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PANEL 7

REACTION PROCESSES IN HIGH PRESSURE FLUID SYSTEMS

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INTRODUCTION

This report presents the results of the physical, metallurgical, chemical, and thermodynamic surveys that have been made on the high-pressure tank and plumbing systems of the Apollo spacecraft. These systems comprise the pressurized oxygen, hydrogen, nitrogen, propellant, and helium tanks and related plumbing of the command, service, and lunar modules. The purposes of the surveys are to lend support to the Apollo 13 investigation, to provide review and to extend knowledge of spacecraft pressure systems, and to contribute to the safety of future manned space flights. To achieve these objectives, descriptive data for all tanks were collected, a metallurgical survey and a comprehensive physical chemical survey of all systems were made, and some detailed thermodynamical calculations were performed.

The overall descriptive survey of the high-pressure tanks used on the Apollo spacecraft systems, including a review of the metallurgy involved in their construction, pointed to (1) the importance of a critical examination of any incompatibilities in materials selections and (2) the need for physical chemistry and catalysis studies of the reaction processes involved in high-pressure fluid systems. The result is a critical assessment of the physical and chemical processes that can occur in high-pressure fluids and an assessment of the hazards and possible failure mechanisms associated with containment of cryogenic materials. Findings based on these surveys are tabulated in the report.

As a general point, it should be noted that there is no such thing as a nonreactive substance. The stability of a substance in its environment is a matter of degree. Theoretically, the reactivity of materials can be assessed in terms of entropy and energy changes along with an implied characteristic time. In practice, either in engineering or in science, the experiment and the insight into the basic phenomena provide the real assessment of reactivity. The successful completion of two lunar landings and, before those, the extensive design, development, and qualification aspects of the Apollo Program can be thought of as experimental verifications. The Apollo 13 incident provides an opportunity for reexamination, objective and refined evaluation, improved design, and establishment of a broader base for future technological objectives.

An independent review of reaction processes in high-pressure fluids used in spacecraft systems was assigned to an independent consultant (Arthur D. Little, Inc., Cambridge, Massachusetts). Interim reports from this consultant are included in the appendixes; the final report from this consultant will be issued as a separate report at a later date.

SECTION A — DESCRIPTION OF TANKS IN USE ON THE APOLLO SPACECRAFT

GENERAL DESCRIPTION

A description of the Apollo command module (CM), service module (SM), and lunar module (LM) is shown in table A-I. For convenience, the tanks have been grouped by module and use. For example, the CM reaction control system (RCS) tanks are grouped together and are the first tanks listed. Abbreviations have been used sparingly to facilitate reading. When used, the abbreviations and letters are explained in footnotes at the bottom of the tables.

Table A-I lists the engineering data that are necessary for the thermodynamic and kinetic calculations of hypothetical reactions in or surrounding the tanks. These data also give a frame of reference for discussions of compatibility, contamination, and catalysis. Finally, they give a concise review of the tankage aboard the Apollo spacecraft.

SERVICE CONDITIONS

The normal service conditions for the CM, SM, and LM tanks are described in table A-II. The data were compiled to permit meaningful calculation of reaction processes in high-pressure systems. Table A-II lists the normal and operating ranges for pressure, temperature, volume or quantity, and flow rates for the tanks to which these parameters are applicable. In those cases where complete information was not available for a given tank, a line is drawn down the column.

The operational parameters never exactly match the normal operating parameters; instead, they vary within a small range. When the variance was evenly about a mean value, the mean value is given with plus and minus limits. In other cases, a range is given.

The operation and qualification data in table A-II were derived from several sources, among which were the following: telemetry data from sensors aboard Apollo 12 and 13; vendors statement of testing (ref. A-1); pressure-vessel operating-criteria specifications (refs. A-2 and A-3); and NASA reduced, collated flight data (ref. A-4).

PREDICTABLE FAILURE MODES

If a tank on the spacecraft system failed, it would do so by one of two brittle fracture failure modes: (1) fragmentation or (2) tearing caused by brittle fracture failure. Brittle fractures occur at strength levels that are below material-yield strength levels and are caused by preexisting flaws. Material toughness, operating stress level, flaw location, and flaw size influence the characteristics of the brittle fracture.

The brittle fracture failure modes for the Apollo tanks are tabulated in table A-III. The failure mode predictions are for preexisting surface flaws, maximum design operating pressures (MDOP), material properties per specification, and vessel dimensions within design tolerances. Alteration of any of the normal vessel characteristics by physical damage to the tank, overpressure, improper heat treatment, or fabrication errors will change the predicted failure mode.

OTHER FAILURE MODES

Another failure mode is the ductile or overstress failure mode. An overstress condition as high as the ultimate strength of the tank material probably will result in fragmentation of the tank. This failure mode is not predictable by fracture mechanics techniques. Mechanisms are discussed briefly in the following paragraphs for reactions that can occur in the tank that may result in ductile or overstress failure.

Ductile failure results from pressure buildup processes inside the enclosed area. Pressurization can be caused by chemical and physical reactions that occur within the confined fluid. Failure can result from any of several reaction mechanisms. Pressure buildup can result from exothermic or heat-liberating reactions in a combined space. The pressure may be increased by the addition of gaseous products resulting from solid or liquid reactants. The pressure also may be increased by an increase of liquid products compared to liquid reactants.

The decomposition of hydrazine induced by rust illustrates the above mechanism. The complete decomposition of hydrazine by metallic oxides yields two molecules of water for each hydrazine molecule reacting.

$$H_2NNH_{2(\ell)} + 2Fe_2O_{3(s)} \longrightarrow 2H_2O_{(\ell)} + N_{2(g)} + 2FeO_{(s)} + \text{Heat}$$

Liquid-product insertion into the confined space will increase the pressure. The production of gaseous nitrogen will contribute to the pressure, and the liberation of heat during the reaction will contribute further to pressure buildup.

Pressure buildup can occur in some systems because of catalytic decomposition of container fluids. Metallic ions, such as Fe^{+++}, Ni^{++}, Al^{+++}, Cr^{+++}, or Cu^{++} can be introduced either as impurities or from the vessel walls. This possibility exists with all hydrazine and substituted hydrazine fuels. The products are a mixture of NH_3, N_2, and H_2. In all cases, an excess of product molecules compared to reactant molecules will result, and the container will experience a pressure increase.

Under other circumstances, tank surfaces that are inert or passivated may be abraded mildly, thus removing the protective layer. The abrasion can occur from particulate contamination and, although the abrasive action itself may not injure the tank to failure, the resulting reaction between the contents and the fresh metal surface may liberate sufficient heat to increase the pressure to overstress failure. Possibilities for this failure mechanism exist, for example, in any oxygen tank under pressure that contains parts constructed of aluminum.

Mechanisms for ductile failure exist in possible reactions between tank contents and incompatible materials of construction, between impurities from pressurant gases and tank contents, or from combustion processes initiated by external energy (electrical) deposited in materials in oxidizer systems that are capable of acting as fuels.

REFERENCES

A-1. Statement of Work for Testing of Block II SPS Pressurant and Propellant Tanks, Project Apollo (u). Rept. SID 65-762A, North American Aviation, Inc., June 25, 1965.

A-2. Apollo Command and Service Module Pressure Vessel Criteria Specifications. Rept. SE-V-0028, NASA Manned Spacecraft Center, Oct. 1968.

A-3. Lunar Module Pressure Vessel Operating Criteria Specifications. Rept. SE-V-0024, NASA Manned Spacecraft Center, Oct. 1968.

A-4. Data collected by General Electric Co.

A-5. Predictions by Boeing Co. (D. G. Cox).

TABLE A-I.- APOLLO PRESSURE VESSELS

(a) Command module tanks

Vessel	Function	Gas or liquid contained	Quantity required	Vessel dimensions, in.	Vessel material	Design pressures, psia			Normal operating pressure, psia
						Limit	Proof	Burst	
Reaction control system									
Pressure tank	Pressurize fuel and oxidizer	Gaseous helium	2	9.2 diam. 0.102	Ti-6Al-4V	5000	6667	7500	4150
Propellant tank	Oxidizer storage	[a]N_2O_4	2	19.907 × 12.6 0.022	Ti-6AL-4V	360	525	540	291
Propellant tank	Fuel storage	Monomethyl-hydrazine	2	17.32 × 12.6 0.022	Ti-6AL-4V	360	525	540	291
Environmental control system									
Surge tank	Astronaut breathing	Gaseous oxygen	1	14.00 × 13.00 0.033/0.078	Inconel 718	1070	1356	1530	900
Storage tank	Astronaut breathing	Gaseous oxygen	3	12.62 × 7.00 0.028/0.045	Inconel 718	1070	1600	1800	900

[a] Inhibited nitrogen tetroxide.

TABLE A-I.- APOLLO PRESSURE VESSELS - Continued

(b) Service module tanks

Vessel	Function	Gas or liquid contained	Quantity required	Vessel dimensions, in.	Vessel material	Design pressures, psia			Normal operating pressure, psia
						Limit	Proof	Burst	
Service propulsion system									
Pressure tank	Pressurize fuel and oxidizer	Gaseous helium	2	40.17 diam. 0.366	Ti-6Al-4V	3685	4910	5540	3600
Propellant tank	Oxidizer storage	N_2O_4	1	153.05 × 45 0.047/0.025	Ti-6Al-4V	225	300	337.5	186
Propellant tank	Fuel storage	UDMH[b] Hydrazine	1	153.05 × 45 0.047/0.025	Ti-6Al-4V	225	300	337.5	186
Propellant tank	Oxidizer sump	N_2O_4	1	152.30 × 51.10 0.054/0.028	Ti-6Al-4V	225	300	337.5	186
Propellant tank	Fuel sump	UDMH Hydrazine	1	152.38 × 51 0.054/0.028	Ti-6Al-4V	225	300	337.5	186
Pressure tank	Pneumatic control actuator fuel and oxidizer	Gaseous nitrogen	2	9.16 × 4.92 0.130	Stainless steel AMS 5745	2900	5000	7500	2900
Reaction control system									
Pressure tank	Pressurize fuel and oxidizer	Gaseous helium	4	12.0 diam. 0.130	Ti-6Al-4V	4500	5985	7000	4150
Primary propellant tank	Oxidizer storage	N_2O_4	4	27.563 × 12.6 0.017	Ti-6Al-4V	248	360	460	185
Primary propellant tank	Fuel storage	Monomethylhydrazine	4	22.722 × 12.6 0.017	Ti-6Al-4V	248	360	460	185
Secondary propellant tank	Oxidizer storage	N_2O_4	4	19.907 × 12.6 0.022	Ti-6Al-4V	248	480	540	185
Secondary propellant tank	Fuel storage	Monomethylhydrazine	4	17.32 × 12.6 0.022	Ti-6Al-4V	248	480	540	185

[b] 50:50 mixture of hydrazine and unsymmetrical hydrazine.

TABLE A-I.- APOLLO PRESSURE VESSELS - Continued

(b) Service module tanks - Concluded

Vessel	Function	Gas or liquid contained	Quantity required	Vessel dimensions, in.	Vessel material	Design pressures, psia			Normal operating pressure, psia
						Limit	Proof	Burst	
Electrical power system									
Cryogenic tank	Fuel-cell storage	Liquid oxygen	2	26.28 diam. 0.020	Inconel 718	1020	1356	1530	900
Cryogenic tank	Fuel-cell storage	Liquid hydrogen	2	28.24 diam. 0.045	Ti-5Al-2.5Sn	285	400	450	225 260
Pressure tank	Pneumatic control actuator fuel cells	Gaseous nitrogen	3	6.0 diam. 0.099	Ti-5Al-2.5Sn	1730	3000	5100	1500

TABLE A-I.- APOLLO PRESSURE VESSELS - Continued

(c) Lunar module tanks

Vessel	Function	Gas or liquid contained	Quantity required	Vessel dimensions, in.	Vessel material	Design pressure, psia			Normal operating pressure, psia
						Limit	Proof	Burst	
Environmental control system									
Storage tank descent and ascent	Astronaut drinking	Water	3		Aluminum 6061	45	60	90	44.5
Storage tank descent	Astronaut breathing	Gaseous oxygen	1	23.522 × 21.722 0.118	Low-carbon steel D6AC	3000	3990	4500	2869
Storage tank ascent	Astronaut breathing	Gaseous oxygen	2	14.500 × 11.968 0.029	Inconel 718	1000	1330	1500	850
Reaction control system									
Pressure tank	Pressurize fuel and oxidizer	Gaseous helium	2	12.00 diam. 0.099	Ti-6Al-4V	3500	4650	5250	3420
Propellant tank	Fuel storage	UDMH Hydrazine	2	32.206 × 12.5 0.020/0.017	Ti-6Al-4V	250	333	375	179
Propellant tank	Oxidizer storage	N_2O_4	1	38.819 × 12.5 0.025/0.017	Ti-6Al-4V	250	333	375	179
Descent propulsion system									
Pressure tank	Pressurize fuel and oxidizer	Gaseous helium	1	14.9 diam. 0.064	Ti-6Al-4V	1750	2328	2625	1750
Propellant tank	Fuel storage	UDMH Hydrazine	2	70.28 × 51.00 0.065/0.033	Ti-6Al-4V	275	360	405	246
Propellant tank	Oxidizer storage	N_2O_4	2	70.28 × 51.00 0.065/0.033	Ti-6Al-4V	275	360	405	246
Pressure tank	Fuel pressurant	Supercritical helium	1	26.9 diam. 0.147	Ti-5A2.5Sn	1710	2274	3400	1555

TABLE A-I.- APOLLO PRESSURE VESSELS - Concluded

(c) Lunar module tanks - Concluded

Vessel	Function	Gas or liquid contained	Quantity required	Vessel dimensions, in.	Vessel material	Design pressure, psia			Normal operating pressure, psia
						Limit	Proof	Burst	
Ascent propulsion system									
Pressure tank	Pressurize fuel and oxidizer	Gaseous helium	2	22.25 diam. 0.198	Ti-6Al-4V	3500	4650	5250	3050
Propellant tank	Fuel storage	UDMH / Hydrazine	1	49.4 diam. 0.032	Ti-6Al-4V	250	333	388	184
Propellant tank	Oxidizer storage	N_2O_4	1	49.4 diam. 0.032	Ti-6Al-4V	250	333	388	184

TABLE A-II.- ANALYTICAL CRITERIA, PRESSURE, TEMPERATURE, FLOW, AND ELECTRICAL DATA

(a) Command module tanks

Tank	Normal operating pressure, psi	Specification qualification temperature, °F	Analytical criteria[a] (b)		Actual operating pressure, psi	Actual operating temperature, °F	Normal operating flow, lb/hr	Actual flow, lb/hr
			Pressure, psi	Temperature, °F				
Reaction control system								
Fuel	295	40 to 90	308	85				
Oxidizer	295	40 to 90	308	85				
Helium	4150	175 to 185 max.	5000	140	4105 to 4158	64 ± 4		
Environmental control system								
GO_2 surge	900	40 to 90	1070	--				
GO_2 backup	900	40 to 90	1070	--				
Portable life support system	950	40 to 90	1110 [c]1500	--				

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[a] Reference A-2.

