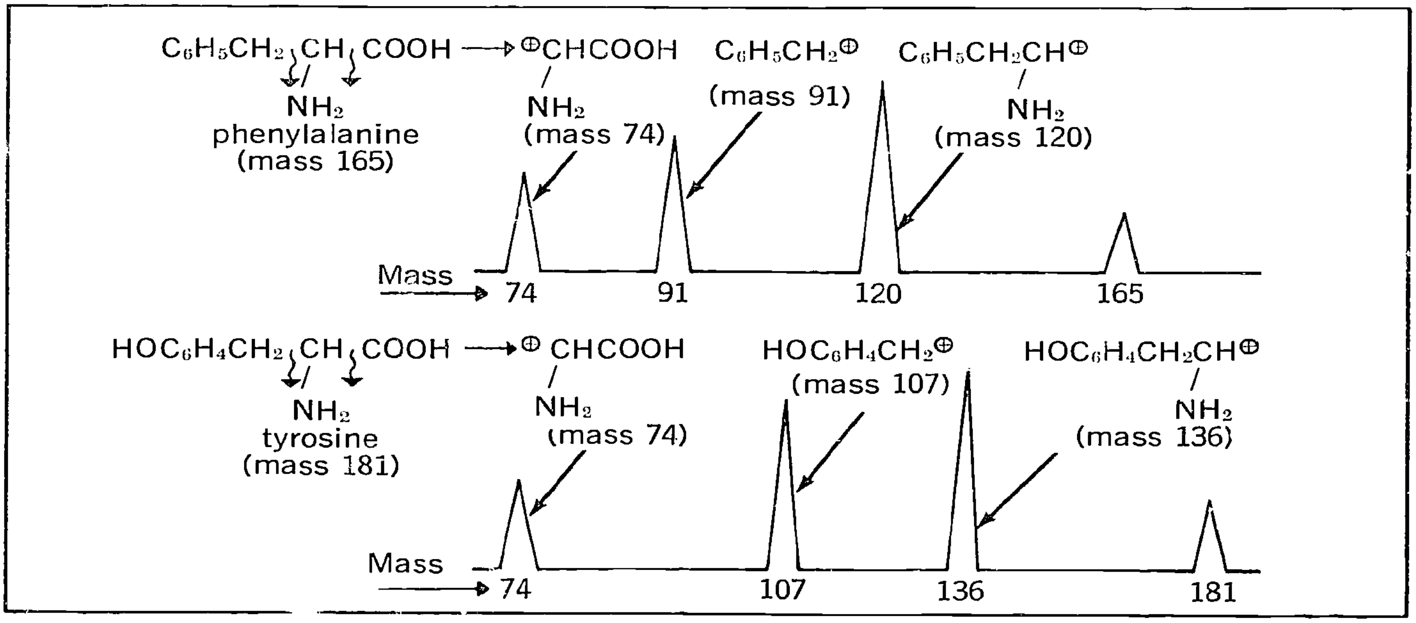


FIGURE 10–1. *Origin and appearance of the mass spectra of two amino acids. Upon electron bombardment, certain bonds in the molecule are broken to form positively charged fragments that the mass spectrometer separates and records according to mass.*

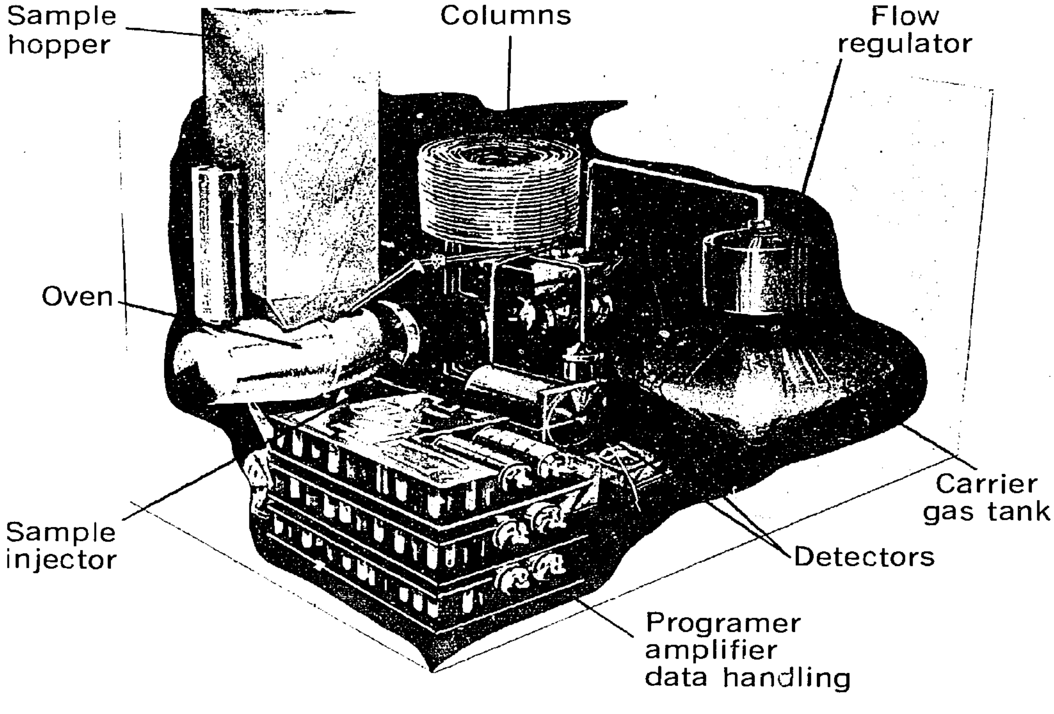


FIGURE 10–2. *Essential components of a gas chromatograph. The sample is injected into the oven where it is volatized. Then the sample and carrier gas flow into the column where the mixture is resolved, allowing component detection.*

Because, in general, these affinities differ from one substance to another, the components of the mixture move through the column at different rates and are resolved. The time required for a given substance to move through the entire length of the column (retention time) is a characteristic and reproducible property, and can thus be used as evidence for identification of the substance (Figure 10-3).

Gas chromatography is presently of interest in life-detection studies for use in "cleaning up" planetary samples prior to mass spectrometric analysis. Because of the large number of volatile components conceivably present in any random sample of planetary material, direct mass spectrometric analysis is likely to yield a spectrum of such complexity as to make interpretation extremely difficult. However, a sample can be first resolved by gas chromatography into fractions containing at most only a few components, and the effluent from the column then passed into a mass spectrometer. Thus the complexity of the spectrum from the mass spectrometer is reduced in proportion to the number of components in each fraction of the effluent. Furthermore, the retention time of each fraction provides additional evidence regarding its structure.

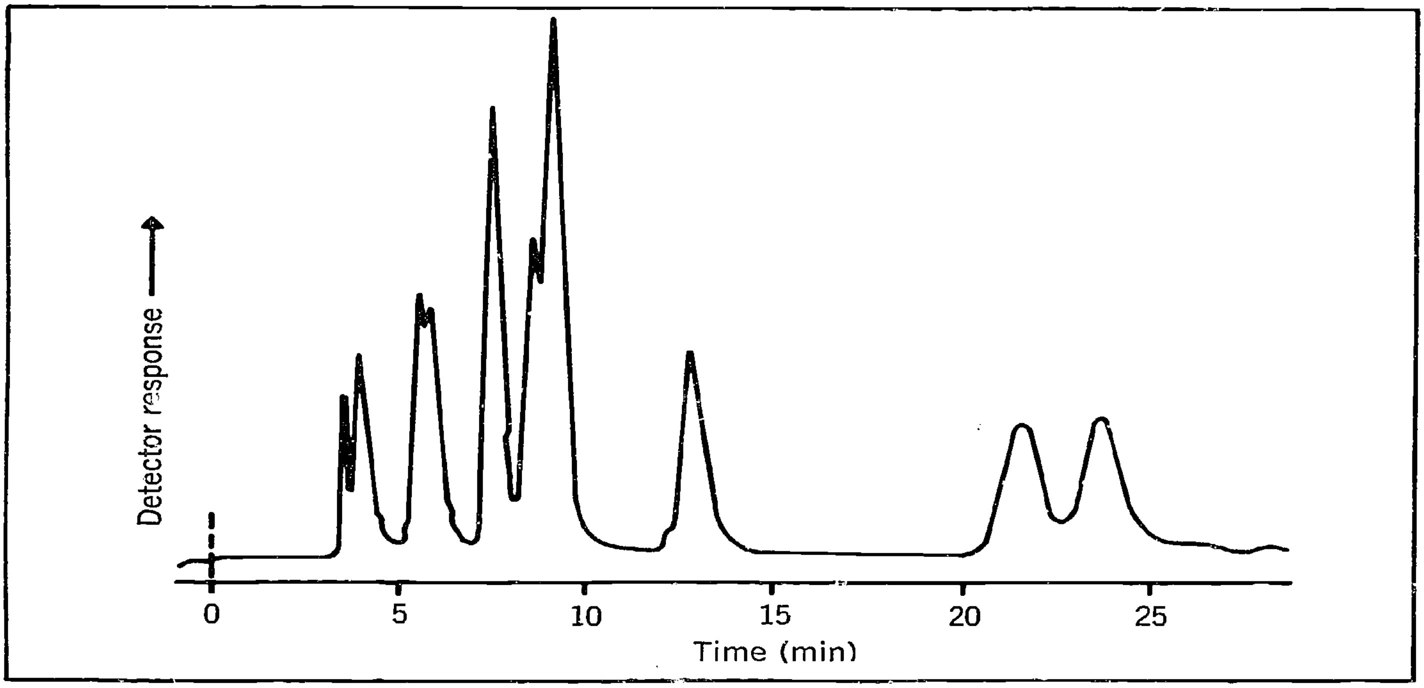


FIGURE 10-3. *Typical gas chromatogram. Zero time is the time of injection of the sample. The time on the minutes scale for each peak is its retention time, and identifies the gas passing through the detector. The area under each peak is proportional to the amount of each component.*

Absorption Spectroscopy

Absorption spectroscopy is based on the selective absorption of electromagnetic radiation by substances. The amount of radiation absorbed varies with the substance, the wavelength, and with the amount of material in the sample (concentration). A plot of the absorbance as a function of wavelength gives an absorption spectrum of the sample. The nature of the absorption spectrum is influenced by the types of chemical bonds present and thus can be used to help identify the constituents of the sample.

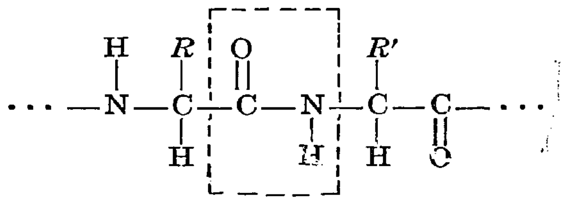
From a practical standpoint, any absorption spectrophotometer is limited in operation to a particular portion of the electromagnetic spectrum. There are instruments for obtaining ultraviolet absorption spectra ($\lambda = 180$ to 400 mμ), others for use in the visible region of the spectrum ($\lambda = 400$ to 800 mμ), and still others for use in the infrared portion of the spectrum ($\lambda = 2.5$ to 15 μ).

Absorption spectra are also useful in quantitative determinations. From the absorption spectra of pure substances, one identifies wavelengths of maximum absorption, and generally, at these wavelengths measurements are made to determine the amount of these substances present in a sample. The relationship between absorbance and amount of material is expressed by the Beer-Lambert law:

$$A = kcl$$

where A is the absorbance, k is a proportionality constant, c is the concentration, and l is the pathlength. For a fixed pathlength, absorbance varies directly with concentration (i.e., a plot of absorbance versus concentration gives a straight line). Similarly, for a fixed concentration, absorbance varies directly with pathlength. Thus, absorbance depends upon the number of particles encountered by the radiation as it passes through the sample. These principles are applied in life-detection systems designed to detect types of biological macromolecules (proteins, nucleic acids, and carbohydrates).

In a protein molecule the monomeric units (amino acids) are linked by means of a peptide bond (the bond between the carboxyl and amine groups of adjacent amino acids):



$$\cdots\text{—}\overset{\mathrm{H}}{\underset{}{\mathrm{N}}}\text{—}\overset{R}{\underset{\mathrm{H}}{\mathrm{C}}}\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\underset{\mathrm{H}}{\mathrm{N}}\text{—}\overset{R'}{\underset{\mathrm{H}}{\mathrm{C}}}\text{—}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\text{—}\cdots$$

This grouping of atoms shows a strong absorbance in the ultraviolet region between 180 mμ and 220 mμ (λ max ~ 195 mμ) (Figure 10-4). Hence, measurement of the absorbance of a planetary sample at 195 mμ should provide evidence for the presence or absence of protein molecules.