[b] The temperature and pressure combination not to be exceeded.

[c] Apollo 16 and subsequent flights.

TABLE A-II.- ANALYTICAL CRITERIA, PRESSURE, TEMPERATURE, FLOW, AND ELECTRICAL DATA - Continued

(b) Service module tanks

Tank	Normal operating pressure, psi	Specification qualification temperature, °F	Analytical criteria (b)		Actual operating pressure, psi	Actual operating temperature, °F	Normal operating flow, lb/hr	Actual flow, lb/hr
			Pressure, psi	Temperature, °F				
Reaction control system								
Fuel (primary)	185	40 to 90	207	85	173 ± 1			
Fuel (secondary)	185	40 to 90	207	85	173 ± 1			
Oxidizer (primary)	185	40 to 90	207	85	169 ± 1			
Oxidizer (secondary)	185	40 to 90	207	85	169 ± 1			
Helium	4150	40 to 90	4500	140	4028 to 4073	74 to 80		
Electrical power system								
LO_2	[d]900	40 to 90	1010	-195	883 to 896	-189 to -199	0.65	0.471 to 0.653
LH_2	255	40 to 90	285	-423	224 to 234	-416 to -417	0.065	0.063 to 0.079
GN_2	1475	40 to 90	1500	75	—	75		
Service propulsion system								
Sump fuel	175	40 to 90	205	85	172 ± 1	70 ± 5		
Sump oxidizer	175	40 to 90	205	85	169	70 ± 5		
Storage fuel	175	40 to 90	205	85	172 ± 1	70 ± 5		
Storage oxidizer	175	40 to 90	205	85	169	70 ± 5		
Helium	3650	175 to 185 max.	3685	140	3530 to 3552	85 to 87		
GN_2	2500	40 to 90	2900	--	2500	60 to [+125?]		

[b] The temperature and pressure combination not to be exceeded.

[d] The normal operating pressure varies from 865 to 935 psi.

TABLE A-II.- ANALYTICAL CRITERIA, PRESSURE, TEMPERATURE, FLOW, AND ELECTRICAL DATA - Concluded

(c) Lunar module tanks[e]

Tank	Normal operating pressure, psi	Specification qualification temperature, °F	Analytical critera[f] (b)		Actual operating pressure, psi	Actual operating temperature, °F	Normal operating flow, lb/hr	Actual flow, lb/hr
			Pressure, psi	Temperature, °F				
Reaction control system								
Fuel	181		192	85	178 to 183			
Oxidizer	181		192	85	178 to 183			
Helium	3420		3500	140	1729 to 2905	65 to 71		
Ascent propulsion system								
Fuel	203		205	85	204 to 240	65 to 95		
Oxidizer	203		205	85	227 to 239	55 to 69		
Helium	3060		3500	140	3086 to 3105	-136 to +69		
Descent propulsion system								
Fuel	253		275	75	236	56 to 71		
Oxidizer	253		275	75	270	55 to 69		
Helium	1663		1750	140	1336			
Supercritical helium	1555		1967	--	1710	-319		
Environmental control system								
Ascent GO_2	850		1000	--	847 to 602		0.3 to 0.4	0.24
Descent GO_2	2690		3060	--	2632 to 598		0.3 to 0.4	0.3 to 0.4

[b] The temperature and pressure combination not to be exceeded.

[e] Data from Apollo 12; gathered by The Boeing Company and General Electric Company (Houston).

[f] Reference A-3.

TABLE A-III.- BRITTLE FRACTURE FAILURE MODES

(a) Command and service module tanks

Gas or liquid contained	Vessel material	Vessel dimensions, in.	Normal operating temperature, °F	MDOP,[a] psi	Predicted failure mode at MDOP[b]
Command module reaction control system					
Gaseous helium	Ti-6Al-4V	9.2 diam 0.102	64 ± 4	5000	Fragment
N_2O_4	Ti-6Al-4V	19.907 × 12.6 0.022	--	360	Fragment
Monomethylhydrazine	Ti-6Al-4V	17.32 × 12.6 0.022	--	360	Fragment
Command module environmental control system					
GO_2 surge	Inconel 718	14.00 × 13.00 0.033/0.078	--	1070	Fragment
GO_2 storage	Inconel 718	12.62 × 7.00 0.028/0.045	--	1210	Leakage
Service module service propulsion system					
Gaseous helium	Ti-6Al-4V	40.17 diam 0.366	85 to 87	3685	Fragment
N_2O_4	Ti-6Al-4V	153.05 × 45 0.047/0.025	70 ± 5	225	Fragment
Aerozine-50	Ti-6Al-4V	153.05 × 45 0.047/0.025	70 ± 5	225	Fragment
N_2O_4 sump	Ti-6Al-4V	152.30 × 51.10 0.054/0.028	70 ± 5	225	Fragment
Aerozine-50 sump	Ti-6Al-4V	152.38 × 51 0.054/0.028	70 ± 5	225	Fragment
GN_2	Stainless steel AM 350	9.16 × 4.92 0.130	60 to 85	2900	Fragment

[a] Maximum design operating pressure.

[b] Reference A-5.

TABLE A-III.- BRITTLE FRACTURE FAILURE MODES - Continued

(a) Command and service module tanks - Concluded

Gas or liquid contained	Vessel material	Vessel dimensions, in.	Normal operating temperature, °F	MDOP,[a] psi	Predicted failure mode at MDOP[b]
Service module reaction control system					
Gaseous helium	Ti-6Al-4V	12.0 diam 0.132	74 to 80	4500	Fragment
N_2O_4 primary	Ti-6Al-4V	27.563 × 12.6 0.017	--	248	Fragment
MMH primary	Ti-6Al-4V	22.722 × 12.6 0.017	--	248	Fragment
N_2O_4 secondary	Ti-6Al-4V	19.907 × 12.6 0.022	--	248	Leakage
MMH secondary	Ti-6Al-4V	17.32 × 12.6 0.022	--	248	Leakage
Service module electrical power system					
Supercritical oxygen	Inconel 718	26.28 diam 0.020	-189 to -199	1020	Leakage
Supercritical hydrogen	Ti-5Al-2.5Sn	28.24 diam 0.045	-416 ± 1	285	Leakage
GN_2	Ti-5Al-2.5Sn	6.0 diam 0.099	75	1730	Leakage

[a] Maximum design operating pressure.

[b] Reference A-5.

TABLE A-III.- BRITTLE FRACTURE FAILURE MODES - Concluded

(b) Lunar module tanks

Gas or liquid contained	Vessel material	Vessel dimensions, in.	Normal operating temperature, °F	MDOP,[a] psi	Predicted failure mode at MDOP[b]
Environmental control system					
Water	Aluminum 6061	--	--	45	Leakage
GO_2	Low-carbon steel D6AC	23.522 × 21.722 0.118	--	3000	Fragment
GO_2	Inconel 718	14.500 × 11.968 0.029	--	1000	Leakage
Reaction control system					
Gaseous helium	Ti-6Al-4V	12.00 diam 0.099	65 to 71	3500	Fragment
Aerozine-50	Ti-6Al-4V	32.206 × 12.5 0.020/0.017	--	250	Fragment
N_2O_4	Ti-6Al-4V	38.819 × 12.5 0.025/0.017	--	250	Fragment
Descent propulsion system					
Gaseous helium	Ti-6Al-4V	14.9 diam 0.064	--	1750	Fragment
Aerozine-50	Ti-6Al-4V	70.28 × 51.00 0.065/0.033	56 to 71	275	Fragment
N_2O_4	Ti-6Al-4V	70.28 × 51.00 0.065/0.033	55 to 69	275	Fragment
Supercritical helium	Ti-5Al-2.5Sn	26.9 diam 0.147	-319	1710	Fragment
Ascent propulsion system					
Gaseous helium	Ti-6Al-4V	22.25 diam 0.198	-136 to +69	3500	Fragment
Aerozine-50	Ti-6Al-4V	49.4 diam 0.032	65 to 95	250	Fragment
N_2O_4	Ti-6Al-4V	49.4 diam 0.032	55 to 69	250	Fragment

[a] Maximum design operating pressure.

[b] Reference A-5.

SECTION B — METALLURGY — APOLLO HIGH-PRESSURE VESSELS

MATERIALS COMPATIBILITY ASSESSMENT

The metallurgical assessment of Apollo pressure vessels includes both the inherent metallurgical characteristics of the tank materials and the two primary potential problem areas — combustion and stress corrosion. Combustion is a concern in any environment that contains either oxygen or a material capable of providing an oxidizing environment. However, corrosion is the most common form of environmental metal degradation. In stressed systems such as those using pressure vessels, stress corrosion can be a damaging problem if not considered properly in design and use. Stress corrosion can cause localized cracks in the metal that can be potential failure sources.

A detailed description of all Apollo pressure vessels has been included in another section of this report. The pressure vessels may be classified into three groups: titanium vessels, steel vessels, and Inconel vessels.

Titanium Vessels

The majority of vessels used for the Apollo Program are fabricated from titanium alloys. The Ti-6Al-4V alloy, in the solution-treated and aged condition, is used for all gaseous helium pressurization vessels and for all vessels that contain propellants in the primary and auxiliary propulsion systems on the command and service module (CSM) and the lunar module (LM). The Ti-5Al-2.5Sn alloy, in the annealed condition, is used for the liquid hydrogen tank, the supercritical helium tank, and the fuel-cell gaseous nitrogen tanks.

The metallurgical compatibility of the titanium alloys with external ambient environments encountered in spacecraft applications has been established previously by tests and proven by use. A review of the effects of these external environments has not provided reason to question this accepted compatibility. The internal environments are included in the following discussions of titanium tanks.

Gaseous helium tanks.- No known metallurgical or compatibility problems are associated with the use of the 6Al-4V titanium alloy with helium. The gaseous helium vessels do not have internal electrical or mechanical devices. This eliminates concern over both the possible problems associated with dissimilar metal combinations and the effects of potential sparking or localized hot spots. Because of the inert nature of helium gas, a compatibility problem is not expected with other components of the high-pressure helium systems if the gas meets the applicable specification limits for impurities.

Propellant tanks.- The oxidizer used in the Apollo propulsion systems is nitrogen tetroxide and the fuel is Aerozine-50, except for the fuel used in the command module (CM) reaction control system (RCS), which uses monomethyl hydrazine. The propellants have been the subject of extensive investigation for compatibility with the tank materials and for stability in the presence of the tank materials. The tanks in the main propulsion systems (service propulsion system (SPS), ascent propulsion system (APS), and descent propulsion system (DPS)) also are exposed to referee propellant fluids (water or trichlorotrifluoroethane) during check-out of the systems. These fluids also have been the subject of extensive investigation for compatibility with tank material. If only the approved fluids and procedures are associated with the use of the tanks, the possibility of stress corrosion is remote. The importance of using only approved fluids is exemplified by the previous methanol and nitrogen tetroxide incompatibilities. Methanol has been eliminated from approved use, and the nitric oxide content of approved nitrogen tetroxide must be at least 0.6 percent to ensure compatibility.

Electrical-apparatus components or connections are isolated from the propellants (for example, in the descent propellant tanks propellant quantity gaging system (PQGS) probe). The possibility of combustion of metallic tank materials is considered remote.

Liquid hydrogen tanks.- The liquid hydrogen tanks are similar in construction to the liquid oxygen tanks, except that the pressure vessel is 5Al-2.5Sn titanium alloy. A variety of metallic materials are used for internal components and accessories. The use of both tin-lead solder and brass is receiving further attention because tin can degrade at cryogenic temperatures, and lead and zinc are individually incompatible with liquid hydrogen. It is not presently known in what potential manner the tin-lead solders or brass (copper-zinc alloy) may react. Experience to date, however, does not support concern over these materials. Another condition requiring attention is the use of iron in fan motors, solenoid and aperture, and switch assemblies. Combustion of any of the metallic materials is unlikely. The hydrogen tank bimetal joint leak encountered on Apollo 12 has been attributed to improper processing in two lots and not to a basic metallurgical problem. The titanium alloy vessel material (Ti-5Al-2.5Sn) and hydrogen are compatible under normal Apollo use conditions in which temperatures are less than -160° F. At room temperature, compatibility is questionable. The allowable maximum temperature for the Apollo liquid hydrogen tanks is 80° F. The use of the alloy (Ti-5Al-2.5Sn) for tanks operating in the warmer temperature range could constitute an incompatible condition.

Supercritical helium tank.- No internal electrical connections or moving parts are in the tank. The combustion of material is improbable under any use conditions. The most probable causes of tank failure are failure of the burst disk to operate (which is remote) or heating of the tank wall to a level at which the wall would fail before the burst disk because of reduced wall strength at the elevated temperature. The latter probability is theoretically possible, and it is understood that this condition may occur under certain operational conditions.

Gaseous nitrogen tanks.- Examination of the gaseous nitrogen fuel-cell tanks has not shown reason to question the service compatibility of a tank with its service environment. Combustion of the tank material is unlikely.

Steel Vessels

The following three types of steel are used for Apollo vessels: AM350, D6AC, and cryoformed 301 stainless steel. The specific applications are discussed in the following paragraphs.

Service propulsion system gaseous nitrogen tanks.- The AM350 steel is used for fabrication of these tanks. There are no internal electrical connections or moving parts. Combustion is highly unlikely. There is no metallurgical reason to question the compatibility of the tanks with their environment under use and test conditions.

Lunar module descent stage oxygen tank.- This tank is fabricated from D6AC steel. The interior of the tank is nickel plated, and the exterior is painted to guard against corrosion. The possibility of combustion is remote. If plating and paint integrity is maintained, environmental corrosion should not be a problem. Crevice corrosion has been avoided in Apollo use but is a potential problem with D6AC steel.

Portable life support system primary oxygen tanks.- Cryoformed stainless steel is used for the primary oxygen tanks on the portable life support system (PLSS). These tanks contain no internal electrical connections or moving parts. Combustion of the tank material is unlikely. Instrumentation is not bonded directly to tank surfaces, and fraying surfaces are avoided. The incidence of crevice corrosion, which has not been experienced on the PLSS tanks, indicates that the design and the environments associated with Apollo usage are compatible.