As in all absorption studies, one must guard against the presence

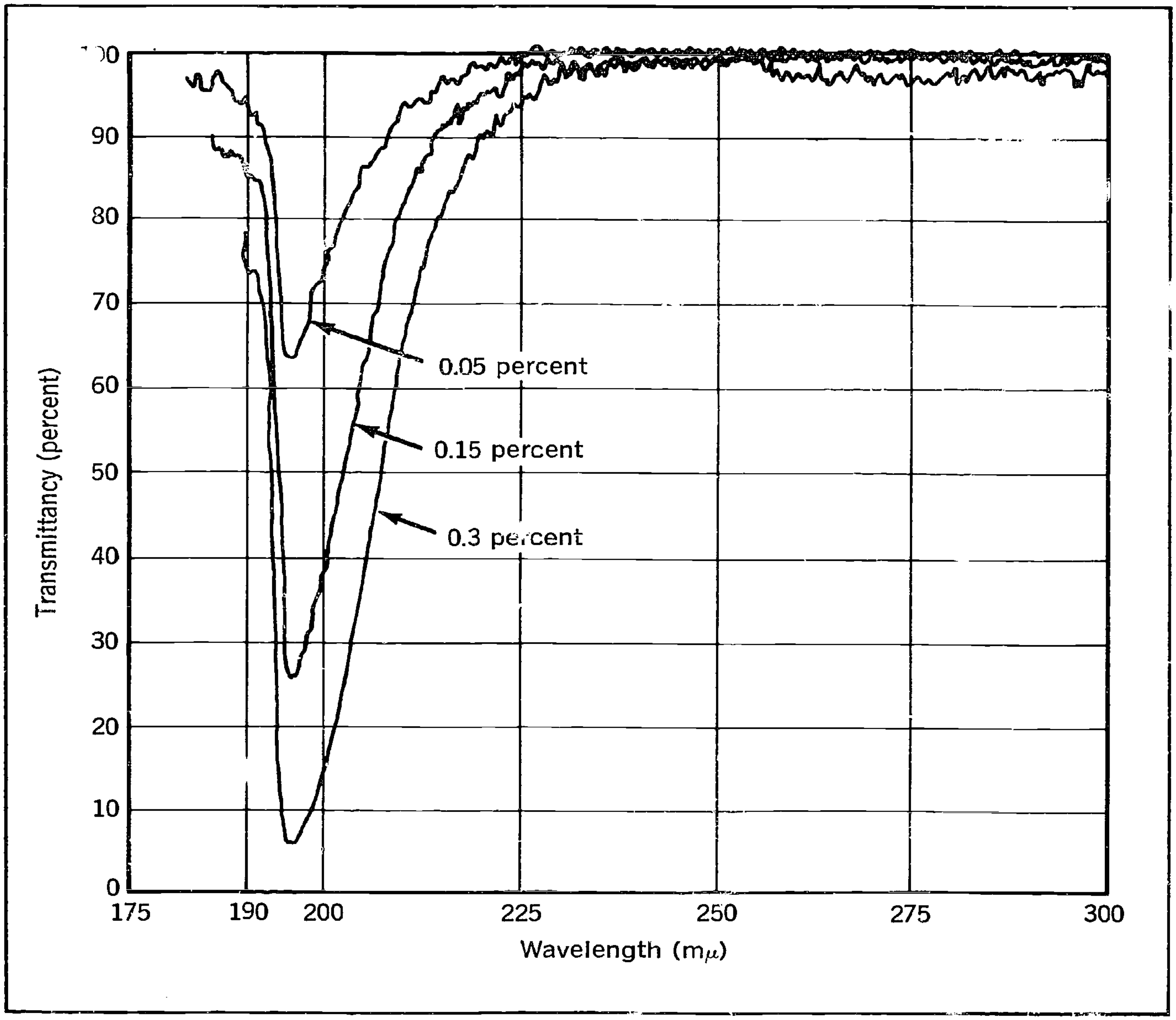
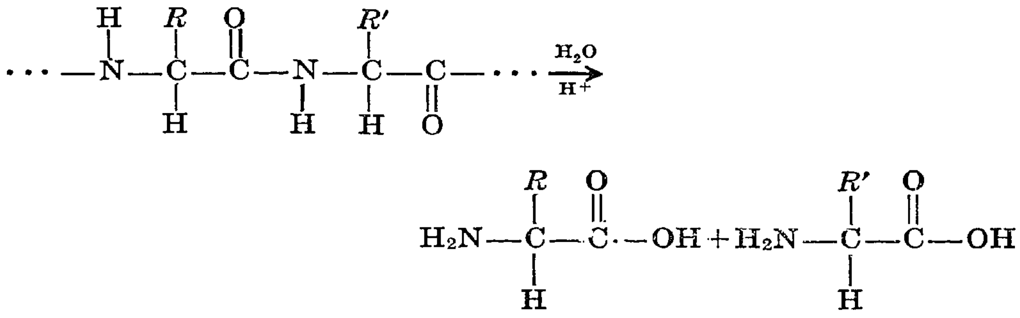


FIGURE 10-4. *Absorption spectra at pH 1 of three different concentrations of alanylglycylglycine (a tripeptide). Notice that the intensity of absorption varies with the number of peptide bonds present, but that the wavelength of maximum absorption is independent of concentration.*

of other substances that also absorb strongly at the wavelength being used. With a heterogeneous sample, such as a planetary surface sample, the possibility of other substances absorbing radiation in the region of 195 mμ is a distinct problem. One suggestion to distinguish peptide bond absorption from extraneous absorption takes advantage of the fact that peptide bonds are susceptible to hydrolysis:



$$\cdots-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\underset{\mathrm{H}}{\underset{|}{\overset{R}{\overset{|}{\mathrm{C}}}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\underset{\mathrm{H}}{\underset{|}{\overset{R'}{\overset{|}{\mathrm{C}}}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\cdots\xrightarrow[\mathrm{H^+}]{\mathrm{H_2O}}$$

$$\mathrm{H_2N}-\underset{\mathrm{H}}{\underset{|}{\overset{R}{\overset{|}{\mathrm{C}}}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}+\mathrm{H_2N}-\underset{\mathrm{H}}{\underset{|}{\overset{R'}{\overset{|}{\mathrm{C}}}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OH}$$

A marked decrease in the initial absorbance following hydrolysis of the sample would thus provide confirmatory evidence for the presence of peptide bonds in the original sample.

An alternate approach is based on the reaction of dyes, such as certain cyanine dyes (e.g., dibenzothiacarbocyanine), with biological macromolecules. The new bonds that are formed between the macromolecule and the dye frequently produce strong absorption in the visible region of the spectrum but at wavelengths distinctly different from the absorption maxima of the isolated macromolecules and dye molecules (Figure 10–5). These absorption bands are termed *J*-bands and are generally located between 450 mμ and 650 mμ. The band at 650 mμ is particularly interesting because only macromolecules of biological origin are known to produce this absorption band.

DETECTION OF THE FUNCTIONAL ATTRIBUTES OF LIFE

All living forms on Earth require a continuous supply of energy for survival. The ultimate source of this energy is the Sun. Light energy, however, cannot be used directly by living organisms to carry on their cellular activities but must first be converted to chemical energy through the process of photosynthesis. Some organisms, called photosynthetic organisms, are able to transform light energy from the Sun into the bond energy of various organic molecules. Nonphotosynthetic organisms can then use these organic molecules, and, through a series of transformations, abstract energy and eliminate the residue. Therefore, it would appear that instruments for the detection of the functional attributes of life could be designed to measure

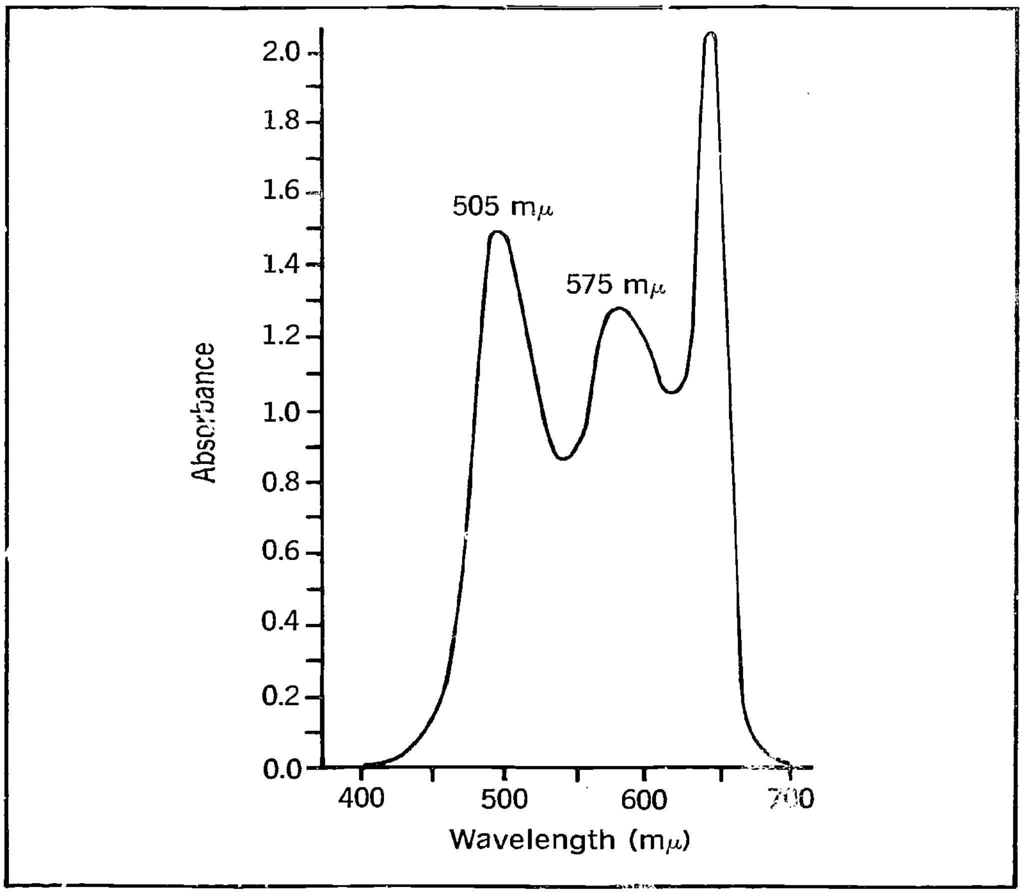


FIGURE 10–5. *Three absorption maxima in the J-band region. The first (505 mμ) is the region of normal dye absorption. The others are due to the interaction of the dye with a 0.002 percent solution of oxidized ribonuclease.*

the disappearance of some foodstuff or the appearance of some waste product in the environment. A third possibility would be to measure some cellular activity, such as growth, that is dependent upon the energy transformations occurring during cellular metabolism. The major drawback to the last approach is that, while such activities are dependent upon cellular metabolism, they are not necessary for cellular metabolism.

The present discussion will center on three devices—Gulliver, Wolf trap, and Multivator—that currently represent the most promising approaches to the detection of metabolic activities on other planets. Each of these devices is designed to detect an end product of metabolic activity in micro-organisms that may be present in planetary soil samples. Of all life forms, micro-organisms are the most ubiquitous on Earth. They are found to thrive under many extremes of environmental conditions

TABLE 10–1 EXTREME ENVIRONMENTAL CONDITIONS PERMITTING GROWTH

Factor	Minimum	Organism	Maximum	Organism
Temperature	$-30°$ C	Algae, yeast	104° C (10^3 atm)	*Desulfovibrio desulfuricans*
Gravity	0 *g*	Plants, animals	1.1×10^5 *g*	*Escherichia coli*
Pressure	10^{-9} mm Hg	*Mycobacterium smegmatis*	1400 atm	Marine organisms
Oxygen	0 percent	Hela cells, anaerobic bacteria	100 percent	Plants, animals
Water	Aw 0.5	Bacteria	Aw 1.0 (1 atm)	Aquatic organisms
NaCl, Na_2SO_4, $NaHCO_3$	....	....	67 percent	Photosynthetic bacteria
pH	0	*Thiobacillus thio-oxidans*	13	*Plectonema nostocorum*

From Young (1).
Aw refers to the weight fraction of water in the growing medium.

(Table 10–1) normally considered lethal to higher forms of life. Thus, micro-organisms must be regarded as the most probable form of life on other planets.