Inconel 718 Vessels

The CM oxygen surge tank and rapid repressurization tanks, the service module (SM) cryogenic oxygen tanks, the LM ascent stage oxygen tank, and the PLSS oxygen purge tanks are fabricated from Inconel 718. Inconel 718 alloy, in tests and by past performance, has demonstrated compatibility with gaseous oxygen.

METALLURGICAL INCOMPATIBILITIES AND IMPURITIES EFFECTS STUDIES

Whenever the free energy change of a system is negative and reaction is limited by kinetics, the possibility exists for catalysis to occur even with trace additions of certain materials. The high-energy liquids (that is, oxygen, hydrogen, nitrogen, nitrogen tetroxide, and hydrazine) would be expected to react with most of the container materials. The only reason these liquids are at all compatible is because of protective films and slow-reaction kinetics. In studying the compatibility of the material in terms of bulk reactions, care should be exercised to determine the course and extent of reactions in materials without protective films. The electrochemical behavior of freshly exposed titanium (that is, fractured specimens) is markedly different from titanium with an oxide coating. The combustion of metals with a protective oxide can be initiated only by breakage of the oxide. Thus, it is known that titanium is a satisfactory container material for hydrogen only if the surface oxide is reformed.

The state of the art of stress-corrosion cracking is such that priori predictions about susceptibility of material-environment combinations cannot be made with a high degree of certainty. The presence of halides in either aqueous, organic, or fused salt environments generally promotes stress-corrosion cracking of metals, but the effect of other environmental species cannot as yet be predicted. Although it is a goal of scientific laboratories to be able to predict stress-corrosion behavior from first principles, the phenomenon is complex and achievement of this goal is still in the future. Trace impurities in the environment can have a large influence on rate of crack propagation. For example, stress-corrosion cracking of some titanium alloys in methanol can be inhibited completely by the addition of a few parts per million of nitrate. The addition of chloride increases susceptibility and crack-propagation velocity. These additions play the role of catalysts, positive and negative. In electrolytically conducting solutions such as water or methanol with dissolved halide salts, crack-propagation velocity is also a function of applied potential. Under open-circuit conditions, this potential may be determined by electrochemical reactions such as dissolved oxygen reduction on the surface of the specimen.

Localized attack usually is initiated and maintained by either nonuniform supply of a reactant to a surface (for example, pitting corrosion in electrochemistry) or by the partial destruction of a protective film. Recent research has been directed to investigating environment-induced cracking. It has been found that the cracking is influenced by the following factors.

1. Metallurgical variables (for example, composition of alloy, heat treatment)

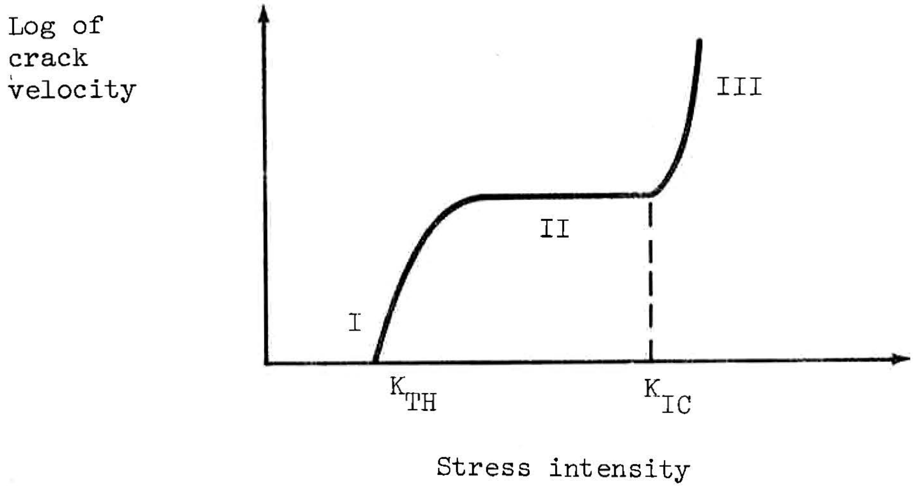
2. Environment variables (for example, chemical composition, impurities)

3. Temperature and pressure

4. Stress

5. Electrochemical variables (for example, electrical potential and conductivity, in systems where the interaction is electrochemical (Aerozine-50 and monomethyl hydrazine, but presumably not oxygen, hydrogen, or nitrogen)).

According to the present state of the art, interpretation of test results requires that the crack-propagation velocity is known for a range of stress intensities. For each test condition, a curve of crack-propagation rate as a function of stress intensity can be plotted, conveniently on logarithmic paper, because recent measurements range from 10^{-7} to 10^{2} cm/sec. On such a plot, if complete, at least three different mechanisms of crack propagation can be distinguished. As shown in the following figure, at high stresses (region III), the crack is unstable mechanically, accelerates, and may approach the velocity of transverse acoustic waves. Fracture mechanics is the science dealing with this phenomenon and with determining the critical stress intensity (K_{IC}) for this to occur. At lower stresses, cracks grow at a rate that is independent of stress intensity (region II). Fracture chemistry is rate-controlling in this region. Fracture may proceed across the grain (titanium alloys) or along the grain boundaries (aluminum alloys). This seems to have little relevance. Region I is important because it determines the lower threshold stress intensity (K_{TH}). Unfortunately, present fundamental knowledge about the mechanisms that control crack propagation in this region is lagging.



Supercritical Oxygen Tank — Inconel 718

Major construction materials are Inconel 718, stainless steel 321, Aluminum 6063 and polytetrafluoroethylene (PTFE) polymer.

References B-1 and B-2 listed PTFE as satisfactory for liquid oxygen service, except if pigmented (ref. B-3) or contaminated. No quantitative information is available on the permissible contamination of PTFE, nor is there anything known about the effect of contamination of the oxygen on the ignition of PTFE. Dissolved contaminants in the tank possibly could be measured by the use of the quantity gage for resistivity measurements. Resistivity has been correlated with impurity content in the case of Freon (ref. B-4) and boron trifluoride (ref. B-5). Of course, solid contaminants could not be traced by this technique. In general, solids become effective as catalysts by impinging on surfaces (ref. B-6) (particulate contaminants) or by intimate contact (as in valve seats, washers, insulations). Inconel 718 is one of the most suitable materials for liquid oxygen service (refs. B-2 and B-7). If the postweld heat treatment were omitted, however, Inconel 718 would be incompatible with liquid oxygen (ref. B-8).

Tiner, et al. (ref. B-9) measured corrosion in ozone difluoride (0.05 percent) liquid oxygen and found that Inconel X, brass, and aluminum 1100 corroded, whereas none of these materials corrode in pure oxygen. It is also significant that Tiner found that corrosion was more pronounced in gaseous oxygen than in liquid oxygen. Boeing (ref. B-8) conducted a stress-corrosion test in liquid oxygen, and Tiner, et al. (ref. B-9) conducted a stress-corrosion test in liquid oxygen that was contaminated deliberately with 0.05 percent ozone difluoride. Neither found significant stress-corrosion susceptibility.

Austenitic stainless steels are compatible with liquid oxygen but somewhat more combustible than Inconel (ref. B-1).

Aluminum alloys usually are listed as compatible, although alloy 6061 occasionally is ignited by impact in liquid oxygen (ref. B-10).

Brass, used to a limited extent, is considered as compatible (ref. B-2), but its catalytic potential should be examined. The same can be stated about copper.

Under impact conditions, tin-lead solder is not compatible with liquid oxygen (ref. B-2).

Gaseous Oxygen Tank, D6AC

This tank is made of low-alloy nickel-molybdenum-vanadium steel, is nonaustenitic, and is stress brittle at cryogenic temperatures. The fracture-toughness values (data from the F111 investigation) are as follows.

Temperature, °F	Oil quenched	Brine quenched
70	90	55
-20	58	40
-65	45	30

Based on the information that the steel was air-quenched and that the service temperature was 50° F, there is no incompatibility in this case.

Comments concerning other materials within the tank are the same as in the case of the supercritical oxygen tank.

Nitrogen Tanks

The major structural materials are Ti-6Al-4V and stainless steel AM350.

Nitrides are known to form; thus, incompatibilities are not impossible. Stress-corrosion-test results, however, indicated hardly any decrease of critical stress intensity.

Helium Tank, Ti-6Al-4H

Not only do noble gases not react with metals, but also the permeability of helium through metals is extremely low. The only cases of helium embrittlement known are caused by alpha-particle irradiation (ref. B-11).

Hydrogen Tank, Ti-5Al-2.5Sn

The interaction of hydrogen with titanium has been studied for many years. There is no evidence for the reaction of liquid hydrogen with titanium alloys (ref. B-12). There is some lowering of the critical stress intensity at low temperatures, but this seems to be related to temperature rather than to the presence of hydrogen (ref. B-13). At room temperature, however, reaction of titanium with oxygen was observed (refs. B-12 and B-14), and the substitution of Ti-5Al-2.5Sn alloys for the unalloyed titanium piping solved the then existing problem. A second research program, however, showed that titanium alloys were equally vulnerable if the surface was abraded or cleaned (ref. B-15). The Ti-5Al-2.5Sn was shown to be more compatible with hydrogen than unalloyed titanium, but less so than Ti-6Al-4V. At the recent American Institute of Metallurgical Engineers Conference, May 11 to 14, 1970, several papers were presented on the interactions of hydrogen with titanium alloys. The following statements can be made.

1. Hydrogen does produce slow crack growth in titanium alloys.

2. The rate of such crack growth is often quite fast (10^{-3} cm/sec (ref. B-16)).

3. Notched and precracked specimens show a more dramatic effect than unnotched speciments (ref. B-16).

4. The purity of the hydrogen is very important. Slow crack growth occurs more readily in high-purity hydrogen.

5. Crack growth occurs even at very low hydrogen pressures (10^{-2} atmospheres).

6. There appears to be some influence of heat treatment and microstructure, but this was not well established.

There were no data reported on the Ti-5Al-2.5Sn alloy; most work was performed on commercial-purity titanium and Ti-6Al-4V. It is obvious that more careful and systematic work on the phenomenon is required before it can be controlled or understood. It is now evident that the traces of oxygen or water present in commercial-purity hydrogen had been a very effective inhibitor in prior experiments. Dell P. Williams (NASA Ames Research Center), states that an embrittling effect has been observed at temperatures as low as -100° C (ref. B-16). The concentration of oxygen in hydrogen necessary for inhibition has not yet been measured but is estimated by Williams to be approximately 100 ppm. A suitable surface treatment might improve the compatibility but would not necessarily improve the fracture toughness.

Some secondary structures within the tank are made of commercial-purity titanium and deserve particularly urgent attention.

Other secondary structures are made of aluminum alloys, 1100, 2024, 3007, 6061 and 7075. Aluminum alloys clearly are the alloys least affected by hydrogen, and there have been no reports that an external hydrogen environment at room temperature degrades the properties of aluminum alloys (ref. B-17).

The PTFE polymer is used as an insulating material within the hydrogen tank. There has been a scientific publication by DuPont (ref. B-18) that, once ignited, PTFE can react with hydrogen. A significant experimental effort is being initiated at MSC to verify this observation.

Nitrogen Tetroxide Tank

The principal structural material is Ti-6Al-4V; the materials for the zero-g can are Al 6061 T6 and Al 2024 T3.

Corrosion.- There is no evidence that noncontaminated nitrogen tetroxide (N_2O_4) corrodes titanium alloys, 300 series stainless steels, or Inconel X (ref. B-19). Most aluminum alloys are considered as compatible, except for 7075 and 2024 (ref. B-8). This point requires further examination. Also, if two different alloys are connected electrically, a galvanic cell is formed in N_2O_4 (ref. B-19). Water reacts with N_2O_4 to form nitric acid, which is corrosive to most structural materials (except 304 stainless steel and titanium). The water is regenerated during the corrosion process (ref. B-21) and, thus, does not exhaust. Corrosion of aluminum alloys becomes significant with a water content of 0.45 percent or more (ref. B-20). The specifications limit the water content to 0.1 percent (ref. B-19). F. D. Hess reviewed potential inhibitors and, in his paper (ref. B-20), recommends NH_4SO_3F for further evaluation.

Grunt, et al. (ref. B-21) conducted accelerated corrosion tests with contaminated N_2O_4. The contaminations were chlorine, water (0.91 percent), oxygen (0.04 percent), NOCL, NOCl + oxygen. He found that these contaminants did not promote corrosion in the case of Ti-6Al-4V. In the case of 6061-T6 aluminum, the addition of water and oxygen did promote corrosion.

Stress corrosion.- Early work in the 1960's indicated that titanium alloys behaved passively in N_2O_4, and there was no evidence of cracking in this environment. However, in 1965, Bell Aerospace Systems Inc. (ref. B-19) reported premature failure of a Ti-6Al-4V alloy tank containing N_2O_4. (The conditions were as follows: temperature 105° F; stress level, 90 000 psi; failure time, 40 hours). Examination of the fracture surface indicated that crack growth had occurred before catastrophic failure and, thus, indicated a stress-corrosion-cracking process had occurred. This failure initiated a detailed investigation of the compatibility of titanium alloys with N_2O_4 and, by 1966, the following statements were made in a DMIC report (ref. B-22).

1. Stress-corrosion cracking usually will occur in N_2O_4 when no significant or measurable amounts of nitric oxide (NO) are present and the system is exposed to moderately high stresses at temperatures in the range of 85° F to 165° F.

2. Stress-corrosion cracking does not occur in N_2O_4 when the N_2O_4 contains an excess of NO.

3. The commercial and military specifications to which N_2O_4 is processed do not control either the oxygen or NO content. As a result of this work, NASA developed a specification for N_2O_4 that controls the NO content.

4. All tests to date have shown complete inhibition of stress-corrosion cracking of titanium in "green" N_2O_4.

5. Further work has indicated that additions of sufficient water to red N_2O_4 will eliminate the stress-corrosion cracking of titanium. (This, in effect, adds NO and eliminates free oxygen because water forms nitric acid and NO in N_2O_4). Nitric acid, however, leads to general corrosion problems.

Since 1966, Battelle (NASA Contract NASr-100(09) and Hercules Inc. (NAS 8-21207) have continued work on this problem. The main conclusions of the Battelle study are summarized below.