Gulliver

The energy-producing reactions of biological systems generally involve oxidation of foodstuffs. If molecular oxygen represents the ultimate oxidizing agent, a common end product is carbon dioxide. For example, the sugar glucose is oxidized in accord with the following net equation:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 690 \text{ kcal}$$

A life-detection device named Gulliver (Figure 10–6) is designed to detect carbon dioxide liberated during metabolism of carbon compounds by organisms. Detection is achieved by using carbon compounds containing the radioactive isotope of carbon, ^{14}C, so that the carbon dioxide produced will be radioactively labeled. Carbon-14 decays by beta emission:

$$^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{0}\beta^{-}$$

and these beta particles can be detected by a Geiger-Mueller (GM) tube. The GM tube is shielded from the synthetic medium

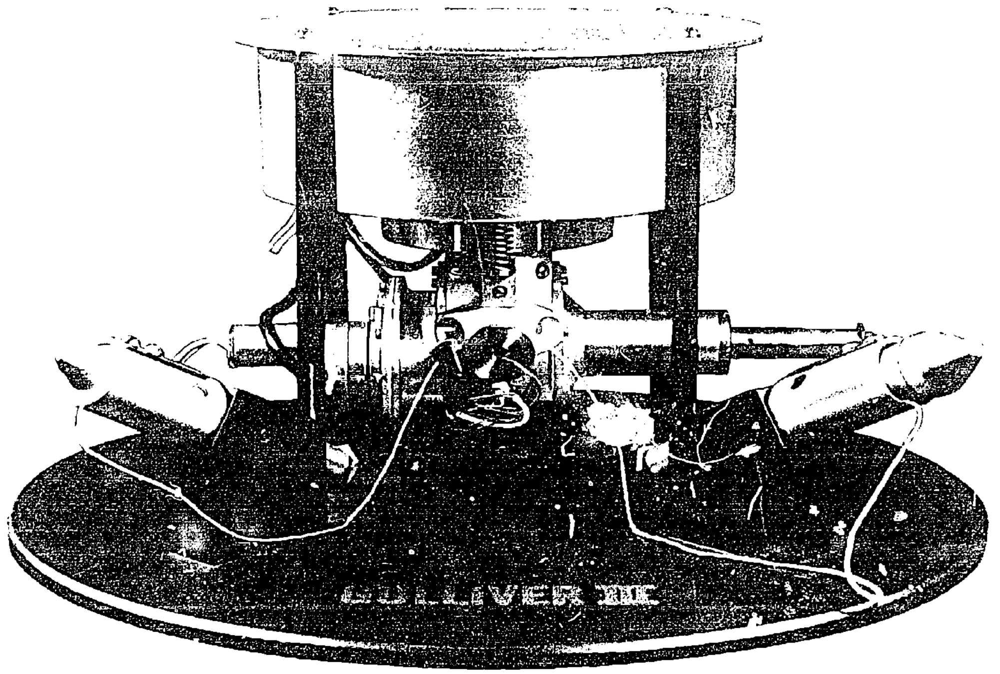


FIGURE 10–6. *A working model of Gulliver. This life-detection device has three "sticky strings" that are carried out in three different directions by bullets. As the strings are reeled back, planetary material clinging to the sticky substance is introduced into a nutrient broth.*

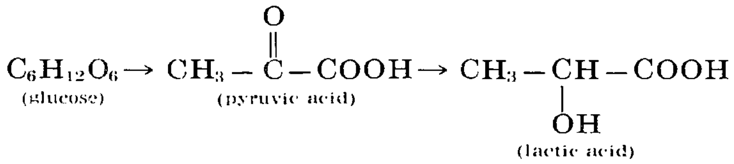
into which the planetary sample is placed but can detect the activity of any carbon dioxide produced in the reaction chamber. Thus, only radioactivity resulting from the oxidation of foodstuffs is monitored by the instrument.

Sampling of the planetary soil is achieved by use of strings coated with a sticky material such as glycerol. The strings are discharged from the device by projectiles and fall to the planetary surface. As the strings are reeled back, particles of the planetary surface are carried along and introduced into the reaction chamber. In the chamber they are mixed with a nutrient solution and the temperature of the solution is adjusted to a level suitable for growth and metabolism of organisms.

Wolf Trap

The Wolf trap is designed to detect two other phenomena that frequently accompany microbial metabolism: (*a*) changes in the pH of the medium that are caused by the formation of various organic acids and (*b*) changes in the turbidity of the medium caused by growth of the micro-organisms.

Organic acids are commonly formed as intermediary products of metabolism. Under conditions of limited oxygen supply, they frequently represent the end products of metabolism. For example, the oxidation of glucose under anaerobic conditions can give rise to pyruvic and lactic acids:



$$\underset{\text{(glucose)}}{C_6H_{12}O_6} \rightarrow \underset{\text{(pyruvic acid)}}{CH_3-\overset{\overset{O}{\|}}{C}-COOH} \rightarrow \underset{\text{(lactic acid)}}{CH_3-\underset{\underset{OH}{|}}{CH}-COOH}$$

Accumulation of these acids in the culture medium produces an increase in acidity that may be detected by use of a pH electrode.

In the Wolf trap (Figure 10–7) a planetary soil sample is introduced into a sealed culture tube. The amount of available oxygen is limited to that which was originally present plus any introduced with the sample. Any micro-organisms that are present

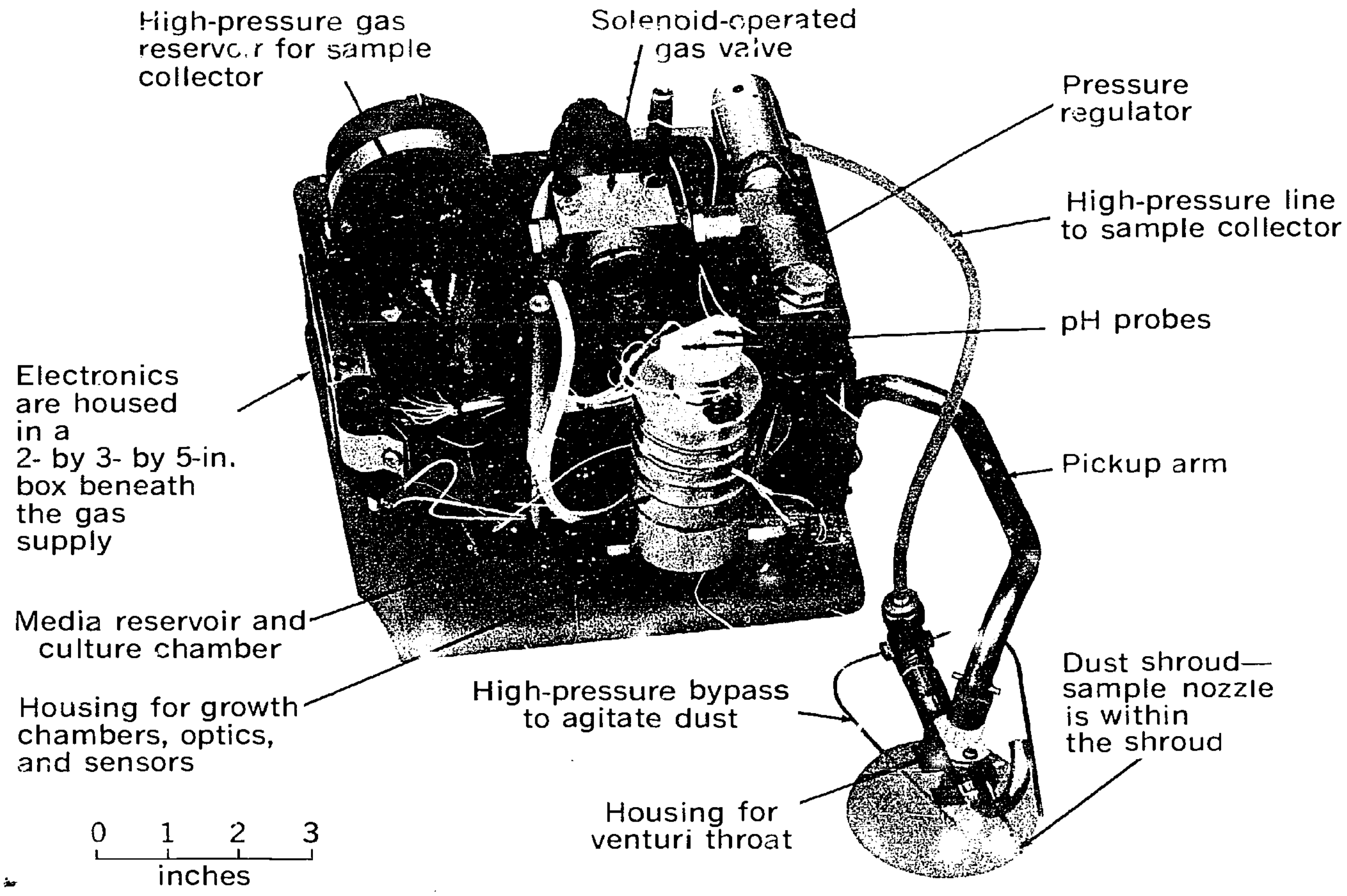


FIGURE 10–7. *Wolf trap with cover removed. The Wolf trap measures 5 by 7 by 7 in. with the cover in place. The sample collector is located on the right in the figure. The sampling mechanism is based upon the sucking up of planetary dust that has been agitated by a stream of air.*

and able to carry on metabolism will thus be forced to do so under conditions of limited oxygen supply. The probability is good, therefore, that changes in the acidity of the medium can be used as an indicator of microbial metabolism.

The Wolf trap is also designed to measure a second indicator of metabolic activity; viz, changes in the turbidity of the culture medium resulting from growth of micro-organisms. As micro-organisms increase in size and/or number, the medium becomes increasingly turbid, and the amount of light that can be transmitted through the sample decreases. A simple spectrophotometric measurement can be used to follow this change in transmittance as a function of time and thereby provide an additional indication of metabolic activity within the sample.

Multivator

A characteristic feature of chemical activities occurring within biological systems is that they are mediated by catalysts known as enzymes. Enzymes exhibit a high degree of specificity with respect to the reaction(s) they catalyze. Thus, if enzyme activity is used as an indicator of cellular metabolism, one must design an experiment for a particular enzyme. Considering that many hundreds of enzymes are known (6), the selection itself is a formidable task.

The Multivator (Figures 10–8 and 10–9) is a multipurpose life-detection system designed to accommodate up to 15 separate experiments. Among the experiments being considered for this probe are several designed to detect enzyme activity. The instrument is designed to introduce a planetary soil sample into a reaction chamber and mix the sample with a substrate that can

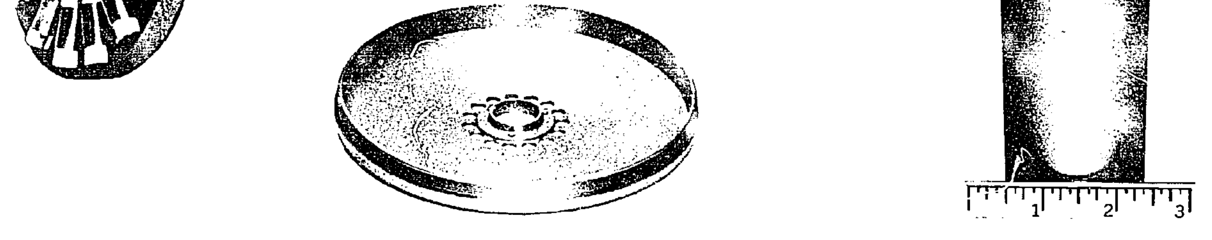


FIGURE 10–8. *Multivator, with housing partially removed (left) and fully assembled (right).*

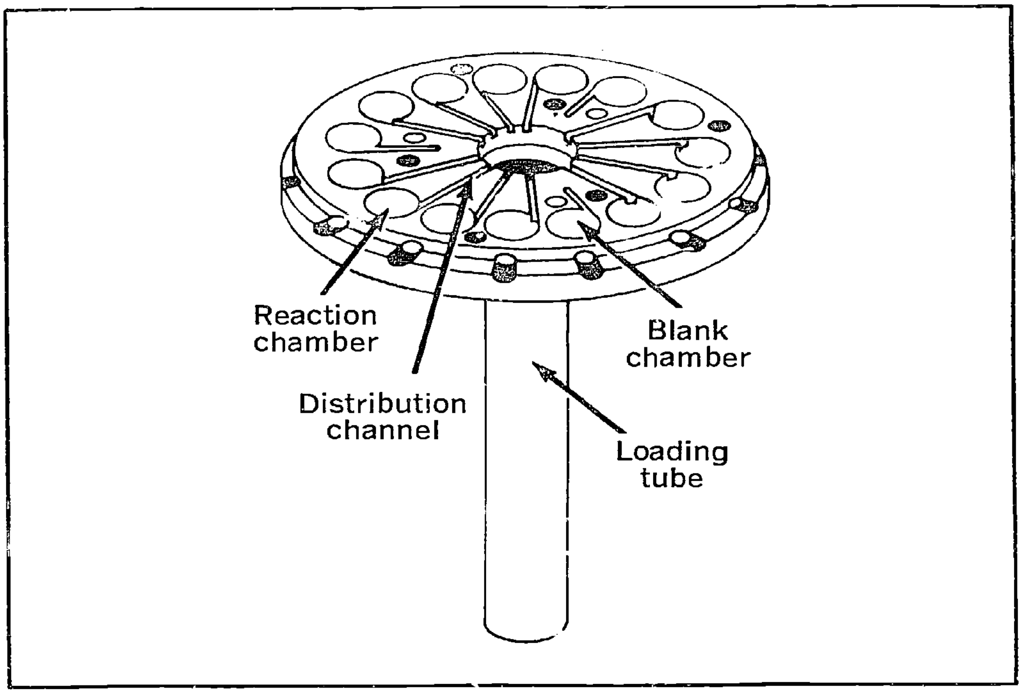
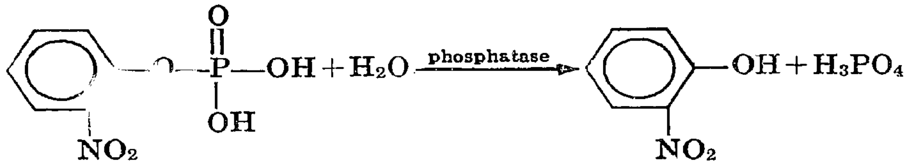


FIGURE 10–9. *Layout of the Multivator assembly. The diagram shows the multiple-chamber feature of the Multivator life-detection system. Dust is drawn up through the loading tube and blown through distribution channels to reaction chambers containing various chemical reagents.*

be hydrolyzed by the enzyme in question. The substrate is selected so that the hydrolysis products will exhibit a characteristic property (color, fluorescence, etc.) that can be easily measured. For example, the enzyme phosphatase, which is quite common in terrestrial forms of life, catalyzes the hydrolysis of compounds known as phosphate esters:

$$\text{an orthophosphoric monoester} + H_2O \xrightarrow{\text{phosphatase}} \text{an alcohol} + H_3PO_4$$

With this enzyme in mind, one possibility would be to use *o*-nitrophenylphosphate as the substrate.



The *o*-nitrophenol liberated by hydrolysis has a yellow color that can be measured spectrophotometrically at about 420 mμ.

ACTIVITIES

USING DYE ABSORPTION TO DETECT PROTEIN

The absorption of dyes by biological macromolecules is the basis of a proposed spectroscopic method for detection of these macromolecules in planetary soil samples. In this experiment the dye methyl orange will be allowed to interact with a protein (albumin).

In aqueous solution the dye molecules (HIn) establish the equilibrium:

$$\underset{\text{(red)}}{HIn} \rightleftarrows H^+ + \underset{\text{(yellow)}}{In^-} \tag{10-1}$$

Under acid conditions the equilibrium is displaced to the left so that the species HIn predominates. The protein in acidic medium exists predominantly as a cation. When the protein and dye are mixed, the protein cations combine with the dye anions:

$$\text{protein}^+ + In^- \longrightarrow \text{Protein}^+\text{-}In^- \tag{10-2}$$

The result is that Reaction (10-1) is shifted to the right. One may follow Reaction (10-2) by measuring the disappearance of HIn species or the appearance of the protein$^+$-In$^-$ complex.

The following solutions are prepared:

1. Solution A – 0.1 g methyl orange dissolved in 100 ml H_2O.
2. Solution B – 2.0 g citric acid dissolved in 100 ml of 0.2 *N* NaOH; adjust to pH 3.5 with 0.1 *N* HCl.
3. Dye solution – mix 1.0 ml of solution A with 99.0 ml of solution B.
4. Albumin solution – dissolve 1.0 g albumin (egg albumin or serum albumin) in 100 ml H_2O.

Add the following volume (milliliters) of reagents in the order indicated (top to bottom) to six clean test tubes:

Reagent	Test tube					
	1	2	3	4	5	6
Dye solution	5.0	5.0	5.0	5.0	5.0	5.0
H_2O	1.0	.8	.6	.4	.2	.0
Albumin solution	.0	.2	.4	.6	.8	1.0

After mixing the contents of each tube thoroughly, the absorbance of each is read at 550 mμ in a spectrophotometer. The absorbance (ordinate) versus the volume of the albumin solution (abscissa) is plotted. Because 550 mμ represents the wavelength of maximum absorption of the HIn species, a decrease in absorbance with increasing concentration of protein is to be expected. In accordance with the Beer-Lambert law, the absorbance versus concentration plot should be approximately linear.

An alternate approach to this experiment would be to measure the absorbancy at a wavelength corresponding to the maximum absorption of the $\text{protein}^{+}\text{-In}^{-}$ complex. The plot should then show an increase in absorbance with the increasing concentration. The wavelength of maximum absorption of the complex may be determined by adding an excess of protein to the dye and then measuring the absorbance at wavelengths between 400 and 600 mμ at 25-mμ intervals. A plot of absorbance versus wavelength yields the wavelength of maximum absorption.

A semiquantitative measure of these effects can be obtained visually by observing the color change with increasing protein concentrations against a white background.

USING TURBIDITY TO DETECT MICRO-ORGANISMS

The Wolf trap life-detection device is designed to detect the attributes of growth and metabolism by measuring changes in the turbidity and pH of the culture medium, respectively. The following experiment illustrates the principles involved. If possible, it should be run under sterile conditions. Water may be sterilized by autoclaving at 121° C and 15-psi pressure for 15 to 20 min. The salt solutions may be sterilized by filtration in a sterile bacterial filter and then added aseptically to the sterile water. If sterilization facilities are not available, control tubes should be run and differences between them and the samples noted.

To detect growth of micro-organisms, soil samples are incubated in a culture medium and the turbidity of the solution is monitored as a function of time. In this experiment a synthetic medium utilizing glucose as the carbon source is employed. Incorporation of an indicator dye into the medium permits simultaneous monitoring of pH changes. A gradual decrease in pH due to formation of organic acids commonly occurs when micro-organisms are growing under conditions of limited oxygen supply. Such a condition may be approximated by allowing the samples to remain stationary during the incubation period.

To prepare the culture medium, first make up two stock solutions:

1. Solution A—15 g Na_2HPO_4 and 7.5 g KH_2PO_4 dissolved in 100 ml distilled H_2O.
2. Solution B—10 g NH_4Cl, 5 g NaCl, and 4.1 g $MgSO_4 \cdot 7H_2O$ dissolved in 100 ml distilled water.

The growth medium is prepared by dissolving 0.4 g of glucose (dextrose) in a solution made by mixing 4 ml of solution A with 1 ml of solution B. This solution is then sterilized by filtration and added to 95 ml of sterile distilled water containing 1 ml of indicator solution. Because the culture medium will initially exhibit a pH of approximately 7, the indicator selected should exhibit a color change in the approximate pH range 4 to 7. Suggested indicator solutions are: 0.4 percent bromcresol purple (pH range 5.2 to 6.8) and 0.2 percent bromthymol blue (pH range 6.0 to 7.6). Ten-ml volumes of the medium are then placed in sterile tubes and capped with cotton plugs.

To prepare the soil samples, 5.0 ml of sterile distilled water is added to a 1.0-g sample of the soil(s) to be tested to form a slurry. The soil particles are allowed to settle until the supernatant liquid is relatively clear. The time required for this step and the degree of clarity will vary with the type of soil sample. Five drops of the supernatant liquid are transferred to the tube containing the 10 ml of culture medium. The stopper is replaced and the tube(s) are allowed to incubate at room temperature or, if possible, at a temperature of 37° C. Growth of micro-organisms will be indicated by increasing turbidity of the medium and/or a change in the color of the indicator dye. The time required for these effects will depend primarily on the number of bacteria introduced into the medium from the soil sample and on their ability to utilize the components of the medium for growth.

If a colorimeter is available, one may graphically follow the change in turbidity as a function of time. This is best done with a separate tube to which no indicator dye has been added. Under these conditions, a wavelength of 600 $m\mu$ may be employed for turbidity measurements.

HYDROLYSIS OF PHOSPHATE ESTERS

The hydrolysis of phosphate esters by the enzyme phosphatase is one of the experiments contemplated for the Multivator life-detection device. The phosphatase enzyme is abundant in most bacteria as well as in the blood of higher animals. In this experiment, blood serum will be used as the source of the enzyme.

The following reagents are prepared:

1. Alkaline buffer solution – 6.4 g of anhydrous Na_2CO_3 and 3.4 g $NaHCO_3$ dissolved in H_2O and diluted to 1 liter.
2. Stock substrate solution – 0.01 *M* solution of *p*-nitrophenyl phosphate in H_2O (the ortho isomer will work equally well).
3. Alkaline buffered substrate – mix equal volumes of the above solutions just prior to use.

One ml of the alkaline buffered substrate is placed into each of two test tubes. To one of the tubes 0.10 ml of serum is added, and to the other tube (control) 0.10 ml of water is added. Both tubes should be allowed to stand for 45 min. Then 10.0 ml of 0.02 *N* NaOH is placed in each tube and the intensity of color in the tubes is compared. The yellow color in the tube containing the serum is produced by the nitrophenol liberated by the hydrolytic action of the phosphatase enzyme. If a spectrophotometer is available, the intensity of color can be measured at 410 $m\mu$.

TOPIC FOR THE DEVELOPMENT OF ADDITIONAL ACTIVITIES

The use of gas chromatography as a means of "cleaning up" planetary soil samples prior to mass spectrometric analysis was discussed in the text. This technique is a very useful tool for the study of complex mixtures, and is finding wide applicability in many areas of chemistry and biology. While the required instrumentation is expensive, "simple" gas chromatographs can be constructed for relatively modest sums. The "Other References" section lists three articles from the *Journal of Chemical Education* that describe methods for the construction and use of gas chromatographs.

LITERATURE CITED

1. Young, R. S. 1962. Exobiology, p. 30. *In* Bioastronautics. NASA SP-18. GPO, $0.30.

2. Bentley, K. E., C. E. Giffin, D. G. Whitten, and W. F. Wilhite. 1965. Detection of life-related compounds on planetary surfaces by gas chromatography-mass spectrometry techniques. American Association for the Advancement of Science, 131st Annual Meeting. (Montreal, Canada, Dec. 26–31, 1964.) JPL–TR–32–713. AIAA A65–15153.

3. Corliss, W. R. 1965. Space probes and planetary exploration, pp. 477–503. D. Van Nostrand Co., Inc., New York.

*4. National Aeronautics and Space Administration. 1963. The search for extraterrestrial life. NASA EP–10. GPO, $0.20.

*5. Quimby, F. H. 1964. Concepts for detection of extraterrestrial life. NASA SP–56. GPO, $0.50.

6. Florkin, M., and E. H. Stotz. 1964. Comprehensive biochemistry, Vol. 13, pp. 50–141. American Elsevier Publishing Co., Inc., New York.

OTHER REFERENCES

Herbener, R. E. 1964. A demonstration device for gas chromatography. Journal of Chemical Education 41: 162.

Lowell, S., and H. Malemud. 1966. Design and construction of a thermal conductivity gas analyzer. Journal of Chemical Education 43: 660.

Silberman, R. 1967. A simple gas-liquid chromatography device. Journal of Chemical Education 44: 590.

*Young, R. S., R. B. Painter, and R. D. Johnson. 1965. An analysis of the extraterrestrial life detection problem. NASA SP–75. NTIS N65–34227#.

*Glasstone, S. 1968. The book of Mars, pp [illegible]-246. NASA SP-179. GPO, $5.75.

FILM

Life on other planets. 1961. 21 min, sound, color. NASA.

Documents with source listed as NTIS are available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Va., 22151. Prices are $3 for hardcopy (printed facsimile, or reproduced from microcopy) for NASA and NASA-supported documents when less than 550 pages and $10 for documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70–12345#).