1. All alloys tested were susceptible in "red" N_2O_4.

2. Both intergranular and transgranular cracking occur.

3. The mode of cracking depends on the stress intensity.

Some fracture-toughness testing has been performed within the Boeing Company (ref. B-14), and a reduction of fracture toughness of only 30 percent was reported in NO-enriched N_2O_4 ("green" N_2O_4), (that is, cracks propagate slower than they would in sea water).

Impact sensitivity.- Reports on the impact sensitivity in N_2O_4 are contradictory. Two 1961 manuals (refs. B-23 and B-24) list aluminum and titanium as incompatible, whereas a more recent report (ref. B-25) lists these two metals as insensitive to impact. This contradiction should be decided by experiment.

Monomethyl Hydrazine and Aerozine-50 Tanks

The major structural material is Ti-6Al-4V.

Corrosion.- Few corrosion data have been found in the available literature. The manufacturers recommend use of 300 series stainless steels and advise against use of copper, lead, zinc alloys, and so forth, without specifying the reasons (ref. B-26). Titanium alloys are "approved" for use with Aerozine-50 (ref. B-26). Tests conducted for a different purpose indicate corrosion of copper, although the test pressure was only 4 torr (ref. B-27).

Stress corrosion.- The decrease of the fracture toughness of Ti-6Al-4V by monomethyl hydrazine (MMH) is only approximately 25 percent, and by Aerozine-50 approximately 20 percent (refs. B-28, B-29, and B-30) (that is, no difficulties are indicated). One publication mentions cracking of 2014 aluminum alloy, indicative of stress corrosion in this alloy (ref. B-31). No further information concerning stress corrosion was found, nor was any information uncovered concerning the effect of impurities on stress corrosion.

Catalytic degradation.- Long-term storage of the propellant is limited by the catalytic effects of the tank walls and the impurities. The worst undesired catalysts are rust, molybdenom, and molybdenum-bearing alloys (ref. B-26), followed by nickel, iron, copper, stainless steel (ref. B-32), and gold (ref. B-8). Aluminum seems to be the most desirable material from this point of view, but the 4.5 percent copper content of the 2000 series aluminum alloys seems to be enough to spoil the inertness of aluminum (ref. B-33). Thus, aluminum alloy 2024 T3 should be eliminated from the "zero-g can." No information was found on the catalytic effect of titanium alloys.

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SECTION C — CHEMISTRY SURVEY

A chemistry survey was made on the Apollo high-pressure fluid systems. This survey includes examination of the tank contents, specifications, and analyses procedures; extent of polymer involvements; and catalytic effects on reaction processes.

CONTENTS, ANALYSES, AND SPECIFICATIONS — HIGH-PRESSURE FLUIDS AND GASES ON APOLLO SPACECRAFT 109

Cryogenic Hydrogen

Characteristics, chemical reactivity, and incompatibilities.- Liquid hydrogen is less dangerous than high-pressure gaseous hydrogen and is similar in hazardous respects to highly volatile gasoline (ref. C-1). The main precaution is to prevent air leakage into the liquid hydrogen containers. If this should happen, the air will solidify on the walls or will sink to the bottom of the tank. Solid air and liquid hydrogen will not explode spontaneously; a spark is required for an explosion. The spark, however, can be produced by the breaking of a crystal of solid air or oxygen or by a malfunctioning heater or motor wire immersed in liquid hydrogen containing solid air.

As a summary of the materials review, the materials inside and outside the tank generally are compatible with liquid hydrogen. The only possible exceptions are solder joints used in the heater and fan assemblies and polymers that can hydrogenize.

Materials considered incompatible with liquid hydrogen are listed in table C-I. They are class IV materials (ref. C-2) that have one or more of the following reactive properties: (1) have corrosion rates greater than 50 mils per year, (2) cause extensive decomposition of the propellant, (3) cause spontaneous combustion, or (4) are impact sensitive.

Solder is not listed in table C-I as an incompatible material in liquid hydrogen. However, solder contains lead in solid solution. Solder is used in two places on the Simmonds probe.

Reports in the literature place lead in the incompatible list for hydrogen use. A telecommunication to Batelle Memorial Institute reveals that this is in error. An error exists in the Defense Metals Information Center Memorandum. Lead is rated compatible with liquid hydrogen (ref. C-3).

Hydrogen manufacture.- The impurities present in hydrogen depend upon the source (reaction used in preparing the hydrogen) and the methods of purification. Hydrogen is manufactured by several methods (ref. C-1), among which are (1) electrolysis of water; (2) separation from flue gas, water gas, or coke-oven gas; (3) thermal decomposition of natural gas; (4) decomposition of steam on heated iron; and (5) action of steam on refinery oil. The water-gas reaction and the electrolysis of water are the two most important methods of production. Several methods of production are listed to show that several impurities must be guarded against and that they will vary with source.

The purest product results from the electrolysis of water; the method of decomposing water on hot iron results in the second purest product. The other methods of production give mixed products, and the purity of the final hydrogen depends upon the efficiency of the purification.

Impurities in hydrogen.- All known substances are essentially insoluble in liquid hydrogen. Helium is possibly soluble to about 1 percent. Impurities in liquid hydrogen, therefore, must be considered as segregated or particulate in nature. As a result, the primary concern is with contamination rather than with dissolved homogeneous impurities.

After purification, the main precaution to be taken is the prevention of air leakage into the liquid hydrogen containers. Twenty percent of air is oxygen, which will collect in the tank.

Hydrogen in either gaseous or liquid form will react violently with strong oxidizers. Because the air impurity will concentrate in liquid hydrogen and because it contains an oxidizer (oxygen), liquid hydrogen must be kept completely out of contact with air.

The impurities in hydrogen should run less than 50 ppm by volume. Most of the impurities will be helium, which is inert. Other impurities expected are oxygen, nitrogen, argon, water, carbon dioxide, carbon monoxide, and methane.

Specifications for hydrogen.- The procurement specifications for liquid and gaseous hydrogen are the same. The requirement is for the material as delivered at the spacecraft interface. The procurement specification for liquid hydrogen is listed in table C-II.

Conclusions.- Analysis of hydrogen for procurement and control should be from a representative sample. Analysis of gases withdrawn from the ullage area above a liquid sample will not give a complete and accurate analysis. Withdrawal of a gaseous sample in effect means that the cryogenic hydrogen has been purified one more time by distillation; therefore, the sample is not representative of the liquid.

Liquid hydrogen represents a potential fire and explosion source, but only in the presence of an oxidizer and an energy source to initiate the reaction. The two potential electrical sources present are the electrical wiring and air crystals in the hydrogen. Breakage can furnish electrical energy.) Two potential oxidizer sources present are air crystals and Polytetrafluoroethylene (PTFE).

Oxygen

Contaminants in oxygen.- Contaminants found in oxygen generally arise as a result of manufacture (air condensation) and failure of complete removal by purification. Some contaminants found are the following (ref. C-4).

1. Acetylene, 0.08 ppm
2. Ethylene, 0.88 ppm
3. Carbon dioxide, 6.6 ppm
4. Nitrous oxide, 2.0 ppm
5. Ethane, 3.56 ppm
6. Aliphatic hydrocarbons, 31 ppm

Concentration effects may occur. This was the case with an onboard converter (ref. C-5). The mechanism is as follows. The original composition of impurities was determined. The tank then was emptied and filled 25 times and the contents were reanalyzed for the impurities. The contaminant concentration effects are illustrated in table C-III.

Hydrocarbons such as methane, ethane, ethylene, acetylene, and higher homologues are potentially dangerous because they can be concentrated and oxidized in liquid oxygen to carbon dioxide (CO_2) and water (H_2O), with liberation of heat. The same consideration applies to ammonia (NH_3).

Carbon dioxide is deleterious for an entirely different reason. Carbon dioxide "snow" exists at all times in missile liquid oxygen (ref. C-6). Carbon dioxide concentration tends to rise with increase in filtration rate. It precipitates (solubility limit = 4.42 ppm in liquid oxygen (LO_2) at -183° C) as the oxygen (O_2) is handled or vaporized while in storage. The CO_2 "snow" will agglomerate where conditions are static (e.g., launch-pad storage tank). In subsequent operations, it may create blockage in the missile LO_2 system.

Contaminants found in container equipment.- Tank and container contamination can be divided into (1) impurities left during equipment cleaning operation and (2) impurities introduced by filling operations. Trichloroethylene and carbon tetrachloride are adsorbed by and often desorbed from container walls. Stabilized grades of trichlorethylene giving residues as small as 1 mg (0.4 in^2 in area) can be detonated by liquid oxygen. Residues from halocarbons should be regarded as potentially hazardous in service. The same generalization can be made about penetrant residues (ref. C-7). Closely controlled rinsing and cleaning is required for final cleaning; and, where possible, inspection methods for oxygen containers other than penetrant inspection should be used.

A table of contaminants detected at Kennedy Space Center on ground-support equipment (GSE) is contained in appendix B. This table illustrates the potential hazards associated with contamination introduced to LO_2 systems in filling and support operations.

Contaminants from pressurizing gases.- Nitrogen and helium are common pressurant gases. Helium is inert and nitrogen is relatively inert. Chemical reactions do not occur between the liquid and the ullage gas. However, both gases contain impurities. Nitrogen is obtained by essentially the same process as oxygen and has generally the same contaminants. Nitrogen can be dissolved in liquid oxygen up to 30 percent under nitrogen pressure (ref. C-8).

Impurities such as carbon monoxide and hydrogen are common in both gaseous nitrogen and gaseous helium (ref. C-9). When present in ullage gases for oxygen, the impurities are oxidized exothermically to form solid $CO_2 + H_2O$, which may contribute to filter blockage. Exothermic oxidation of impurities generally occurs at ppm concentration, and the reaction is imperceptible. However, if impurity concentration can occur for any reason, the resultant oxidation-reduction reaction may be deleterious to the system. The procurement specifications for liquid oxygen are shown in table C-IV; the impurities likely to be found in liquid oxygen are shown in table C-V.

The contaminant gases likely to produce a pressure rise are listed in table C-V along with relevant physical data (refs. C-10 and C-11).

The service module oxygen storage tank (part number 282-0046) pressure is nominally 900 psia, and system pressure has a range of 865 to 935 psia. The temperature of the tank appears to run at -200 ± 20° F, as judged by the time-line information. Comparison of the data in table C-VI with the tank-operating parameters shows that the temperature in the tank is below the critical temperature of all hydrocarbon impurities. It is below the sublimation point and normal melting point of acetylene and methyl chloride, respectively. As a result, the impurities will exist as solids and liquids in the normal system. Any process that raises the temperature above 204° F will cause the impurities to become gases.

Gasification of hydrocarbons in the oxygen tank is undesirable for two reasons: (1) A change of volume will occur for the hydrocarbons, with resultant increase in pressure. For the amounts of hydrocarbons present (<14 ppm), this physical process is insignificant. However, the impurity change from solid to gas will allow the impurities to oxidize at comparatively rapid rate.

$$4\ CH_4 + 7\ O_2 \longrightarrow 4\ CO_2 + 6\ H_2O + 21\,495\ \text{Btu/lb}$$

Similar reactions occur for the other hydrocarbons. The products of such reactions are condensable at the temperature and pressure of the tank. The reactions, however, are exothermic and offer a possibility of furnishing activation energy for other reactions.

An impurity-concentration process may occur through normal liquid oxygen boiloff in any storage tank from the time of production to the time of ultimate use aboard the spacecraft.

Nitrogen

Characteristics and chemical reactivity of nitrogen.- Nitrogen usually is considered an inert gas. It neither supports combustion nor sustains respiration. At high temperatures, however, it will combine with hydrogen, oxygen, and the other elements, and it will combine with some of the more reactive metals to form nitrides.

Nitrogen manufacture.- Nitrogen is produced commercially at air-separation plants by liquifaction of atmospheric air and removal of nitrogen by fractionation. As a result, impurity content in nitrogen is very similar to that in oxygen.

Nitrogen impurities.- Typical impurity levels for nitrogen are given below for a purity level of 99.998 per cent nitrogen (ref. C-12).

1. Acetylene, 0.05 ppm
2. Argon, 5.0 ppm
3. Carbon dioxide, 0.5 ppm
4. Helium, 5.0 ppm
5. Hydrogen, 1.0 ppm
6. Methane, 0.5 ppm
7. Nitrous oxide, 0.1 ppm
8. Oxygen, 1.0 ppm
9. Water, 1.0 ppm
10. Carbon monoxide, 1.0 ppm

These values are typical of the concentrations that are expected for this designated purity level. Actual analyses will vary from batch to batch.

Specifications for nitrogen.- The procurement for gaseous and liquid nitrogen is the same. The requirement is for the material as delivered at the spacecraft interface. The specifications for nitrogen are listed in table C-VI.

Conclusions.- The nitrogen in the electrical power system is used to flush the fuel cells of water, unused oxygen, and hydrogen. As a result, the chemical purity of the nitrogen is not critical except for oxygen and hydrocarbon content. The hydrocarbon content is controlled to 5 ppm or less, and, in a flowing vented system, this control is adequate. The oxygen content even at 150 ppm is not hazardous in a flowing system if adequate arrangements are made for venting and isolation from electrical energy sources.

Because nitrogen is used for flushing and blanketing, aerosols and particulate matter are critical. If particulates are present, abrasion can open fresh surfaces for possible reaction with oxygen or hydrogen, plugged filters and faulty valve action also can result.

Monomethylhydrazine

Characteristics and chemical reactivity of monomethylhydrazine.- Propellant-grade monomethylhydrazine (MMH) contains a minimum of 98 percent MMH (CH_3NHNH_2), the remainder being primarily water. Monomethylhydrazine is weakly alkaline, a strong reducing agent, and very hygroscopic. It will react accordingly with carbon dioxide, oxygen, and water, all of which are present in air. For example, carbon dioxide reacts with MMH to form a carbonic acid salt. Monomethylhydrazine will react with other acidic and oxidative materials (ref. C-13).

A film of MMH in contact with metallic oxides such as rust or other oxidizing agents (including oxygen in the air) may ignite from the heat evolved in the oxidation reaction. Catalysts such as copper, iron, or their alloys can cause decomposition on contact, with ignition possible (ref. C-14). Contact with mercury forms azide-type materials, which are very sensitive to shock. Zinc and alloys containing more than 0.5 weight-percent of molybdenum are not compatible with MMH.

Monomethylhydrazine manufacture.- The general method for making MMH starts with ammonia (NH_3) and uses chloramine (NH_2Cl) as the intermediate.

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH$$

$$NH_2Cl + CH_3NH_2 \longrightarrow CH_3NHNH_2 + HCl$$

$$HCl + NaOH \longrightarrow H_2O + Na^+ + Cl^-$$

The synthesis is analogous to the Raschig synthesis for hydrazine. It is particularly well suited for the manufacture of MMH and is the manufacturing method generally used.