**Recommended general sources of information.*

appendixes

APPENDIX A BRIEF SPACE GLOSSARY*

ablating material. A material, especially a coating material, designed to provide **thermal** protection to a body in a fluid stream through loss of mass.

ablation. The removal of surface material from a body by vaporization, melting, chipping, or other erosive process; specifically, the intentional removal of material from a nose **cone** or **spacecraft** during high-speed movement through a planetary atmosphere to provide **thermal** protection to the underlying structure. See **ablating material.**

ablator. A material designed to provide **thermal** protection through **ablation.**

abort. 1. To cut short or break off an action, operation, or procedure with an aircraft, space vehicle, or the like, especially because of equipment failure; as *to abort a mission; the launching was aborted.* 2. An aircraft, space vehicle, or the like that aborts. 3. An act or instance of aborting.

absorption. 1. The process by which radiant energy is absorbed and converted into other forms of energy. 2. In general, the taking up or assimilation of one substance by another. See **adsorption.** 3. In vacuum technology, gas entering into the interior of a solid.

additive. Any material or substance added to something else. Specifically, a substance added to a **propellant** to achieve some purpose, such as a more even rate of combustion; or a substance added to fuels or lubricants to improve them or give them some desired quality, such as tetraethyl lead added to a fuel as an antidetonation agent; or graphite, talc, or other substances added to certain oils and greases to improve lubrication qualities.

adiabatic. Without gain or loss of heat.

adiabatic process. A **thermodynamic** change of state of a system in which there is no transfer of heat or mass across the boundaries of the system. In an adiabatic process, compression always results in warming; expansion, in cooling.

adsorption. The adhesion of a thin film of liquid or gas to the surface of a solid substance. The solid does not combine chemically with the adsorbed substance.

aerodynamic heating. The heating of a body produced by passage of air or other gases over the body; caused by friction and compression processes and significant chiefly at high speeds.

aerodynamics. 1. The science that deals with the motion of air and other gaseous fluids, and with the forces acting on bodies when the bodies move through such fluids or when such fluids move against or around the bodies, as *his research in aerodynamics.* 2. (*a*) The actions and forces resulting from the movement or flow of gaseous fluids against or around bodies, as *the aerodynamics of a wing in supersonic flight.* (*b*) The properties of a body or bodies with respect to these actions or forces, as *the aerodynamics of a configuration.* 3. The application of the principles of gaseous fluid flows and of their actions against and around bodies to the design and construction of bodies intended to move through such fluids, as *a design used in aerodynamics.*

**Most of the entries in this glossary are taken from the* Dictionary of Technical Terms for Aerospace Use, *NASA SP-7, 1965, GPO, $3. An abridgment of SP-7 is entitled* Short Glossary of Space Terms, *second edition, NASA SP-1, 1966, GPO, $0.25.*

aerospace. (From **aeronautics** and **space.**) 1. Of or pertaining to both the Earth's atmosphere and **space**, as in *aerospace industries*. 2. Earth's envelope of air and space above it; the two considered as a single realm for activity in the flight of air vehicles and in the launching, guidance, and control of ballistic missiles, Earth satellites, dirigible space vehicles, and the like.

aerospace medicine. That branch of medicine dealing with the effects of flight through the atmosphere or in **space** upon the human body and with the prevention or cure of physiological or psychological malfunctions arising from these effects.

airbreathing. An engine or aerodynamic vehicle required to take in air for the purpose of combustion.

albedo. The ratio of the amount of electromagnetic **radiation** reflected by a body to the amount incident upon it, often expressed as a percentage, as *the albedo of the Earth is 34 percent.*

alveolar air. The respiratory air in the **alveoli** (air sacs) deep within the lungs.

alveolar oxygen pressure. The oxygen pressure in the **alveoli.** The value is about 105 mm Hg.

alveoli. The terminal air sacs deep within the lungs. The inhaled oxygen diffuses across the thin alveolar membranes (the walls of the air sacs) into the blood stream, and at the same time carbon dioxide diffuses from the blood into the alveoli and is exhaled through the lungs.

ambient (symbol *a*, used as a subscript). Surrounding; especially, of or pertaining to the environment about a flying aircraft or other body, but undisturbed or unaffected by it, as in *ambient air*, or *ambient temperature*.

apogee. 1. That point in a geocentric **orbit** which is most distant from the Earth. That orbital point nearest the Earth is called **perigee.** 2. Of a **satellite** or **rocket**: To reach its apogee (sense 1), as in *the Vanguard apogees at 2560 miles.*

artificial gravity. A simulated gravity established within a **space** vehicle by rotation or acceleration.

astro. A prefix meaning *star* or *stars* and, by extension, sometimes used as the equivalent of *celestial*, as in *astronautics*.

astrobiology. The study of living organisms on celestial bodies other than the Earth.

astronaut. 1. A person who rides in a **space** vehicle. 2. Specifically, one of the test pilots selected to participate in Project Mercury, Project Gemini, Project Apollo, or any other U.S. program for manned space flight.

astronautics. 1. The art, skill, or activity of operating **spacecraft.** 2. In a broader sense, the science of space flight.

astronomical unit (abbr AU). A unit of length, usually defined as the distance from the Earth to the Sun, 149,599,000 km.

backup. 1. An item kept available to replace an item that fails to perform satisfactorily. 2. An item under development intended to perform the same general functions of another item under development.

ballistics. The science that deals with the motion, behavior, and effects of projectiles, especially bullets, aerial bombs, **rockets**, or the like; the science or art of designing and hurling projectiles to achieve a desired performance.

ballistic trajectory. The trajectory followed by a body being acted upon only by gravitational forces and the resistance of the medium through which it passes.

biosatellite. An artificial satel**lite** specifically **d**esigned to contain and support man, animals, or other living material in a reasonably normal manner for an adequate period of time and which, particularly for man and animals, possesses the proper means for safe return to the Earth. See **closed ecological system.**

bipropellant. A **rocket propellant** consisting of two unmixed or uncombined chemicals (fuel and **oxidizer**) fed to the combustion chamber separately.

blackbody radiation. The electromagnetic radiation emitted by an ideal blackbody; it is the theoretical maximum amount of radiant energy of all wavelengths that can be emitted by a body at a given temperature. The spectral distribution of blackbody radiation is described by Planck's law and the related radiation laws. If a very tiny opening is made into an otherwise completely enclosed space (Hohlraum), the radiation passing out through this hole when the walls of the enclosure have come to thermal equilibrium at some temperature will closely approximate ideal blackbody radiation for that temperature.

boilerplate model. A metal copy of a flight vehicle, the structure or components of which are heavier than the flight model.

booster. 1. Short for **booster engine** or **booster rocket**. 2. **launch vehicle**.

booster engine. An engine, especially a booster rocket, that adds its **thrust** to the thrust of the sustainer engine.

booster rocket. 1. A **rocket engine**, either solid or liquid, that assists the normal propulsive system or sustainer engine of a **rocket** or aeronautical vehicle in some phase of its flight. 2. A **rocket** used to set a vehicle in motion before another engine takes over. (In sense 2 the term **launch vehicle** is preferred.)

burning rate (symbol r). The velocity at which a **solid propellant** in a rocket is consumed. (Burning rate is measured in a direction normal to the propellant surface and is usually expressed in inches per second.)

burnout. 1. An act or instance of fuel or oxidant depletion or, ideally, the simultaneous depletion of both; the time at which this occurs. Compare **cutoff**. 2. An act or instance of something burning out or of overheating; specifically, an act or instance of a **rocket** combustion chamber, **nozzle**, or other part overheating and resulting in damage or destruction.

capsule. 1. A boxlike component or unit, often sealed. 2. A small sealed pressurized cabin with an internal environment that will support life in a man or animal during extemely high-altitude flight, space flight, or emergency escape. 3. A container carried on a rocket or spacecraft, as an instrument capsule holding instruments intended to be recovered after a flight.

cermet (ceramic + **metal**). A body consisting of ceramic particles bonded with a metal; used in aircraft, rockets, and spacecraft for high-strength, high-temperature applications. Also called *ceramal* (*ceram*ic + *al*loy).

charring ablator. An **ablation** material characterized by the formation of a carbonaceous layer at the heated surface that impedes heat flow into the material by its insulating and reradiating characteristics.

chemical fuel. A fuel that depends upon an **oxidizer** for combustion or for development of **thrust**, such as liquid or solid **rocket** fuel or internal-combustion-engine fuel; distinguished from nuclear fuel.

chemisorption. The binding of a liquid or gas on the surface or in the interior of a solid by chemical bonds or forces.

chugging. A form of combustion instability in a **rocket engine**, characterized by a pulsing operation at a fairly low frequency, sometimes defined as occurring between particular frequency limits; the noise made in this kind of combustion. Also called *chuffing*.

cislunar. (Latin *cis*, on this side.) Of or pertaining to phenomena, projects, or activity in the space between the Earth and the Moon's orbit. Compare **translunar**.

closed ecological system. A system that provides for the maintenance of life in an isolated living chamber through complete reutilization of the material available, in particular, by means of a cycle wherein exhaled carbon dioxide, urine, and other waste matter are converted chemically or by photosynthesis into oxygen, water, and food.

cold welding. The spontaneous welding together of metal objects when the objects are placed in contact in an unheated condition.

communications satellite. A **satellite** designed to reflect or relay electromagnetic signals used for communication.

composite materials. Structural materials of metals, ceramics, or plastics with built-in strengthening agents, which may be in the form of filaments, foils, powders, or flakes of a different, compatible material.

composite propellant. A **solid rocket propellant** consisting of a fuel and an oxidizer neither of which would burn without the presence of the other.

configuration. A particular type of a specific aircraft, rocket, etc., that differs from others of the same model by virtue of the arrangement of its components or by the addition or omission of auxiliary equipment as *long-range configuration, cargo configuration.*

control rocket. A **vernier** engine, **retrorocket**, or other such rocket, used to change the attitude of, guide, or make small changes in the speed of a rocket, spacecraft, or the like.

cosmic dust. Finely divided solid matter with particle sizes smaller than a **micrometeorite**, thus with diameters much smaller than a millimeter, moving in interplanetary space.

COSPAR (abbr)=Committee on Space Research, International Council of Scientific Unions.

countdown. 1. A step-by-step process that culminates in a climactic event, each step being performed in accordance with a schedule marked by a count in inverse numerical order; specifically, this process is used in leading up to the launch of a large or complicated **rocket** vehicle, or in leading up to a captive test, a readiness firing, a mock firing, or other firing test. 2. The act of counting inversely during this process. (In sense 2, the countdown ends with *T*-time; thus *T minus 60 min* indicates there are 60 min to go, excepting for holds and recycling. The countdown may be hours, minutes, or seconds. At the end it narrows down to seconds, 4–3–2–1–0.)

cryogenic propellant. A **rocket** fuel, **oxidizer**, or propulsion fluid which is liquid only at very low temperatures.

cryogenic temperature. In general, a temperature range below the boiling point of nitrogen (−195° C); more particularly, temperatures within a few degrees of absolute zero.

cutoff or **cut-off.** 1. An act or instance of shutting something off; specifically, in rocketry, an act or instance of shutting off the **propellant** flow in a **rocket** or of stopping the combustion of the propellant. Compare **burnout**. 2. Limiting or bounding, as in *cutoff frequency*.

debug. 1. To isolate and remove malfunctions from a device, or mistakes from a routine or program. 2. Specifically, in electronic manufacturing, to operate equipment under specified environmental and test conditions to eliminate early failures and to stabilize equipment prior to actual use. Also called *burn-in*.

docking. The act of coupling two or more orbiting objects; the operation of mechanically connecting together, or in some manner bringing together, orbital **payloads**.

elasticizer. An elastic substance or fuel used in a **solid rocket propellant** to prevent cracking of the propellant grain and to bind it to the combustion-chamber case.

elastomeric. Having a rubberlike quality.

electric propulsion. A general term encompassing all the various types of propulsion in which the **propellant** consists of charged electrical particles that are accelerated by electrical or magnetic fields, or both; for example, electrostatic propulsion, electromagnetic propulsion, electrothermal propulsion.

entry corridor. Depth of the region between two trajectories that define the design limits of a vehicle that will enter a planetary atmosphere.

environmental chamber. A chamber in which humidity, temperature, pressure, fluid contents, noise, and movement may be controlled so as to simulate different environments.

escape velocity. The radial speed that a particle or larger body must attain to escape from the gravitational field of a planet, moon, or star.

exhaust velocity. Average velocity at which the exhaust gases are expelled from the **nozzle** of a **rocket**.

exobiology. The field of biology that deals with the effects of extraterrestrial environments on living organisms and with the search for extraterrestrial life

exotic fuel. Any fuel considered to be unusual, as a boron-base fuel.

expansion ratio. Ratio of the exit area of a **nozzle** to its throat area.

fallaway section. A section of a **rocket** vehicle that is cast off and separates from the vehicle during flight, especially such a section that falls back to the Earth.

film cooling. The cooling of a body or surface, such as the inner surface of a **rocket** combustion chamber, by maintaining a thin fluid layer over the affected area.

fixed satellite. A satellite that orbits the Earth from west to east at such a speed as to remain fixed over a given place on the Earth's equator at approximately 35,900-km altitude. See **stationary orbit, synchronous satellite.**

flashback. A reversal of flame in a system, counter to the usual flow of the combustible mixture.

free fall. 1. The fall or drop of a body, such as a **rocket**, not guided, not under **thrust**, and not retarded by a parachute or other braking device. 2. The free and unhampered motion of a body along a Keplerian trajectory, in which the force of gravity is counterbalanced by the force of inertia. See **weightlessness, Kepler laws.**

free radical. An atom or group of atoms broken away from a stable molecule by application of external energy and containing an unpaired electron.

g or G. An acceleration equal to the acceleration of gravity, 980.665 cm/sec^2, approximately 32.2 ft/sec^2 at sea level; used as a unit of stress measurement for bodies undergoing acceleration.