Monomethylhydrazine impurities.- As a result of the manufacturing process and the chemical characteristics of MMH, the following compounds are probable impurities. (Where percentages are given, the results are representative of MMH samples in reference C-15.)

1. Water, = 0.56 percent
2. Nitrogen, = 0.09 percent

3. Nitrous oxide, = trace
4. Chloramine, = 0.1 percent
5. Ammonia, = 0.10 percent
6. Methylamine, = 0.07 percent
7. Triethylamine, = 0.07 percent
8. Monomethylhydrazine carbonate, = trace
9. Methylene monomethyldydrazine = 0.97 percent

The contaminant present in the largest amount is usually water, with the others present in lesser amounts. None of the other impurities will cause detrimental reactions.

Filterable solids are not required to be counted or identified, but a gravimetric record is kept. Copper and iron metals, particularly iron oxide (FE_2O_3, rust), can cause pressure buildup by catalysis and oxidative decomposition of the fuel. The following metals have been found in residues from representative MMH samples at the ppm level stated (ref. C-15): magnesium, 10; iron, 0.005; copper, 0.01; aluminum, <0.0005; and silicon, <0.01. The only metal found in any appreciable concentration was magnesium. Iron and copper, which should not be allowed to come in contact with MMH, were present in less than 1×10^{-7} parts and would cause no trouble.

Specifications for MMH.- The procurement specification for monomethylhydrazine is listed in table C-VII.

Conclusions.- The fact that some solids can cause catalytic and oxidative decomposition means that consideration should be given to quality analysis and control of residues in the fuel. Also, the titrimetric procedure described provides largely for the analysis of major components, but without differentiation of the various amine impurities. Chromatographic techniques have been developed for the separation and analysis of MMH impurities. They should be implemented to control the fuel better.

Nitrogen Tetroxide

Characteristics, chemical reactivity, and incompatibilities of nitrogen tetroxide.- Nitrogen tetroxide (N_2O_4) is an equilibrium mixture of nitrogen tetroxide and nitrogen dioxide $N_2O_4 \rightleftharpoons 2NO_2$. Propellant-grade inhibited H_2O_4 tetroxide contains 98.5 percent by weight of N_2O_4. Nitric oxide (NO), the inhibitor, is present in 0.6 minimum to 1.0 maximum percent by weight. The water equivalent for propellant N_2O_4 is maintained at 0.2 percent by weight or less, delivered. The 0.2-percent limit, by common acceptance, defines dry nitrogen tetroxide.

Dry nitrogen tetroxide can be contained readily by several metals and their alloys. The metals are listed in reference C-16. Wet nitrogen tetroxide is, in general, more corrosive than dry nitrogen tetroxide because of the nitric acid formed. Marked corrosion appears on metals exposed to N_2O_4 containing approximately 3 percent water. Under wet conditions, stainless steel (300 series) is the only recommended tank material. When the moisture content is 0.1 percent or less (dry), the following materials can be used: carbon steels, aluminum, stainless steels, nickel, and Inconel (ref. C-13). Lists of compatible materials that fail to differentiate metal compatibility caused by water content should be suspect.

Materials incompatible with N_2O_4 and materials that are satisfactory for limited service in N_2O_4 are listed in table C-VIII.

Polytetrafluoroethylene (Teflon) is listed as a compatible material. However, Teflon swelling in N_2O_4 has been noted (ref. C-17). The swelling characteristic is troublesome in packing and glands and is indicative of absorption or reactions in the polymer. In either case, the swelling is indicative of long-term incompatibility and a potential hazard anytime after it occurs.

Titanium originally was placed on the incompatible list because of stress-crack corrosion tendency in "red" N_2O_4. With the advent of "green" N_2O_4 (nitric oxide inhibited), titanium was removed from the list. However, upon further test, it was found that titanium Al-4V is vibration sensitive in inhibited N_2O_4 (ref. C-18).

Nitrogen tetroxide manufacture.- The purity of the nitrogen tetroxide and the types of impurities to expect are dependent upon the manufacturing method used. At the present, there are three methods of manufacture. The preparation of N_2O_4 by oxidation of nitrosyl chloride is cheap but it yields gaseous chlorine as a byproduct. A second method, the decomposition of metal nitrites, furnishes a pure product, but it is more expensive. The usual method is to produce ammonia by the synthetic ammonia process and then oxidize it with air over platinum catalyst (ref. C-19). The method is straightforward and produces no troublesome contaminants.

Impurities of nitrogen tetroxide.- When N_2O_4 is purchased from several sources, chlorine, nitrosyl chloride, water, nitric acid, and particulate matter will be the major impurities. Nitric acid results from the reaction of water and the equilibrium mixture $N_2O_4 \rightleftarrows NO_2$ (ref. C-20). The overall reaction proceeds as follows.

$$3N_2O_4 + 2H_2O \longrightarrow 4HNO_3 + 2NO$$

As a result, the elimination of water to 0.1 percent or less is desirable to prevent nitric acid formation with subsequent attack on the plumbing. It is stated generally that there are no reactions between N_2O_4 and components of the air. The statement is generally true. However, N_2O_4 will react with any reducing agent in the air to which it has been exposed. Carbon monoxide (CO) generally is present in air in populated areas. The reaction between CO and N_2O_4 will produce carbon dioxide.

Because of the acidic nature of the reaction products of N_2O_4, particulate contamination is a problem in long-term N_2O_4 service containers. Reports of valve malfunction in N_2O_4 systems have been received that indicate blockage by solid tank oxidation products.

Specifications for nitrogen tetroxide.- The procurement specification for nitrogen tetroxide is listed in table C-IX.

Conclusions.- Nitrogen tetroxide is a powerful oxidizer that is hypergolic with some organic compounds. By itself, it is not flammable. Nitrogen tetroxide is capable of a second type of reaction; namely, nitration with organic materials. When the reaction can occur, substances are produced that are extremely shock-, heat-, or electrically-sensitive. The materials of construction for the N_2O_4 tank are chosen to preclude the nitration reaction.

Water and particulate matter offer the greatest possibility for adverse effects in the system. The particulate matter only becomes a problem on long-term storage in steel containers. Further test work is required to determine the compatibility effects of inhibited N_2O_4 on titanium 6Al-4V underloadings.

Hydrazine-Unsymmetrical Dimethylhydrazine — Aerozine-50

Characteristics, chemical reactivity, and incompatibilities.- Aerozine-50 is a 51:47 percent (nominally 50:50) mixture of hydrazine and unsymmetrical dimethylhydrazine (UDMH). The two are miscible in all proportions but, if mixing is not thorough, layering will take place. If the mixture freezes, the UDMH and hydrazine will separate into two layers that will not blend again without a mixing operation.

The two components have the following vapor pressures: hydrazine, 0.31 psia at 80° F and UDMH, 3.1 psia at 80° F. The order-of-magnitude-higher vapor pressure of the larger molecular weight substance can be explained on the basis of hydrogen bonding. The hydrazine molecules are more strongly held to one another by the greater availability of hydrogen atoms to form hydrogen bonds with the unshared electron pair on each of the nitrogen atoms. Methyl substitution decreases the hydrogen bonding capability of the UDMH in comparison with hydrazine.

As a result of the relatively high vapor pressure, UDMH will form explosive mixtures at 7° F and hydrazine will do likewise at 104° F. The mixture is unstable in the presence of some metals and metal oxides. In a series of stability tests, Aerozine-50 and hydrazine ignited in single drop tests in powdered Fe_2O_3 at 120° to 125° F, and in multiple drops on rusty iron at 235° to 245° F (ref. C-19). The Bureau of Mines, in a series of tests with hydrazine, found that ignition in air occurred approximately at room temperature (ref. C-21).

Hydrazine vapor can be exploded by a spark or flame if it is in the flammable limits, which at 212° F, are the following: lower limit, 4.7; upper limit, 100 (percent by volume). Thus, the vapor can be exploded by a spark over a wide concentration range. For UDMH, the flammability limits at 77° F are the following: lower limit, 2.3; upper limit, 80 (percent by volume).

Aerozine-50 is hygroscopic and absorbs water rapidly from the air. Slight wetting of hydrazine appears to decrease the sensitivity of the material decomposition; but unfortunately, the water degrades propellant performance.

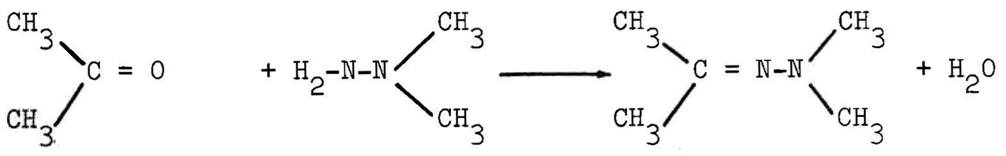
Both components of Aerozine-50 are powerful reducing agents, strong bases, and hygroscopic. As a result, Aerozine-50 absorbs water rapidly from the air, reacts with oxidizers in air (such as oxygen), and reacts with acidic gases such as NO_2, CO_2, and HCl. Inert gas blanketing is required to protect Aerozine-50 from reactive constitutents in the atmosphere. Nitrogen is inert in this application and is an excellent blanketing gas.

Hydrazine exhibits more material incompatibility than UDMH. As a result, the compatibilities must be the guide for material selection. Materials are listed in table C-X. Titanium is not listed and is an exception, as the suitability of titanium has been established by tests.

Aerozine manufacture.- Both components of Aerozine generally are made by the Raschig or modified Raschig process. Either ammonia or urea is reacted with hypochlorite; the resulting chloramine is then reacted with ammonia to produce hydrazine or with dimethyllamine to form UDMH. There are other methods of production, but these are the most common. The products will carry the byproduct impurities characteristic of the processes for both components.

Impurities in Aerozine-50.- Very little work has been done on the chemical analysis of Aerozine-50. Generally, the analysis is carried out on the individual components and then the components are blended carefully. The usual contaminants found in hydrazine are listed in table C-XI, with a typical analysis (ref. C-22). In addition to the reactivities noted previously, UDMH readily undergoes autoxidation (ref. C-23). Major products are methylene-1, 1-dimethylhydrazine (formaldehyde dimethylhydrazine), nitrogen, and water. Minor products are ammonia, dimethylamine, dimethylnitrosamine, diazomethane, nitrous oxide, methane, carbon dioxide, and formaldehyde. The reaction is catalyzed by metals and metal salts, accelerated by ultraviolet light, and inhibited by 1,3-butadiene. Copper, molybdeum and iron oxide catalyze hydrazine decomposition at room temperatures.

The components of Aerozine-50 can react with several types of materials to form impurities in solution. When Aerozine-50 is brought in contact with CO_2, products form, but they are not solids as are the products that form when CO_2 comes in contact with 100 percent UDMH. Thus, CO_2 is to be considered a source of chemical contamination but not of particulate contamination in Aerozine-50. Both components will react readily with carbonyl compounds (ketones and aldehydes) to form azomethine type of materials.



Acetone

UDMH

As a result, all common solvents such as methylethyl ketone and acetone should be excluded from use on the Aerozine-50 system. A qualitative observation (ref. C-20) indicates that metal surfaces cleaned with halogen solvents such as trichloroethylene are reactive to Aerozine-50.

Specification for Aerozine-50.- The requirements for Aerozine-50 are listed in table C-XII. The specification is for procurement.

Conclusions.- The UDMH and hydrazine components of Aerozine-50 are very reactive and must be isolated in unreactive vessels under inert gas blankets for safe storage. The components will react in the following ways.

1. Reduction of oxidizing agents
2. Neutralization of acids
3. Dessication of gases
4. Reaction to form azomethines of the hydrazone type

Most of the impurities found present in Aerozine-50 are products of hydrazine reactivity. Metal impurities listed above can cause catalytic decomposition with pressure buildup, and rust can cause oxidative decomposition with the liberation of heat.

Helium

Characteristics, chemical reactivity, and incompatibilities.- Helium is colorless, odorless, and tasteless. It is inert and compatible with all materials of construction. It is a monatomic compound with completely filled electron orbitals. As a result of the small molecular size and lack of reactivity, it is difficult to contain.

Helium preparation (separation from natural gas).- The only helium plants now in operation are run by the Bureau of Mines. The helium is produced by cryogenic distillation to 99.995 percent purity from natural gas. The few impurities are characteristic of the source and separation process.

Impurities in helium.- The usual impurities are listed below in order of decreasing amounts (ref. C-24).

1. Nitrogen
2. Hydrocarbons
3. Water
4. Oxygen
5. Argon

6. Carbon dioxide

7. Carbon monoxide

The purpose of helium on board the spacecraft is as pressurant for fuel systems. While the presence of hydrocarbons in helium is not dangerous, the hydrocarbons can be carried into the oxidizer tanks during pressurization. Care must be taken that hydrocarbon lubricants used for equipment hookup also be excluded from the system.

From a practical standpoint, particulate and aerosol contaminants in helium pose more of a problem than impurities. The gas generally is delivered with purity exceeding 99.99 percent. The largest percentage of impurities consist of nitrogen and argon. These are inert and will cause no trouble. Particulate contamination is capable of plugging filters and causing improper valve action.

Specifications.- The requirements for helium are listed in table C-XIII. Procurement shall be to specification MSFC-SPEC-364B.

Conclusions.- Helium is used to pressurize propellant tanks. The important requirements for helium are that it contain an insignificant amount of compounds capable of reacting with either fuels or oxidizers and that it contain insignificant amounts of particulate.

The only impurities of consequence are hydrogen, oxygen, and hydrocarbons. Each is stringently controlled, and no problem is anticipated when the helium is sampled properly.

In a cryogenic helium tank, every impurity present will be in solid particulate form. All substances with the exception of hydrogen have larger specific gravities than helium. In a quiescent tank, segregation can occur, and the impurities in any given sample withdrawn from the container will depend upon the level from which the sample was taken.

Agitation should be employed wherever possible before sampling, and the analysis should encompass aliquots from top, middle, and bottom portions of the sample.

PHYSICAL CHEMISTRY SURVEY

Descriptive data on the high-pressure systems and the information obvious from the Apollo 13 accident required a physical chemistry survey of the several tank systems. This survey indicated the following results.

Polytetrafluoroethylene Reactivity

Polytetrafluoroethylene when heated decomposes (unzippers) into the monomer (C_2F_4), elemental fluorine (F_2), fluoro-methane (CF_4), and other fragments (ref. C-25). If oxygen is present, the monomer oxidizes to COF_2 (ref. C-26). If metals in suitable physical state for reaction are present, the metal is converted to its fluoride (and oxide if oxygen is available) (ref. C-27). If ceramics, such as silicates and glass, are present, reaction to silicon fluoride and metal fluorides occurs (ref. C-27). Oxygen, fluorine, and hydrogen all react with polytetrafluoroethylene at approximately 650° C (1202° F) for virgin unfilled polymer and at approximately 430° C (806° F) for filled polymer, dependent on fillers used. The basic reactions are as follows.

$(-CF_2-)_n \longrightarrow C_2F_4 + (F_2 + CF_4 + C)$ Unzippering

$(-CF_2-)_n + O_2 \longrightarrow COF_2$ Oxidation by oxygen

$(-CF_2-)_n + H_2 \longrightarrow HF + C$ Hydrogenation

$(-CF_2-)_n + F_2 \longrightarrow CF_4$ Incipient combustion from pyrolysis

$(-CF_2-)_n + OF_2 \longrightarrow CF_4 + O_2$ From sparks and arcing

$(-CF_2-)_n + Al \longrightarrow AlF_3 + C_2F_4 + CF_4$

Electrostatic Charging of Surfaces in High-Pressure Fluid Systems

The question of initiation of chemical breakdown of materials in high-pressure oxygen atmospheres caused by surface charging has been raised by Dr. George Yeh, Villanova University (April 22, 1970).

The problem of surface charging remains. The charging of a surface caused by a flow of fluid over it depends on the velocity of the fluid, the electrical resistance of the fluid, and the presence of ions in a diffuse double layer on the surface.

A double layer should not form on pure PTFE. It does not show contact electrification (ref. C-28). Even a clean (oxide-covered) metal surface should not form a diffuse double layer, because there are no ions in pure oxygen. Therefore, any charging must be caused by impurity ions either from the solid surface or from the oxygen. Adsorption of these ions can form a double layer, the outer layer of which can be swept away by the motion of the fluid.

An additional mechanism of charging would be caused by the presence of particles in the fluid that would impinge on the surface and exchange charge. This should not happen on pure PTFE unless mechanical damage occurs, but it is possible on metal surfaces.

Water is one of the likely contaminants, in that it is ubiquitous, could form a double layer, and could form ice particles in cryogenic systems. There are two possible effects caused by a charge on the surface. One is to produce an electric discharge in the fluid and the other is to activate the molecules and reduce the reaction energy. Because the electric field needed to initiate discharge in gases is approximately 10^4-10^5 volts/cm and because activation of molecules by high field alone takes more than 10^6 volts/cm, as shown by field ion microscopy, the discharge mechanism would occur first.

Harper (ref. C-28) states that surface-charge densities of 1 to 10 esu/cm^2 are possible by contact and frictional electrification. This leads to fields of as much as 3×10^4 volts/cm. This is enough to cause at least local electrical breakdown. The ions produced can attack the solid and initiate combustion. In oxygen, this also could produce ozone which could react elsewhere in the system.

In the case of metal surfaces, the potential over the surface remains constant (unless covered by an insulating oxide). This would cause charge to flow away from regions of high fluid flow but also to flow to asperities where higher local fields could result.

The question, then, is why this does not happen often, because it is essentially impossible to keep the systems pure enough to prevent any contamination of the surfaces. The answer must be that the kind of contaminants necessary to produce a diffuse ionic double layer or to produce proper particles is not present, or that the flow velocity does not become high enough to cause charging of the surface. The latter seems more likely, especially if any region of high flow rate over a metal surface would be connected electrically to large areas of metal where the flow rate is low. The negative and positive charge carriers would tend to combine over the whole surface and thus reduce the surface charge. Isolated metal parts should certainly be avoided where fast flow is occurring.

Polytetrafluoroethylene valve seats are known to decompose by flowing oxygen contaminated with Lubriseal and garnet (ref. C-29). In this case, both the mechanical damage caused by the garnet particles and the lower ignition temperature of the Lubriseal may have been necessary.

For electrostatic charging of surfaces in a high-pressure fluid system to present an ignition or explosion hazard, there must exist an explosive mixture, a charge generator, and a sufficient spark intensity. If the system (PTFE:oxygen), is considered to be a potentially flammable system, then a charge generator would require a fluid flow greater than 1 meter per second (ref. C-30) and a fluid conductivity of 10^{-12} $\text{ohm}^{-1}\text{cm}^{-1}$. For conductivities much less than this, there are insufficient ions present to build up a charge; and, for flows greater than this, the conductivity is too high. The presence of a second phase, however, (particularly water as ice crystals) can be dangerous from standpoint of inducing electrostatic effects. A spark intensity of more than 2×10^{-4} joules generally is necessary to initiate an explosion (ref. C-30). If flow rates can attain as much as 1 meter per second and if the conductivity of the fluid is much less than 10^{-12} $\text{ohm}^{-1}\text{cm}^{-1}$ or if ice crystals may be present in the fluid mass, then experimental studies should be carried out to assess the chance of discharge.

Polytetrafluorothylene Degradation

Polytetrafluoroethylene polymer, $(\text{-CF}_2\text{-})_n$, is a granular polymer containing 1- to 3-micron-size granules with discontinuities between them. Electron microscope studies (ref. C-31) reveal that the polymer PTFE consists of spiral helices arranged in lamellar construction as folded-over chains. Fillers and coloring agents, as well as impurities (such as OH and COOH fragments), remaining from polymerization are concentrated between the lamellae. High temperatures on the polymer (greater than 500° C (932° F)) or pressure-induced shock stresses cause degradation, as evidenced by growth of holes and void places in the polymeric structure. Regions surrounding these voids become crystalline and provide focal points for combustion activity. Polytetrafluoroethylene is known to disappear in high-pressure-oxygen-gas systems because of the action of oxygen gas flow under pressure and heating. The National Bureau of Standards (ref. C-32) made disks, placed these in an oxygen bomb, and admitted gas to various pressures from 1620 to 2537 psig. Samples of PTFE that reacted did so starting at approximately 733° C, and it was found that the PTFE simply had disappeared completely. The following proportion of samples run reacted as follows: 1 percent of PTFE samples reacted at 1620 to 1790 psig; 2.7 percent of PTFE samples reacted at 1620 to 2537 psig.

The following substances commonly are used to fill PTFE and to color code parts.

Color	Material used
Blue	Cobalt, chromium, aluminum oxides
Red	Cadmium and selenium sulfides
Black	Manganese, copper, iron, and chromium oxides
Brown	Iron and zinc oxides
Violet	Cobalt and silicon oxides

Filled and colored materials should not be used in PTFE for high-pressure oxygen gas systems, or in wires carrying electricity in such systems. Rocketdyne reports that PTFE in high-pressure oxygen reacts starting at 430° C (806° F) over the pressure range from 2000 to 7500 psig.

Nitrogen tetroxide, N_2O_4, does not react with PTFE, and use of PTFE with wet (less than 0.1 percent water) or dry N_2O_4 is reported to be safe (ref. C-33). Therefore, polytetrafluoroethylene is completely compatible with N_2O_4, and is the most unreactive polymer with N_2O_4 known. The foregoing reports apply, however, only to virgin PTFE in dry machined or extruded form, free of foreign material and structural damage. Nitrogen tetroxide is so unreactive chemically with PTFE because N_2O_4 cannot be reduced to lower oxides of nitrogen (i.e., to N_2O_3) as long as any N_2O_4 is present to oxidize the trioxide back to the tetroxide. However, caution should be exercised to maintain PTFE free of foreign materials. Coatings of PTFE fabricated from powders particularly are susceptible to contamination in the micron-particle size. Use of chlorinated solvents on PTFE coatings should be forbidden because the chlorine cannot be removed from PTFE surfaces by conventional means and the polymer thus treated and used in oxidizers and liquid fuels can be hazardous (ref. C-33).

Safe usage of Teflon involves preventing high temperature levels (greater than 500° (932° F) for unfilled virgin Teflon and above 430° C (806° F) for filled Teflon) from occurring within the polymeric structure between the lamellae. This means prevention of excessive heating on the outside surfaces of the polymer and elimination of mechanisms for sparking or arcing or high-pressure induced shocking. Because fillers and coloring agents used in making Teflon components usually are semiconductors of electricity, avoidance of arcing situations is particularly important in preserving the integrity of Teflon parts. Rapidly shocking the Teflon component, such as happens on a "chattering" high-pressure gas valve, is to be avoided, because rapid cycles of adiabatic compression build up heat within the polymer.

Extent of polymer degradation upon exposure (1) to high-pressure shock treatment, (2) to oxidation, or (3) to hydrogenation can be followed by employing electron-microscope techniques (ref. C-31). Degradation induced by fillers or coloring agents, as well as by aging, similarly can be delineated using the proper electron-microscope techniques. Such degradation would be indicated by enlarged pore spaces. Correlation of the size and numbers of voids in the Teflon structure with known histories of the specimens, compared to virgin polymer samples, would provide insight to incipient reactivity.

It is concluded that no hazard is expected in using PTFE polymer in high-pressure oxygen gas systems provided the following maintain.

1. Unpigmented virgin Teflon is used wherever physical conditions permit.

2. Temperatures are not permitted to rise above 430° C (806° F).

3. Electric sparks or arcing at polymer sites cannot occur.

4. Halocarbon cleansing agents are removed completely.

CATALYSIS AND CHEMICAL REACTIVITY

The possibilities of catalytic acceleration of chemical reactions in the spacecraft pressurized containers have been reviewed. The following have been identified as reactions where significant catalytic action may occur.

Reactive Degradation of PTFE

It has been pointed out previously in this report how the reactivity of PTFE varies markedly. Polytetrafluoroethylene component parts, as received, vary in the amounts of fillers, fibers, residual polymerization catalysts, dyes, decomposition products, contaminants, crystallinity, and porosity (refs. C-7 and C-34). Teflon-impregnated fiberglass may be catalysed and made more reactive because of the dispersent used in applying it (ref. C-35).

These variables can all act as catalysts and thus affect combustion of PTFE. Metals that come in intimate contact as in valve seats may also act as catalysts.

The effect is not limited simply to oxygen, because fluorocarbon polymers (PTFE) can react with other fluids, such as impure nitrogen tetroxide, or with hydrogen, hydrazine, and its derivitives. The reaction of a fluorocarbon lubricant with hydrazine in the presence of stainless steel is known (ref. C-2). Systematic study of PTFE polymer degradation in spacecraft service appears needful.

Decomposition of Hydrazine and Derivitives

This catalytic reaction is well known (refs. C-2, C-16, C-36, and C-37). Many metals, (molybdenum being perhaps the most sensitive) and certain nonmetals are mentioned. Catalysts tend to fall into two categories: (1) those multivalent metals that influence oxidation-reduction and (2) the acid-base catalysts that influence cracking and rearrangement reactions. Both types seem effective for decomposition of hydrazine.

Heterogeneous catalysts are exceedingly sensitive to surface treatments. The optimum treatment to desensitize metal surfaces towards hydrazine is a mildly alkaline treatment (hydrazine itself in aqueous solution) (ref. C-37).

Reaction Between Fluids and Impurities

The oxidants, O_2 and N_2O_4, can react with reductants, such as organic molecules. The reductants H_2 and N_2H_4 can react with oxidants, such as O_2 and CO_2.

Conclusions

Highest attention to standards of purity in the fluids and fluorocarbons is important. Attention to surface treatment of metals that should leave them smooth and passive also is important. Passivation is largely empirical at present. It would seem that rigorous application of present knowledge to purification and surface preparation would increase safety, and research into reaction mechanisms would be beneficial and desirable for long-range improvements.

POLYMER INVOLVEMENT

Supercritical Hydrogen Tank

An examination was made of the materials used in construction of the supercritical hydrogen tank. A list of materials was obtained for that purpose from North American Rockwell.* The complete list of materials as per NR ME282-0047 Tank, H_2 Cryogenic Storage Subsystem, is not reproduced here. However, materials that can, under certain circumstances, be incompatible or combustible are listed in table C-XIV. The combustible materials present in the assembly are listed and the material location in the storage system is given. Most of the materials are polymeric in nature, but there are a few, such as Drilube, that are not. It is emphasized that "combustible" as used here means materials that will react exothermically (liberation of heat) with an oxidizer such as oxygen. They are not materials that will necessarily react exothermically with hydrogen to give flames or an explosion.

A material that will react with hydrogen to give an exothermic reaction must function as an oxidizer. Materials that are capable of supporting combustion by acting as the fuel are listed in the table. One of the materials (PTFE) can act as the source of an oxidizer, fluorine (F_2) (ref. C-25), under certain circumstances. Polytetrafluoroethylene will react oxidatively and in an exothermic manner with hydrogen (ref. C-26). The product of the reaction is hydrofluoric acid, HF.

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*Data from NR were obtained through the efforts of General Electric, Houston.

Supercritical Oxygen Tank

An examination was made of materials used in construction of the supercritical oxygen tank in the service module electrical power system. A list of materials was obtained for that purpose from North American Rockwell.* The polymeric materials found in the supercritical tank assembly per ME282-0046 are listed in table C-XV.

Only polymer involvements are discussed in this section. The majority of the polymeric parts used in the tank are PTFE. The PTFE purity and composition varies over wide ranges. Bleached and clear, clean virgin polymer is used in some parts; and, although it will combust in oxygen, it has passed LO_2 impact sensitivity tests when free of surface contamination such as fingerprints. Other parts made of PTFE are filled and dyed and must be considered LO_2-impact sensitive; therefore, they are high risk items and should not be used.**

Minimal amounts of other organic materials possibly could be present, such as flux residue remaining from motor wire hookup. If present, they should be considered contaminants and not materials present. Rosin flux reacts readily with oxygen and could be a possible ignition source.

In addition to polymers and organic materials inside the cryogenic tank, there are several materials between the cryogenic tank and the outer-shell tank that are capable of combustion. For example, the Dexiglas-aluminum insulation is LO_2 sensitive in the as-received condition. When loose particles are removed, it becomes relatively insensitive (ref. C-38). Owens-Corning E glass with 3 percent M700 binder also is used in the between-tank area. The binder is unsaturated, uncured polyester resin, which is combustible in oxygen. Thus, rupture of the inner tank will expose reactive polymers at ambient temperature (approximately 70° F) to oxygen.

It should be pointed out that there are several inorganic materials used inside the tank that can react with liquid oxygen. Drilube 822 is used as a thread lubricant for the quantity gage, and excess material is supposed to be removed. The material is LO_2-impact sensitive and any unremoved excess could react. Aluminum is LO_2 compatible unless it is

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*Data from NR were obtained through the efforts of General Electric, Houston.