gantry. A frame structure that spans over something, as an elevated platform that runs astride a work area, supported by wheels on each side; short for gantry crane or **gantry scaffold.**

gantry scaffold. A massive scaffolding structure mounted on a bridge or platform supported by a pair of towers or trestles that normally run back and forth on parallel tracks, used to assemble and service a large **rocket** as the rocket rests on its **launch pad.** Often shortened to **gantry.**

garbage. Miscellaneous objects in **orbit**, usually material ejected or broken away from a **launch vehicle** or **satellite.**

gas cap. The gas immediately in front of a body as it travels through the atmosphere.

geo. A prefix meaning Earth, as in *geology, geophysics.*

geodesy. The science that deals mathematically with the size and shape of the Earth and the Earth's external gravity field, and with surveys of such precision that overall size and shape of the Earth must be taken into consideration.

gox. Gaseous oxygen.

gradient. The rate of change with respect to distance of a variable quantity such as temperature.

gravity well. An analogy in which the gravitational field is considered as a deep pit out of which a **space vehicle** has to climb to escape from a planetary body.

guidance. The process of directing the movements of an aeronautical vehicle or **space vehicle,** with particular reference to the selection of a flightpath.

gyro. A device that utilizes the angular momentum of a spinning mass (rotor) to sense angular motion of its base about one or two axes orthogonal to the spin axis. Also called *gyroscope.*

hard landing. An impact landing of a **spacecraft** on the surface of a planet or a natural **satellite** destroying all equipment except possibly a very rugged package.

hardness. Resistance of metal to plastic deformation usually by indentation. However, the term may also refer to stiffness or temper, or to resistance to scratching, abrasion, or cutting.

heat exchanger. A device for transferring heat from one fluid to another without intermixing the fluids.

heat shield. 1. Any device that protects something from heat. 2. Specifically, the protective structure necessary to protect a reentry body from **aerodynamic heating.** See **heat sink.**

heat sink. 1. In **thermodynamic** theory, a means by which heat is stored, or is dissipated or transferred from the system under consideration. 2. A place toward which the heat moves in a system. 3. A material capable of absorbing heat; a device utilizing such a material and used as a **thermal** protection device on a **spacecraft** or **reentry vehicle**. 4. In nuclear propulsion, any thermodynamic device, such as a radiator or condenser, that is designed to absorb the excess heat energy of the working fluid. Also called *heat dump*.

hold. To stop counting during a **countdown** and to wait until an impediment has been removed so that the countdown can be resumed.

hyperoxia. A condition in which the total oxygen content of the body is increased above that normally existing at sea level.

hypersonic. 1. Pertaining to hypersonic flow. 2. Pertaining to speeds of **Mach** 5 or greater.

hypersonic flow. In **aerodynamics**, flow of a fluid over a body at speeds much greater than the speed of sound and in which the shock waves start at a finite distance from the surface of the body.

igniter. A device used to begin combustion, such as a spark plug in the combustion chamber of a jet engine, or a squib used to ignite the fuel in a **rocket**.

ignition delay. The time lapse occurring between the instance of an igniting action of a fuel and the onset of a specified burning reaction. Also called *ignition lag*.

impact area. The area in which a **rocket** strikes the surface of the Earth or other celestial body.

injection. The introduction of fuel, fuel and air, fuel and **oxidizer**, water, or other substance into an engine induction system or combustion chamber.

instrumentation. 1. The installation and use of electronic, gyroscopic, and other instruments for the purpose of detecting, measuring, recording, telemetering, processing, or analyzing different values or quantities as encountered in the flight of a **rocket** or **spacecraft**. 2. The assemblage of such instruments in a rocket, spacecraft, or the like. 3. A special field of engineering concerned with the design, composition, and arrangement of such instruments.

ion. 1. A charged atom or molecularly bound group of atoms; sometimes also a free electron or other charged subatomic particle. 2. In atmospheric electricity, a[illegible] several types of electrically charged submicroscopic particles norm[illegible] atmosphere. Atmospheric ions are of two principal types, sm[illegible]ons, although a class of intermediate ions has occasionally be[illegible] chemistry, atoms or specific groupings of atoms that have gai[illegible] one or more electrons, as *the chloride* [illegible] *ammonium ion*. Such ions exist in aqueous solutions and in certain crystal structures.

Kepler laws. The three empirical laws governing the motions of planets in their orbits, discovered by Johannes Kepler (1571–1630): (*a*) the orbits of the planets are ellipses, with the Sun at a common focus; (*b*) as a planet moves in its orbit, the line joining the planet and Sun sweeps over equal areas in equal intervals of time (also called law of equal areas); and (*c*) the squares of the periods of revolution of any two planets are proportional to the cubes of their mean distances from the Sun.

launch pad. The load-bearing base or platform from which **a rocket vehicle** is launched. Usually called **pad**.

launch vehicle. A **rocket** or other **vehicle** used to launch a **probe**, **satellite**, or the like.

launch window. The postulated opening in the continuum of time or space, through which a **spacecraft** or **missile** must be launched to achieve a desired encounter, rendezvous, impact, or the like.

liftoff. The action of a **rocket vehicle** as it separates from its **launch pad** in a vertical ascent.

liquid-propellant rocket engine. A **rocket** engine using a **propellant** or propellants in liquid form. Also called *liquid-propellant rocket*.

lox. 1. Liquid oxygen. Used attributively as in *lox tank, lox unit*. Also called *loxygen*. 2. To load the fuel tanks of a **rocket vehicle** with liquid oxygen. Hence, loxing.

Mach number (symbols M, N_{Ma}). (Pronounced *mock*, after Ernest Mach, 1838–1916, Austrian scientist.) A number expressing the ratio of the speed of a body or of a point on a body with respect to the surrounding air or other fluid, or the speed of a flow, to the speed of sound in the medium; the speed represented by this number.

main stage. 1. In a multistage **rocket**, the **stage** that develops the greatest amount of **thrust**, with or without **booster engines**. 2. In a single-stage rocket vehicle powered by one or more engines, the period when full thrust (at or above 90 percent) is attained. 3. A sustainer engine, considered as a stage after booster engines have fallen away, as in *the main stage of the Atlas*.

mass ratio. The ratio of the mass of the **propellant** charge of a **rocket** to the total mass of the rocket when charged with the propellant.

meteorological rocket. A **rocket** designed primarily for routine upper air observation (as opposed to research) in the lower 250,000 ft of the atmosphere, especially that portion inaccessible to balloons; i.e., above 100,000 ft. Also called *rocketsonde*.

micrometeorite. A very small meteorite or meteoritic particle with a diameter generally less than a millimeter.

miniaturize. To construct a functioning miniature of a part or instrument. Said of telemetering instruments or parts used in an Earth **satellite** or **rocket vehicle**, where space is at a premium. Hence, *miniaturized, miniaturization.*

missile. Any object thrown, dropped, fired, launched, or otherwise projected with the purpose of striking a target. Short for *ballistic missile, guided missile.* (Should not be used loosely as a synonym for **rocket** or **spacecraft.**)

mixture ratio. In liquid-propellant rockets, the relative mass flow rates to the combustion chamber of **oxidizer** and fuel.

mockup. A full-sized replica or dummy of something, such as a **spacecraft**, often made of some substitute material such as wood, and sometimes incorporating actual functioning pieces of equipment, such as engines.

module. 1. A self-contained unit of a **launch vehicle** or **spacecraft** that serves as a building block for the overall structure. The module usually is designated by its primary function as command module, lunar landing module, etc. 2. A one-package assembly of functionally associated electronic parts, usually a plug-in unit, arranged so as to function as a system or subsystem; a black box. 3. The size of some one part of a **rocket** or other structure, as the semidiameter of a rocket's base, taken as a unit of measure for the proportional design and construction of component parts.

monopropellant. A **rocket propellant** consisting of a single substance, especially a liquid, capable of producing a heated jet without the addition of a second substance.

multipropellant. A **rocket propellant** consisting of two or more substances fed separately to the combustion chamber. See **bipropellant.**

multistage rocket. A **vehicle** having two or more **rocket** units, each unit firing after the one in back of it has exhausted its **propellant.** Normally, each unit, or **stage,** is jettisoned after completing its firing. Also called a *multiple-stage rocket* or, infrequently, a *step rocket.*

normal shock wave. A **shock wave** perpendicular, or nearly perpendicular, to the direction of flow in a **supersonic** flow field. Sometimes shortened to *normal shock*.

nose cone. The cone-shaped leading end of a **rocket vehicle**, consisting (*a*) of a chamber or chambers in which a **satellite**, instruments, animals, plants, or auxiliary equipment may be carried, and (*b*) of an outer surface built to withstand high temperatures generated by **aerodynamic heating**.

nozzle (symbol n used as subscript). 1. A duct, tube, pipe, spout, or the like through which a fluid is directed and from the open end of which the fluid is discharged; designed to meter the fluid or to produce a desired direction, velocity, or shape of discharge. 2. That part of a **rocket thrust** chamber assembly in which the gases produced in the chamber are accelerated to high velocities.

nuclear-electric rocket engine. A **rocket engine** in which a nuclear reactor is used to generate the electricity used in an electric propulsion system or as a heat source for the working fluid.

nuclear reactor. An apparatus in which nuclear fission may be sustained in a self-supporting chain reaction. Commonly called *reactor*. Formerly called *pile*.

nuclear rocket engine. A **rocket engine** in which a nuclear reactor is used as a power source or as a source of **thermal energy**.

orbit. 1. The path of a body or particle under the influence of a gravitational or other force. For instance, the **orbit** of a celestial body is its path relative to another body around which it revolves. 2. To go around the Earth or other body in an orbit (sense 1).

orbital period. The interval between successive passages of a **satellite** through the same point in its **orbit**. Often called *period*.

orbital velocity. 1. The average velocity at which an Earth **satellite** or other orbiting body travels around its primary. 2. The velocity of such a body at any given point in its orbit, as in *its orbital velocity at the apogee is less than at the perigee*. 3. = circular velocity.

outgassing. The evolution of gas from a material in a vacuum.

oxidizer. Specifically, a substance (not necessarily containing oxygen) that supports the combustion of a fuel or **propellant**.

pad = launch pad.

parameter. A constant or variable term in a function that determines the specific form of the function but not its general nature. For example, the a in $f(x) = ax$.

parking orbit. An orbit of a **spacecraft** around a celestial body, used for assembly of components or to wait for conditions favorable for departure from the orbit.

passive. Containing no power sources to augment output power; e.g., passive electrical network, passive reflector (as in the Echo **satellite**). Applied to a device that draws all its power from the input signal.

payload. 1. Originally, the revenue-producing portion of an aircraft's load; e.g., passengers, cargo, mail, etc. 2. By extension, that which an aircraft, **rocket**, or the like carries over and above what is necessary for the operation of the vehicle for its flight.

perigee. That orbital point nearest the Earth when the Earth is the center of attraction. See **orbit**.

photon engine. A projected type of **reaction engine** in which **thrust** would be obtained from a stream of electromagnetic **radiation**.

physiological acceleration. The acceleration experienced by a human or an animal test subject in an accelerating **vehicle**.

plasma. An electrically conductive gas comprised of neutral particles, [illegible] particles, and free electrons but which, taken as a whole, is electrically neutral.

plasma engine. A **reaction engine** using magnetically accelerated **plasma** as **propellant**.

pressurized. Containing air, or other gas, at a pressure higher than ambient.

primary. Short for primary body. The celestial body or central force field about which a **satellite** or other body orbits, or from which it is escaping, or toward which it is falling.

probe. 1. Any device inserted in an environment for the purpose of obtaining information about the environment. 2. In geophysics, a device used to make a sounding. 3. An instrumented **vehicle** moving through the upper atmosphere or space or landing upon another celestial body to obtain information about the specific environment. 4. A slender device or apparatus projected into a moving fluid, as for measurement purposes.

propellant (symbol p, used as a subscript). Any agent used for consumption or combustion in a **rocket** and from which the rocket derives its **thrust**, such as a fuel, **oxidizer**, **additive**, catalyst, or any compound or mixture of these; specifically, a fuel, oxidant, or a combination or mixture of fuel and oxidant used in propelling a rocket.

purge. To rid a line or tank of residual fluid, especially of fuel or oxygen in the tanks or lines of a rocket, after a test firing or simulated test firing.

radiation. 1. The process by which electromagnetic energy is propagated through free **space** by virtue of joint undulatory variations in the electric and magnetic fields in space. This concept is to be distinguished from conduction and convection. 2. The process by which energy is propagated through any medium by virtue of the wave motion of that medium, as in the propagation of sound waves through the atmosphere, or ocean waves along the water surface. 3. = radiant energy. 4. = electromagnetic radiation, specifically, high-energy radiation such as gamma rays and X-rays. 5. Corpuscular emissions, such as α- or β-radiation. 6. = nuclear radiation. 7. = radioactivity.

radiation pressure (symbol P_r). Pressure exerted upon any material body by electromagnetic **radiation** incident upon it.

radiation shield. 1. A device used on certain types of instruments to prevent unwanted **radiation** from biasing the measurement of a quantity. 2. A device used to protect human beings from the harmful effects of nuclear radiation, cosmic radiation, or the like. 3. = **heat shield.**

radiator. 1. Any source of radiant energy, especially electromagnetic **radiation.** 2. A device that dissipates the heat from something, as from water or oil, not necessarily by radiation only.

ramjet engine. A type of jet engine with no mechanical compressor and consisting of a specially shaped tube or duct open at both ends. The air necessary for combustion is shoved into the duct, is compressed by the forward motion of the engine, passes through a diffuser, and is mixed with fuel and burned, the exhaust gases issuing in a jet from the rear opening. The ramjet engine cannot operate under static conditions. Often called a *ramjet.*

reaction engine. An engine that develops thrust by its reaction to a substance ejected from it; specifically, such an engine that ejects a jet or stream of gases created by the burning of fuel within the engine.

recombination. The process by which positive and negative **ions** join to form neutral molecules or other neutral particles; also the process by which radicals or dissociation species join to form molecules.

reentry. The event occurring when a **spacecraft** or other object comes back into the **sensible atmosphere** after being rocketed to higher altitudes; the action involved in this event.

reentry vehicle. Any **payload**-carrying **vehicle** designed to leave the **sensible atmosphere** and then return through it to Earth.

regenerative cooling. The cooling of a part of an engine by the fuel or **propellant** being delivered to the combustion chamber; specifically, the cooling of a **rocket-engine** combustion chamber or **nozzle** by circulating the fuel or **oxidizer**, or both, around the part to be cooled.

rendezvous. 1. The event of two or more objects meeting with zero relative velocity at a preconceived time and place. 2. The **point** in space at which such an event takes place, or is to take place.

retrofire. To ignite a **retrorocket.**

retrorocket. (From retroacting.) A rocket fitted on or in a **spacecraft, satellite,** or the like to produce **thrust** opposed to forward motion.