**See the section entitled "Physical Chemistry Survey", in this report.

abraded and fresh, clean surfaces are exposed to LO_2. It is then reactive. Tin-lead solder (60:40) also is used; this particular type of solder has failed Army Ballistics Missile Agency (ABMA) LO_2 impact sensitivity tests (ref. C-7).

Nitrogen Tetroxide Tank

An examination was made of materials used in the nitrogen tetroxide tanks. The oxidizer is used on the command module, service module, and lunar module. A list of materials for that purpose was obtained from North American Rockwell.* The polymeric materials found in the nitrogen tetroxide tanks per ME 282-0004 and ME282-0006 are listed in tables C-XVI and C-VII. A detailed list of materials for the lunar module tanks is not available at this time. All identified polymeric materials are Teflon or Rulon-A in the lunar module tanks (ref. C-39).

Polytetrafluoroethylene is considered compatible with nitrogen tetroxide. However, PTFE has a tendency to swell in liquid nitrogen tetroxide (ref. C-17). The tendency is indicative of a physical absorption process, and the question arises whether long-term exposure to N_2O_4 will make PTFE impact-sensitive to N_2O_4. For comparison purposes, Mylar film becomes more sensitive to ABMA LO_2 impact after immersion in LO_2 for 8 hours rather than the usual short time used in the standard test. It is not known at the present time whether the same is true of PTFE.

When a comparison is made of the compatibility of materials with N_2O_4, it is immediately evident that several factors control the effect observed. For example, water exerts a significant effect on most materials. Aluminum is compatible for use in dry N_2O_4 (H_2O content 0.2 to 1.0 percent); but, with larger percentages of water (3.2 percent), aluminum cannot be used. The excess water produces significant amounts of HNO_3, and aluminum loses compatibility because of corrosion.

Comparing PTFE in dry N_2O_4 in static and flowing condition, it is rated class I and is compatible under static conditions, but it is downrated to class IV in flowing N_2O_4 (ref. C-16).

The type of nitrogen tetroxide used plays a decisive role in compatibility. Titanium is incompatible in "red" nitrogen tetroxide

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*Data from NR were obtained through the efforts of General Electric, Houston.

(uninhibited) and cannot be used. However, it is rated compatible in "green" nitrogen tetroxide (inhibited with nitric oxide, NO), which is the type of N_2O_4 used on the spacecraft.

Conditions of test produce varying effects. For example, titanium 6Al 4V is reported to be impact insensitive (ref. C-16) in N_2O_4, but it is reported (ref. C-18) to be very sensitive to vibration in N_2O_4. Most data available on reactions in N_2O_4 are in the presence of an impact energy source and do not take into consideration other energy sources that are capable of producing more harmful results.

Material compatibility in nitrogen tetroxide is dependent on diluents and additives in the N_2O_4 and on the means of energy deposition in the test material. Each material must be tested under conditions approaching as closely as possible those conditions that will exist in use.

Monomethylhydrazine and Aerozine-50

An examination was made of materials used in construction of the monomethylhydrazine and Aerozine-50 tanks. A list of materials was obtained for that purpose from North American Rockwell and Grumman Aerospace Corporation. Data were obtained through the efforts of The Boeing Company and General Electric Company, Houston.

Monomethylhydrazine.- The monomethylhydrazine tank contains only tetrafluoroethylene polymer (Teflon, TFE) and fluoroethylene polymer (Teflon, FEP). They are used as gaskets, bladders, spacers, bushings, and pads. Teflon is the only nonmetallic material present, and it is compatible with monomethylhydrazine. It has been reported that Teflon possibly shows some reactivity (decomposition) with MMH at 160° F (ref. C-2).

There is no oxidizer present, and no electrical wiring is present. The tank operates considerably below any possible Teflon-MMH decomposition temperature, and no problems are foreseen.

Aerozine-50.- The polymers present in the Aerozine-50 tank are Teflon TFE and FEP, epoxy fiber glass, and epoxy polymer used at a Kovar glass seal. All are on the fuel-probe assembly. Teflon TFE is rated compatible and satisfactory for repeated short time use to 160° F. The FEP is not as stable, but can be used at approximately 60° F. However, the epoxy resins generally are unsatisfactory above 60° F in Aerozine-50. A potential compatibility problem exists with the epoxy resin, and testing is required to determine whether epoxy resin should be used in this application.

Fuel and Oxidizer Tanks — Service Propulsion System

An examination of the sump-tank fuel and oxidizer tanks showed no reactive polymers in use directly in the tanks. Both the fuel and oxidizer tanks use butyl and Teflon O-rings in connections. The nitrogen tetroxide is capable of oxidizing the butyl rubber, and the Aerozine-50 will dissolve the butyl rubber. In approximately 1 hour, some reaction is evident. As a result, the butyl rubber must be classed as imcompatible and should not be used in this application.

Environmental Control System Oxygen Tank — 900 psi Pressure

The cabin repressurization assembly contains three polymeric and organic materials. They are a butyl rubber O-ring, Teflon TFE retainer, and Krytex 240 AC lubricating grease. The surge tank assembly uses a butyl rubber O-ring as a seal.

It is understood that the nonmetallics passed the AiResearch surge test, but organic materials should be avoided with both liquid and gaseous oxygen because of the possibilities of explosions. The use of Teflon TFE as a retainer material appears to be acceptable, but the butyl O-ring appears questionable.

Gaseous Nitrogen Pressure Vessels

Gaseous nitrogen pressure vessels for docking ordnance and recovery systems and for the electrical power system (fuel cell blanket and purge) were examined. The only polymers used are butyl rubber in a bladder and an adhesive in the nitrogen system of the electrical power system. Both are inert to nitrogen in the temperature and pressure ranges used. No incompatibilities were found.

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TABLE C-I.- LIQUID HYDROGEN INCOMPATIBLE MATERIALS

(CLASS IV)

Metals	Nonmetals
Aluminum 40-E	Natural rubber
Magnesium	Neoprene rubber
Lead	Cork
Zinc	Wood
Iron	Polyvinyl chloride
High carbon steel	Saran
	Polyvinyl alcohol

TABLE C-II.- LIQUID HYDROGEN

[Procured to specification MSFC-SPEC-356A]

Characteristics	Requirement as delivered to spacecraft interface
Purity, percent by volume, minimum	99.995
Gaseous impurities, ppm by volume, maximum	50
Selected impurities, ppm by volume, maximum[a]	9.0
Nitrogen, ppm by volume, maximum	2.0
Methane, ppm by volume, maximum	2.0
Specific impurities[b]	
Oxygen and argon, ppm by volume, maximum	1.0
Helium, ppm by volume, maximum	39.0
Carbon monoxide, ppm by volume, maximum	1.0
Carbon dioxide	- -

[a] Restricted sample analysis.

[b] Sample subjected to complete analysis.

TABLE C-III.- OXYGEN CONTAMINANT CONCENTRATION EFFECTS

Composition	Impurities, concentration, ppm						
	CH_4	CH=CH	CH_2=CH_2	CH_3=CH_3	C_4	NH_3	CO_2
Original composition	15	Trace	0	0	0	0.6	Trace
After 25 refills	62	0.05	Trace	Trace	Trace	12	5

TABLE C-IV.- PROCUREMENT SPECIFICATION FOR LIQUID OXYGEN

[Specification MSFC-SPEC-356A]

Characteristic	Requirement as delivered to spacecraft interface — grade A for fuel cells
Purity, percent by volume	99.995
Total hydrocarbons, ppm as methane	14
Methane, ppm	10
Ethane, ppm	2
Propane and higher hydrocarbons, ppm as propane	1
Alkyne hydrocarbons, ppm as acetylene	0.05
Moisture, ppm	3.0
Nitrous oxide, ppm	1.0
Halogenated hydrocarbons, ppm	1.0
Odor	None
CO and CO_2, total ppm	1

TABLE C-V.- CHARACTERISTICS OF HYDROCARBON IMPURITIES FOUND IN LIQUID OXYGEN

Impurity	Melting point, °F	Boiling point, °F	Critical temperature, °F	Critical pressure, psi	Critical density
Methane	-296	-258	-116	673	0.162
Ethane	-278	-127	90	709	.21
Propane	-306	-44	206	617	- -
Acetylene	-115.6 (10 psig)	-118 (sublimes)	97	907	.231
Halogenated hydrocarbons (methyl chloride)	-144	-11	289	969	.37

TABLE C-VI.- SPECIFICATION FOR GASEOUS AND LIQUID NITROGEN

[Procured to specification MSFC-SPEC-356A]

Characteristic	Requirement as delivered to spacecraft interface
Purity, percent by volume, minimum . . .	99.983
Total impurities, ppm by volume, maximum	170
Oxygen, ppm by volume, maximum	150
Total hydrocarbon content (as methane), ppm by total volume, maximum[a]	5
Moisture content, ppm by volume, maximum	11.5

[a] Specification MSFC-PROC-404 shall be used to test total hydrocarbons, moisture, and particulate of gases as delivered to spacecraft.

TABLE C-VII.- SPECIFICATION FOR MONOMETHYLHYDRAZINE

[Procured to specification MIL-P-27404]

Characteristic	Requirement as delivered to spacecraft interface
MMH assay, percent by weight, minimum	98.0
Density at 77° F (25° C), g/ml	0.872 + 0.0004
Transmittancy	(a)
Water plus soluble impurities, percent by weight, maximum . . .	2.0
Total filtrable solids, mg/liter maximum	1

[a] Engineering evaluation only.

TABLE C-VIII.- NITROGEN TETROXIDE LIMITED SERVICE AND INCOMPATIBLE MATERIALS LIST

Metals	Polymeric and Organic Materials
Incompatible	
2024 aluminum	Micarta
K-Monel	Mylar
Brass	Buna N
Bronze	Hypalon
Silver	Oxylube
Copper	
Titanium	
Zinc	
Cadmium	
Nickel	
Limited Service	
Mild steels	LS-53 fluorosilicone rubber
	Polyethylene
	Koraseal
	Saran

TABLE C-IX.- SPECIFICATION FOR NITROGEN TETROXIDE

[Procured to specification MIL-P-27404]

Characteristic	Requirement as delivered to the spacecraft interface
Nitrogen tetroxide assay (N_2O_4), percent by weight, minimum	98.50
Nitric oxide (NO) assay, percent by weight, minimum to maximum[a]	0.60
Water, equivalent, percent by weight, maximum	0.20
Chloride as nitrosyl chloride (NOCl), percent by weight maximum	0.08
Density, lb/gal (g/cc) at 68° F[b]	12.08 (1.205)
Total filterable solids (TFS), mg/l maximum	10

[a] Nitric oxide content is controlled to 0.7 to 1.0 percent when delivered to the GSE. Nitric oxide content can be increased by the addition of MON-10. (MON — mixed oxides of nitrogen (N_2O_4 + NO)).

[b] Density to be determined to a precision of ±0.003 g/mc.

TABLE C-X.- MATERIALS FOR HYDRAZINE

Metals		Nonmetals
Allowable		
Stainless steel - 303, 304, 316, 321, 347 Nickel Aluminum, 25 and 35		Teflon Polyethylene, high density Kel-F, unplasticized
Prohibited		
Hastelloys	Lead	
Monel	Copper	
Aluminum 40E	Iron	
Magnesium	Copper alloys	
Zinc	S.S.W. more than 0.5 percent molybdenum	

TABLE C-XI.- CONTAMINANTS FOUND IN HYDRAZINE

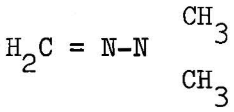
Impurity	Concentration in UDMH, percent by weight	Concentration in hydrazine, percent by weight
N_2	0.04	0.09
NH_3	.02	.15
H_2O	.33	.68
Dimethlylamine	--	.03
 $H_2C = N\text{-}N\begin{matrix}CH_3\\CH_3\end{matrix}$	3.2	--

TABLE C-XII.- SPECIFICATION FOR PROPELLANT, 50 PERCENT HYDRAZINE/50 PERCENT UNSYMMETRICAL DIMETHYLHYDRAZINE

[Procurement to specification MIL-P-27402A]

Characteristics	Requirement as delivered to the spacecraft interface
Aerozine-50 N_2H_4, percent	51.0 ± 0.8
UDMH plus other amines, percent, minimum	47.0
Water plus other soluble impurities, percent, maximum	1.8
N_2H_4-UDMH plus other amines, percent, minimum	98.2
Conductivity, mhos/cm at 40° F (minimum)	10
Density, gm/nil-required precision	±0.003
Transmittancy	([a])
TFS, mg/maximum	10

[a] MIL-P-27404 will be used for engineering evaluation only.

TABLE C-XIII.- SPECIFICATION FOR HELIUM

Characteristics	Requirement as delivered to spacecraft interface
Purity, percent by volume, minimum	99.990
Total impurities, ppm	94
Hydrogen content, ppm by volume, maximum	1
Nitrogen content, ppm by volume, maximum	50
Other gases, ppm by volume, maximum[a]	19
Oxygen and argon, ppm by volume, maximum	10 (oxygen only)
Moisture content, ppm by volume, maximum[b]	9
Total hydrocarbons, ppm by volume, maximum	5 (as methane)

[a] Should hydrogen, nitrogen, moisture, total of oxygen and argon, and total hydrocarbons be at the maximum permissible values, then only 19 ppm of other gases could be permitted.

[b] Specification MSFC-PROC-404 shall be used to test total hydrocarbons, moisture, and particulate matter of gases as delivered to spacecraft. Normally, liquid helium is not filtered.