Reynolds number. Experiment indicates that there is a combination of four factors that determines whether the flow of a viscous fluid through a pipe is laminar or turbulent. This combination is known as the Reynolds number N_{Re} and is defined as

$$N_{Re}=\frac{\rho v D}{\eta}$$

where ρ is the density of the fluid; v, the average velocity; η, the viscosity; and D, the diameter of the pipe.

rocket. 1. A projectile, pyrotechnic device, or flying **vehicle** propelled by a **rocket** engine. 2. A rocket engine; any one of the combustion chambers or tubes of a multichambered rocket engine.

rocket engine. A **reaction engine** that contains within itself, or carries along with itself, all the substances necessary for its operation or for the consumption or combustion of its fuel, and that does not require intake of any outside substance and hence is capable of operation in outer **space**. (Chemical rocket engines contain or carry along their own fuel and **oxidizer**, usually in either liquid or solid form, and range from simple motors consisting only of a combustion chamber and exhaust **nozzle** to engines of some complexity incorporating, in addition, fuel and oxygen lines, pumps, cooling systems, etc., and sometimes having two or more combustion chambers. Experimental rocket engines have used neutral gas, ionized gas, and plasmas as **propellants**. See **liquid-propellant rocket engine, solid-propellant rocket engine.**)

rocket propellant. 1. Any agent used for consumption or combustion in a **rocket** and from which the rocket derives its **thrust**, such as a fuel, **oxidizer**, **additive**, catalyst, or any compound or mixture of these. 2. The ejected fluid in a nuclear rocket.

satellite. 1. An attendant body that revolves about a primary body; especially in the solar system, a secondary body, or moon, that revolves about a planet. 2. A manmade object that revolves about a spatial body, such as Explorer 1 orbiting about the Earth. 3. Such a body intended and designed for orbiting, as distinguished from a companion body that may incidentally also **orbit**, as in *the observer actually saw the orbiting rocket rather than the satellite.* 4. An object not yet placed in orbit, but designed or expected to be launched into an orbit.

screaming. A form of combustion instability, especially in a **liquid-propellant rocket engine**, of relatively high frequency and characterized by a high-pitched noise.

scrub. To cancel a scheduled firing, either before or during **countdown.**

sensible atmosphere. That part of the atmosphere that offers resistance to a body passing through it.

sensor. The component of an instrument that converts an input signal into a quantity that is measured by another part of the instrument.

shear strength. In materials, the stress required to produce fracture in the cross-sectional plane, the conditions of loading being such that the directions of force and resistance are parallel and opposite although their paths are offset by a specified minimum amount.

shock tube. A relatively long tube or pipe in which very brief high-speed gas flows are produced by the sudden release of gas at very high pressure into a low-pressure portion of the tube; the high-speed flow moves into the region of low pressure behind a **shock wave.**

shock wave. A surface or sheet of discontinuity (i.e., of abrupt changes in conditions) set up in a **supersonic** field of flow, through which the fluid undergoes a finite decrease in velocity accompanied by a marked increase in pressure, density, temperature, and entropy; e.g., as occurs in a supersonic flow about a body. Sometimes called a *shock.*

sintering. The bonding of adjacent surfaces of particles in a mass of powders, usually metal, by heating.

sloshing. The back-and-forth movement of a liquid fuel in its tank, creating problems of stability and control in the **vehicle.**

solar cell. A photovoltaic cell that converts sunlight into electrical energy.

solar radiation. The total electromagnetic **radiation** emitted by the Sun.

solar wind. Streams of **plasma** flowing approximately radially outward from the Sun.

solid propellant. Specifically, a **rocket propellant** in solid form, usually containing both fuel and **oxidizer** combined or mixed, and formed into a monolithic (not powdered or granulated) grain.

solid-propellant rocket engine. A **rocket engine** fueled with a **solid propellant.** Such engines consist essentially of a combustion chamber containing the **propellant,** and a **nozzle** for the exhaust jet, although they often contain other components, as grids, liners, etc.

sonic. In **aerodynamics**, of or pertaining to the speed of sound.

sounding rocket. A **rocket** that carries aloft equipment for making observations of or from the upper atmosphere. Compare **probe**, sense 3.

space. 1. The part of the universe lying outside the limits of the Earth's atmosphere. 2. The volume in which all celestial bodies, including the Earth, move.

space-air vehicle. A vehicle operable either within or above the **sensible atmosphere**. Also called *aerospace vehicle*.

space medicine. A branch of **aerospace medicine** concerned specifically with the health of persons who make, or expect to make, flights into **space** beyond the **sensible atmosphere**.

space probe. See **probe**.

space simulator. 1. Any device used to simulate one or more parameters of the space environment used for testing space systems or components. 2. A closed chamber capable of approximately the vacuum and normal environments of space.

spacecraft. Devices, manned and unmanned, that are designed to be placed into an **orbit** about the Earth or into a trajectory to another celestial body.

specific impulse (symbol I_{sp}). A performance parameter of a **rocket propellant**, expressed in seconds or pound-seconds per pound, equal to the **thrust F** in pounds divided by the weight flow rate of the propellant in pounds per second.

spinoff or **spin-off.** Benefits or results that are a byproduct of another endeavor.

spin stabilization. Directional stability of a **spacecraft** obtained by the action of gyroscopic forces that result from spinning the **body** about its axis of symmetry.

sputtering. Dislocation of surface atoms of a material from bombardment by high-energy atomic particles.

stage. 1. A self-propelled separable element of a rocket vehicle. See **multistage rocket**. 2. A step or process through which a fluid passes, especially in compression or expansion. 3. A set of stator blades and a set of rotor blades in an axial-flow compressor or in a turbine; an impeller wheel in a radial-flow compressor.

stagnation point. A point in a field of flow about a body where the fluid particles have zero velocity with respect to the body.

stationary orbit. An **orbit** in which the **satellite** revolves about the primary at the angular rate at which the primary rotates on its axis. From the primary, the satellite thus appears to be stationary over a point on the primary.

stoichiometric. Of a mixture of chemicals, having the exact proportions required for complete chemical combination, applied especially to combustible mixtures used as **propellants**.

superalloy. An alloy developed for very high temperature service where relatively high stresses (tensile, thermal, vibratory, and shock) are encountered and where oxidation resistance frequently is required.

supersonic. Of or pertaining to, or dealing with, speeds greater than the acoustic velocity. Compare with **ultrasonic**.

sustainer engine. A **rocket engine** that maintains the velocity of a rocket **vehicle** once it has achieved its programed velocity by use of **booster** or other engine.

synchronous satellite. An equatorial west-to-east **satellite** orbiting the Earth at an altitude of approximately 35,900 km at which altitude it makes one revolution in 24 hr, synchronous with the Earth's rotation.

telemetry. The science of measuring a quantity or quantities, transmitting the results to a distant station, and there interpreting, indicating, and/or recording the quantities measured.

termolecular reaction. A reaction in which three molecules come together in the formation of the complex which dissociates to give the products of the reaction.

terrestrial. Of or pertaining to the Earth.

thermal. 1. Of or pertaining to heat or temperature. 2. A vertical air current caused by differential heating of the terrain.

thermal emission. The process by which a body emits electromagnetic **radiation** as a consequence of its temperature only.

thermodynamic. Pertaining to the flow of heat or to **thermodynamics**.

thermodynamics. The study of the flow of heat.

thermonuclear. Pertaining to a nuclear reaction that is triggered by particles of high **thermal** energy.

thrust. 1. The pushing or pulling force developed by an aircraft engine or a **rocket engine**. 2. The force exerted in any direction by a fluid jet or by a powered screw, as *the thrust of an antitorque rotor*. 3. (symbol **F**). In rocketry, $F = mv$ where m is **propellant** mass flow and v is exhaust velocity relative to the vehicle. Also called *momentum thrust*.

torr. Provisional international standard term to replace the English term millimeters of mercury and its abbreviation mm Hg.

tracking. 1. The process of following the movements of an object. This may be done by keeping the reticle of an optical system or a radar beam on the object, by plotting its bearing and distance at frequent intervals, or by a combination of the two. 2. A motion given to the major lobe of an antenna so that a preassigned moving target in **space** remains in the lobe's field as long as it is within viewing range.

translunar. Outside the Moon's **orbit** about the Earth.

transmittance. The fraction of **radiation** incident on an object which is transmitted through the object.

ultrasonic. In acoustics, of or pertaining to frequencies above those that affect the human ear; i.e., more than 20,000 vibrations per second.

umbilical cord. Any of the servicing electrical or fluid lines between the ground or a tower and an uprighted **rocket vehicle** before the launch. Often shortened to *umbilical*.

upper stage. A second or later **stage** in a **multistage rocket**.

Van Allen belt, Van Allen radiation belt. (For James A. Van Allen, 1915– .) The zone of high-intensity particulate **radiation** surrounding the Earth beginning at altitudes of approximately 1000 km. (The radiation of the **Van Allen belt** is composed of protons and electrons temporarily trapped in the Eart[illegible] field. The intensity of radiation varies with the [illegible] from [illegible]

vehicle. Specif[illegible] [illegible]chine, or device, such as an aircraft or **rocket**, designed to carry a burden through air or **space**; more restrictively, a rocket vehicle. (This word has acquired its specific meaning from the need for a term to embrace aircraft, rockets, and all other flying craft, and has more currency than other words used in this meaning. See **launch vehicle**.)

vernier engine. A **rocket engine** of small **thrust** used primarily to obtain a fine adjustment in the velocity and trajectory of a **rocket vehicle** just after the thrust **cutoff** of the last sustainer engine; used secondarily to add thrust to a **booster** or **sustainer engine**. Also called *vernier rocket*.

weightlessness. A condition in which no acceleration, whether of gravity or of other force, can be detected by an observer within the system in question.

zero-*g* = weightlessness.

APPENDIX B SOME NASA SPACECRAFT FAMILIES

Apollo: The third series of the U.S. manned spacecraft, and the spacecraft designed for manned flight to the Moon. Spacecraft weights have ranged from 33,800 to 93,885 lb.

Biosatellite: Family of recoverable scientific satellites employed for testing the effects of weightlessness, radiation, and lack of the Earth's 24-hr rhythm on biological specimens.

Echo: A family of two passive NASA communication satellites. Once in orbit, these satellites were inflated automatically by a gas generator to become large spherical balloons 100 and 135 ft in diameter, respectively. These large metallized balloons reflected radio signals between ground stations. Precision tracking of the Echo satellites also provided information about the density of the upper atmosphere.

Explorer: A long series of scientific satellites that began before NASA was created. The Army Explorer 1 was the first U.S. satellite to be launched, on January 31, 1958. Explorers 2, 3, and 4 were also Army satellites; the rest were launched by NASA. The Explorer satellites have varied widely in design and purpose. They supply information on micrometeorites, temperature in space, radiation, magnetic fields, gamma rays, etc., near the Earth and around the Moon.

Gemini: The second series of manned NASA Earth satellites. Two astronauts occupied each Gemini capsule, hence the series name. The prime purpose of the Gemini flights was to check equipment and techniques to be used during the Apollo missions to the Moon. During the Gemini program, NASA performed the first rendezvous experiments and the first extravehicular activities (walks in space). Gemini capsule weights varied between 7000 and 14,000 lb. The Gemini program ended in November 1966. There were 12 Gemini missions, of which the first two were unmanned.

Lunar Orbiter: A series of five lunar probes placed in orbit around the Moon to reconnoiter possible landing sites for Apollo astronauts. The probes took a large number of high-quality pictures of the Moon's surface.

Mariner: A family of planetary probes designed to fly by Mars and Venus, making scientific measurements in interplanetary space on the way. In the vicinity of a planet, the Mariner probes scanned the planet with instruments and performed radio occultation experiments.

Mercury: The first U.S. manned spacecraft. The Mercury capsule supported only one astronaut in comparison to two in Gemini. The primary purpose of the flight was to demonstrate that man could not only survive in space but could perform useful tasks. Capsule weights ranged from 2300 to 3033 lb. The Mercury program included six flights, ending in May 1963. The first two flights were unmanned.

Nimbus: A family of large, research and development, meteorological satellites. The Nimbus satellites tested a number of cameras and infrared instruments for operational weather satellite programs.

OAO: NASA's Orbiting Astronomical Observatories are large sophisticated satellites for studying the stars in the ultraviolet region of the spectrum and for carrying out associated experiments in space science.

OGO: NASA has built a family of Orbiting Geophysical Observatories. Each of these large satellites can carry 20 or more experiments in the fields of geophysics, space physics, and astronomy. Like the other observatories, OGO's are large and relatively sophisticated, weighing between 1000 and 1300 lb. Some of the OGO's are injected into polar orbits and are called POGO's. Those in high-eccentric orbits are called EGO's.

OSO: The Orbiting Solar Observatories are the smallest of the observatory class and carry fewer experiments. Weight varies between 450 and 650 lb. Some experiments are located in the spinning wheel section; others are in the sail, which is kept pointed at the Sun.

Pegasus: The three Pegasus satellites have sometimes been called Micrometeoroid Explorers, but they are much larger than any Explorer-class satellite, weighing about 23,000 lb each. These satellites were orbited as byproducts of the Saturn I launch tests. Each was a Saturn SIV upper stage that carried a large folded array of capacitor-type micrometeoroid detectors deployed once orbit was attained.

Pioneer: The first five Pioneer probes were aimed to fly in the general direction of the Moon, but not to hit it. They either fell back to Earth, or continued on into solar orbit. The second series, beginning with Pioneer 6, is aimed at deep-space exploration. These later Pioneers carry magnetometers, solar-wind instrumentation, radiation counters, and other instruments.

Rangers: The first two Rangers were intended to test techniques to be used on lunar and planetary spacecraft as well as measure the particles and fields present in interplanetary space. They were to be aimed in the general direction of the Moon. The next three Rangers were to "rough-land" a seismometer package on the lunar surface. The final four Rangers were designed to take closeup pictures of the lunar surface before crash landing on it, providing data for planning the lunar landing of Apollo astronauts. The Rangers weighed between 675 and 810 lb.

Surveyor: A series of seven soft-landing lunar probes built to reconnoiter the Moon's surface in preparation for the Apollo manned landing. The first Surveyors were primarily picture-taking spacecraft. The later models added experiments in soil mechanics and analyzed the surface composition. Weights varied between 596 and 630 lb at lunar landing.

Syncom: A family of experimental, active, synchronous-orbit communication satellites. The Syncoms were first injected into highly elliptic orbits. Near apogee, a rocket fired and placed them in equatorial synchronous (stationary) orbits. An onboard gas-jet propulsion unit was required to maintain their orbital positions. Weight: about 85 lb each. The Syncom-type satellites are now operational and are called Intelsats. They are operated as part of an international operations network.

Tiros: This long, successful series of experimental weather satellites demonstrated conclusively that satellite cloud-cover and infrared pictures would be useful in improving the accuracy of weather forecasting. The Tiros successes formed the basis for the Tiros Operational Satellite (TOS), which the Environmental Science Services Administration calls Environmental Survey Satellites or ESSA's. The Tiros satellites are hatbox shaped, weigh between 260 and 300 lb, and are spin stabilized. The Tiros satellites are now part of the Environmental Science Services Administration's weather forecasting system.

Vanguard: A family of three scientific satellites. Begun in 1955, the Vanguard satellite program planned to launch at least one small artificial satellite during the International Geophysical Year. Vanguard 1 was launched on March 17, 1958, under the auspices of the U.S. Navy. The project was transferred to NASA in October 1958.

APPENDIX C SELECTED THERMODYNAMIC QUANTITIES FOR 298° K[1]

Formula	ΔH_f°, kcal/mole	Formula	ΔH_f°, kcal/mole
H (*g*)	52.09	P_4O_{10} (*s*)	− 720.0
H_2O (*g*)	− 57.80	PCl_3 (*g*)	− 73.22
H_2O (*l*)	− 68.32	SO_2 (*g*)	− 70.96
H_2O_2 (*g*)	− 31.83	SO_3 (*g*)	− 94.45
H_2O_2 (*l*)	− 44.84	SCl_2 (*l*)	− 12.0
HCl (*g*)	− 22.06	K_2O (*s*)	− 86.4
Li_2O (*s*)	− 142.4	KCl (*s*)	− 104.18
LiCl (*s*)	− 97.70	CaO (*s*)	− 151.9
BeO (*s*)	− 146.0	$CaCl_2$ (*s*)	− 190.0
$BeCl_2$ (*s*)	− 122.3	$ScCl_3$ (*s*)	− 220.8
B_2O_3 (*s*)	− 302.0	TiO_2 (*s*, rutile)	− 218.0
BCl_3 (*l*)	− 100.0	$TiCl_4$ (*s*)	− 179.2
C (*g*)	171.70	V_2O_5 (*s*)	− 373
CO (*g*)	− 26.42	VCl_3 (*s*)	− 138.0
CO_2 (*g*)	− 94.05	Cr_2O_3 (*s*)	− 269.7
CCl_4 (*g*)	− 25.5	$CrCl_2$ (*s*)	− 94.6
NH_3 (*g*)	− 11.04	MnO_2 (*s*)	− 124.2
N_2H_4 (*l*)	12.05	$MnCl_2$ (*s*)	− 115.4
NO_2(*g*)	8.09	Fe_2O_3 (*s*)	− 196.5
N_2O_4 (*g*)	2.31	$FeCl_2$ (*s*)	− 81.6
HNO_3 (*g*)	− 31.92	CoO (*s*)	− 57.2
HNO_3 (*l*)	− 41.40	NiO (*s*)	− 58.4
O (*g*)	59.16	$NiCl_2$ (*s*)	− 75.6
O_3 (*g*)	34.00	CuO (*s*)	− 37.1
F (*g*)	18.3	$CuCl_2$ (*s*)	− 49.2
Na_2O (*s*)	− 99.4	ZnO (*s*)	− 84.0
NaCl (*s*)	− 98.33	$ZnCl_2$ (*s*)	− 99.4
MgO (*s*)	− 143.84	Ga_2O_3 (*s*)	− 258
$MgCl_2$ (*s*)	− 153.40	$GaCl_3$ (*s*)	− 125.4
Al_2O_3 (*s*)	− 399.09	GeO_2 (*s*)	− 128.4
$AlCl_3$ (*s*)	− 166.2	$GeCl_4$ (*l*)	− 128.0
SiC (*s*)	− 26.7	As_2O_5 (*s*)	− 218.6
SiO_2 (*s*, quartz)	− 205.4	$AsCl_3$ (*l*)	− 80.1
$SiCl_4$ (*l*)	− 150.0	SeO_2 (*s*)	− 55.2

---

[1] *Data for other substances can be found in the* Handbook of Chemistry and Physics, *The Chemical Rubber Co., Cleveland, Ohio.*

APPENDIX D NASA SERVICES FOR SCHOOLS AND STUDENTS

PUBLICATIONS AND FILM LISTS

Because of the fast-moving pace of the space program, teachers are advised to obtain the latest NASA publications and film lists, which are revised at frequent intervals.

To request a publications list, a film list, or information about other NASA educational services, write to the Educational Programs Office at the NASA research center that serves your area. (See the list, page 228.)

In the bibliography at the end of each unit, most of the NASA publications listed may be purchased from the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402 (identified by GPO) or from the National Technical Information Service (formerly the Clearinghouse for Federal Scientific and Technical Information), 5285 Port Royal Road, Springfield, Va. 22151 (identified by NTIS).[1] Those wishing publications with AIAA as a source should write to Technical Information Service, American Institute of Aeronautics & Astronautics, Inc., 750 Third Avenue, New York, N.Y. 10017.

For those NASA publications for which a NASA center is listed as the source, write the Educational Programs Office at the center.

For the films listed at the end of a unit, order from NASA Headquarters, Code FAD, Washington, D.C. 20546, unless the source for the film is listed as a specific NASA center. In such case, write to the Educational Programs Office of the center as listed on page 228.

Most of the films listed give broad, general coverage of topics and therefore can be used to provide background information and inspirational material. It is suggested that a film be previewed in order to determine its appropriateness.

---

[1] *Documents are available from NTIS at a standard price of $3 for hardcopy (printed facsimile, or reproduced from microcopy) of less than 550 pages for NASA and NASA-supported documents and $10 for NASA and NASA-supported documents in excess of 550 pages but less than 1100 pages. Documents in excess of 1100 pages are priced individually by NTIS. Microfiche is also available from NTIS for $0.95 for those documents identified by the # sign following the accession number (e.g., N70-12345#).*

NASA EDUCATIONAL SERVICES

For information about the services listed below, write to the NASA Educational Programs Office at the center serving your geographical area.

Curriculum Updating	This program is designed to advise and assist elementary and secondary schools, and institutions preparing teachers for these schools, in adapting and updating courses that deal with space-related information. The service may include assistance in developing resource units, curriculum bulletins, course syllabi, and reading and audiovisual materials.
Educational Visits	The opportunity for school classes to visit the various NASA installations is limited by personnel and program requirements. Certain installations hold periodic open-house activities, others are able to accommodate a limited number of scientifically oriented student groups for special tours.
Exhibits	NASA educational exhibits range from posters to full-size models to slide presentations housed in a theater-type environment.
Space Science Education Project (Spacemobile)	The Spacemobile is a unit composed of a lecturer with science teaching background, equipment for space science demonstrations and 20 to 25 models of NASA spacecraft and launch vehicle transported in a panel truck. It provides a means for filling requests from schools for classroom and assembly-hall lectures and demonstrations about NASA activities.
Speaker Services	Speakers from NASA Headquarters and from the various NASA field centers are available without charge, subject to program limitations, to student and teacher groups for discussing NASA programs.
Teacher Education Courses, Institutes, Seminars and Workshops	This program encourages and assists State departments of education, school districts, professional associations and institutions of higher education in providing opportunities for preservice and in-service elementary and secondary school teachers to gain greater understanding of developments in space sciences.
Youth Programs	Youth programs aim to encourage and assist schools and non-school organizations with space-related activities designed to familiarize participants with developments in the space sciences and related technologies. These include model rocketry, spacecraft model building, Youth Science Congresses, Science Fairs, Boy Scout activities, and Title I and other programs for the culturally deprived.

NASA EDUCATIONAL PROGRAMS OFFICES

If You Live In:	Write to Educational Office at:
Alaska, Arizona, California, Hawaii, Idaho, Montana, Nevada, Oregon, Utah, Washington, or Wyoming	NASA AMES RESEARCH CENTER Moffett Field, Calif. 94035
Alabama, Arkansas, Iowa, Louisiana, Mississippi, Missouri, or Tennessee	NASA GEORGE C. MARSHALL SPACE FLIGHT CENTER Marshall Space Flight Center Alabama 35812
Connecticut, Delaware, District of Columbia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, or Vermont	NASA GODDARD SPACE FLIGHT CENTER Greenbelt, Md. 20771
Florida, Georgia, Puerto Rico, or Virgin Islands	NASA JOHN F. KENNEDY SPACE CENTER Kennedy Space Center Florida 32899
Kentucky, North Carolina, South Carolina, Virginia, or West Virginia	NASA LANGLEY RESEARCH CENTER Langley Station Hampton, Va. 23365
Illinois, Indiana, Michigan, Minnesota, Ohio, or Wisconsin	NASA LEWIS RESEARCH CENTER 21000 Brookpark Road Cleveland, Ohio 44135
Colorado, Kansas, Nebraska, New Mexico, North Dakota, Oklahoma, South Dakota, or Texas	NASA MANNED SPACECRAFT CENTER Houston, Tex. 77058

☆ U. S. GOVERNMENT PRINTING OFFICE : 1971 O - 421-602