C-XIV.- COMBUSTIBLE MATERIALS IN SERVICE MODULE ELECTRICAL POWER SYSTEM CRYOGENIC HYDROGEN-TANK ASSEMBLY

[NR part ME282-0047]

Part name	Part number	Material	Location	Combustible
Insulation, H_2 tank	13532-3523	0.0005 gold-coated Kapton-type "H film"	Between tanks	Yes
Insulation strap	13532-3512	Type E glass fiber and type 700 binder	Between tanks	Yes
Insulation spider	13532-3567	0.0005 gold-coated Kapton-type "H film"	Between tanks	Yes
Washer-radiation shield	118708-1	DuPont "Vespel" SP-1 polyimide resin	Between tanks	Yes
Insulation shield	13532-3539	Type E glass fiber and type 700 binder	Between tanks	Yes
Washer, Teflon	13532-3520	Teflon rod Mil-P-19468	Between tanks	Yes
Adapter, Teflon	13532-3525	Teflon rod Mil-P-19468	In tank	Yes
Heater assembly fan motor	13532-2052	Drilube	In tank	Yes
Heater assembly fan	13532-2052-17	Teflon rod	In tank	Yes
Heater assembly fan	13532-2052-47	Teflon TFE, AWG 14	In tank	Yes
Teflon bar stock	398386	25 percent glass-fiber-filled TFE Teflon	Simmonds probe in tank	Yes
Plug inner tube	398387	25 percent glass-fiber-filled TFE Teflon	Simmonds probe in tank	Yes
Sleeve insulation - bottom	398184	25 percent glass-fiber-filled TFE Teflon	Simmonds probe in tank	Yes
Tubing, Teflon	398157	25 percent glass-fiber-filled TFE Teflon	Simmonds probe in tank	Yes
Spacer, sleeve Spacer	398173 398172	25 percent glass-fiber-filled TFE Teflon	Simmonds probe in tank	Yes
Rod, Teflon Rod, Teflon Rod, Teflon	398155 398161 398192	25 percent glass-fiber-filled TFE Teflon	Simmonds probe in tank	Yes

TABLE C-XIV.- COMBUSTIBLE MATERIALS IN SERVICE MODULE ELECTRICAL POWER SYSTEM CRYOGENIC HYDROGEN-TANK ASSEMBLY - Continued

[NR part ME282-0047]

Part name	Part number	Materials	Location	Combustible
Grommet	398218-001 -002	25 percent glass-fiber-filled TFE Teflon	Simmonds probe in tank	Yes
Solder flux	398263	Core 66 flux 44	Simmonds probe in tank	Yes
Sleeve	398283	ASTM size-D thin-wall extruded TFE Teflon	Simmonds probe in tank	Yes
Flux, rosin	398288	Rosin-base Type-A, Mil-I-14256	Simmonds probe in tank	Yes
Electrical plug	13532-4509		Outside tank	
Seal, Vacco filler	13532-4504-5	Teflon	In line (outside tank)	Yes
Wiring harness tubing	23532-2709	Teflon TFE Type E AWG 14 heat-shrinkable tubing	In tank	Yes
Wiring harness wire insulation	13532-1709	Teflon-coated wire	In tank	Yes
Wiring harness plug	13532-2709	PTS06A-19-915 (Bendix Corp.)	Outside tank	—
Wiring harness boot	13532-2709	Potting boot for receptacle - nylon	—	Yes
Wiring harness boot	13532-2709	Apiezon M	—	Yes
Wiring harness potting compound	13532-2709	RTV 108 silicone polymer	—	Yes
Probe and heater installation	13532-2801	Drilube, MMS-N306A, type 822	In tank	Yes

TABLE C-XIV.- COMBUSTIBLE MATERIALS IN SERVICE MODULE ELECTRICAL POWER SYSTEM CRYOGENIC HYDROGEN-TANK ASSEMBLY - Concluded

[NR part ME282-0047]

Part name	Part number	Material	Location	Combustible
Miscellaneous materials		Stycast, 2850 ft	—	Yes
Miscellaneous materials		Lacquer, red-MIL-L-7178 509	—	Yes
Tie, self-locking		MS17821-4-9	—	

TABLE C-XV.- POLYMERIC MATERIALS IN SERVICE MODULE ELECTRICAL POWER SYSTEM

SUPERCRITICAL OXYGEN-TANK ASSEMBLY

[NR part ME282-0046]

Part name	Material	Location	Remarks
Solder flux	Flux fed 0-0-499	In LO_2 tank	Combustible
Solder flux	Flux Mil-F-14256	In LO_2 tank	Combustible
Solder flux	(Alcoa)AMS-3412		
Lubricant	Liquinite FEP Teflon, powdered dispersion	In LO_2 tank	Combustible
Insulation	Teflon - Rulon "A"	In LO_2 tank	Combustible
Insulation	Teflon-impregnated glass cloth - "Armalon"	In LO_2 tank	Bleached — passed Unbleached — failed
Upper insulation	Teflon TFE, 25 percent glass filled	In LO_2 tank	Will decompose
	Virgin Teflon - MIL-P-19462	In LO_2 tank	Combustible
Electrical tubing	Teflon, heat shrinkable, AWG 14	In LO_2 tank	Combustible
Electrical tubing	Teflon, heat shrinkable, clean, white AWG 9	In LO_2 tank	Bleached — probably safe, but test
Electrical tubing	Teflon, heat shrinkable, red	In LO_2 tank	Filled or colored Teflon is generally LO_2 sensitive.
Lacquer	Duco 9P-16	—	Combustible
Magnet wire	Teflon overcoated (copper on ceramic)	In LO_2 tank	Combustible

TABLE C-XV.- POLYMERIC MATERIALS IN SERVICE MODULE ELECTRICAL POWER SYSTEM

SUPERCRITICAL OXYGEN-TANK ASSEMBLY - Concluded

[NR part ME282-0046]

Part name	Material	Location	Remarks
Conductor wire	Teflon-coated silver-plated copper AWG 20	In LO_2 tank	Insulation is color coded - sensitive
Conductor wire	Teflon coated: AWG 20, 22, 24, 26	In LO_2 tank	Combustible
Conductor wire	Teflon coated MIL-W-16878: black, orange, green, yellow, red, white, blue	In LO_2 tank	Colored Teflon - generally LO_2 sensitive
Tank insulation	Aluminized Mylar	Between tanks	Mylar - Combustible and LO_2 sensitive
Tank insulation	Owens Corning E glass with M 700 binder (3 percent of 700 binder is uncured polyester resin)	Between tanks	Resin - combustible Insulation - LO_2 sensitive

TABLE C-XVI.- POLYMERIC MATERIALS IN COMMAND AND SERVICE MODULES NITROGEN TETROXIDE TANKS

[NR parts ME 282-0004 and -0006]

Part name	Part number	Materials	Location	Remarks
Vent line	8271-471127	Teflon, TFE	In tank	Combustible; heat source required; will swell
Eyelet	8271-471131	Teflon, TFE	In tank	Combustible; heat source required; will swell
Retaining gasket	8271-471140	Teflon, TFE	In tank	Combustible; heat source required; will swell
Pad	8271-471132	Teflon, TFE	In tank	Combustible; heat source required; will swell
Bladder	8271-471148	Teflon, TFE/FEP	In tank	Combustible; heat source required; will swell
Pad	8271-471246	Teflon, TFE/FEP	In tank	Combustible; heat source required; will swell
Gasket	8271-471225	Teflon, TFE	In tank	Combustible; heat source required; will swell
Spacer	8271-471236	Teflon, TFE	In tank	Combustible; heat source required; will swell
Bushing	8271-471213	Teflon, TFE	In tank	Combustible; heat source required; will swell
Gasket	462-4	Teflon, TFE	In tank	Combustible; heat source required; will swell
Gasket	8271-471045	Teflon, TFE	In tank	Combustible; heat source required; will swell

TABLE C-XVII.- POLYMERIC MATERIALS IN SERVICE PROPULSION SYSTEM NITROGEN TETROXIDE PROBE

Part name	Part number	Material	Location	Remarks
Ring support	386548	Teflon TFE MIL P-2296	Oxidizer probe	Combustible; heat source required; will swell
Washer	389679	Teflon, TFE - type 2 class "G"	Oxidizer probe	Combustible; heat source required; will swell
Bushing, split	389650	Teflon, TFE - type 2 class "G"	Oxidizer probe	Combustible; heat source required; will swell
Spacer, Ed. shield	389683	Teflon, TFE - type 2 class "G"	Oxidizer probe	Combustible; heat source required; will swell
Spacer, collar	389682	Teflon, TFE - type 2 class "G"	Oxidizer probe	Combustible; heat source required; will swell
Ring mount	389695, 389696	Teflon, FEP	Pt. sensor assembly	Combustible; heat source required; will swell
Insulated collar	389682	Teflon, FEP	Oxidizer probe	Combustible; heat source required; will swell
Half collar	389681	Teflon, FEP	Oxidizer probe	Combustible; heat source required; will swell
Scuff cap	386432	Teflon, TFE	Oxidizer probe	Combustible; heat source required; will swell
Lock pin	386941	Teflon, TFE	Oxidizer probe	Combustible; heat source required; will swell

SECTION D — THERMODYNAMICS RESTRICTIONS ON ENERGY PROCESSES IN THE APOLLO 13 CRYOGENIC OXYGEN TANK NUMBER 2

INTRODUCTION

The purpose of this report is to specify limitations on energy processes which may have occurred in the Apollo 13 cryogenic oxygen tank number 2 prior to the incident of apparent tank failure. Limitations are established on the basis of thermodynamics and the recorded pressure history. Ultimate and reasonable limitations have been established for the energy added to the oxygen. The primary conclusion of this analysis is that the electrical energy supplied to the tank, in the significant time period, is insufficient to explain the observed pressure rise; therefore, a chemical reaction must have occurred within the tank. Although the analyses provide guidance for the assessment of propagation paths for potential reactions, verification of a particular path requires experimental data at simulated conditions for each significant event in the assumed propagation.

DATA AND ASSUMPTIONS

The pressure and temperature data during the time of interest are shown in figures A-1 and A-2. The mass of oxygen in the tank was taken to be 242 pounds at time t. Additional assumptions are (1) the mass loss from the tank is that caused by a nominal usage of 1.8 lb_m/hr; (2) the mass lost is at bulk-cryogenic-fluid conditions; (3) the pressure from flight data corresponds to the actual tank pressure; (4) the bulk temperature at the time t_0 was 270° R; (5) the oxygen was uniform and homogeneous at time t_0. The work done on the tank by the fluid is included, along with a nominal heat leakage. Energy which is potentially lost to heating up the structure or components is not included. Thermodynamic properties of supercritical oxygen were obtained from Stewart (ref. D-1) and checked with the independent results of Weber (ref. D-2).

THERMODYNAMIC MODELS

Two models are proposed to represent the absolute minimum and maximum energy requirements for the pressure rise. The maximum limit is established by assuming that the energy added is distributed uniformly throughout a homogeneous (constant density) fluid. The minimum is obtained by assuming an isentropic compression of the bulk fluid by a negligible mass of infinitely hot fluid. The cumulative energy addition for these two limits are shown in figure D-3. The bulk-fluid temperatures calculated for these two limits are shown compared to the temperature data in figure D-2. It is noted that the temperature datum is a point measurement and generally is not equal to the bulk-fluid temperature. The energies that all required to reach a pressure of 1008 psi (time t_5) are (1) isentropically, 10.2 Btu, and (2) uniform heating, 139 Btu. These include approximately -1 Btu for nominal heat leakage, 1.5 Btu for work on the tank, and 3 Btu lost because of nominal usage. The accuracy of the isentropic case is very sensitive to the initial condition. If the temperature at t_0 is taken to be $270^\circ {}^{+5^\circ}_{-15^\circ}$ R, the resulting cumulative energy addition for the lower limit is $10.2\,{}^{+8.7}_{-4.6}$ Btu. Also, this small energy change associated with the lower limit case is within the accuracy of our knowledge of the thermodynamic properties of oxygen at these conditions.

DISTRIBUTION OF ENERGY

Although the limitations established for energy addition are only a fraction of the total fluid energy, the upper and lower limits are an order of magnitude apart. However, because supercritical oxygen has a very low thermal conductivity and because the tank is in a zero-gravity state, it is possible to establish much more restrictive limitations for the energy addition caused by a chemical reaction. Basically, the uniform heating limit is inconsistent with the lack of free convection which would be present in a gravitational field, and the isentropic limit is inconsistent with the source of energy being a chemical reaction.

At any given time the thermodynamic state of the fluid is constrained by the pressure, tank volume, mass in the tank and the minimum possible entropy. If the fluid is completely mixed, the entropy is highest, but the average fluid temperature is too low to support a possible chemical reaction. Consider the total fluid mass M_T to be divided into two parts. Fluid 1 (mass M_1) contains the source of energy addition, all irreversible effects and the highest entropy. Fluid 2 is at the lowest possible entropy consistent with an isentropic compression from the state at time t_0. Fluid 2 is representative of the bulk of the fluid, whereas fluid 1 is a hot bubble which is defined by an imaginary adiabatic surface. This adiabatic surface could assume any geometry and is not constrained to be like any physically observable surface.

At a given time the energy in the fluid is uniquely constrained by the distribution of mass between these two fluids. The net energy added to the total fluid as a function of the mass ratio of hot fluid 1 to the total fluid mass is shown in figure D-3. The ratio of energy added to the maximum energy addition limit as a function of the same mass ratio is shown in figure D-4. Also shown in figure D-4 is the relative mass of oxygen consumed for a complete combustion of Teflon. For mass ratios of greater than 10^{-4}, the mass of oxygen in fluid 1 always is more than an order of magnitude greater than the mass of oxygen consumed in this reaction. Therefore, it is concluded that the approximation that the hot fluid 1 has the thermodynamic characteristics of oxygen is reasonable for mass ratios of greater than 10^{-4}.

The energy distributions in a two-fluid model were considered at times t_2 and t_5. The volume of fluid V_1 relative to the total volume V_T of 4.735 ft^3 and the average temperature of fluid 1 are shown as a function of mass ratio in figures D-5 and D-6, respectively. The most significant point in these results is that the temperature of fluid 1 is very sensitive to the mass ratio. The average temperature of fluid 1 for times t_2 and t_5 as a function of the net energy added to the oxygen is shown in figure D-7. If it is assumed that the energy source is oxidizing Teflon, there are two restrictions which can be put on the peak temperature of fluid 1. The lower limit is that Teflon first must depolymerize before reacting with oxygen, and this does not occur appreciably below a Teflon temperature of 500° C (1391° R). The upper limit on temperature results from equilibrium calculations of C_2F_4 in an adiabatic closed system with a starting mol ratio, O_2/C_2F_4, of 1.0. This gives a maximum peak temperature of 4834° R. Because this temperature decreases with increasing O_2/C_2F_4 ratio, and because this ratio in fluid 1 certainly is greater than 1.0, this is the maximum flame temperature to be expected. To relate these peak temperatures to the average temperature of fluid 1, generally it is necessary to consider a particular geometry of fluid 1. To avoid this restriction, it was assumed that the temperature profile of fluid 1 was symmetric about the average temperature and between the peak and fluid 2 temperatures. Thus, the two limits for fluid 1 average temperature are 830° R and 2550° R. These two limitations imposed by a Teflon source restrict the energy input to a fairly narrow region as shown in figure D-8. Although these limits are established on the basis of Teflon combustion, they represent a factor of 3 in fluid 1 average temperature; therefore, the energy input is not very sensitive to a particular reaction selection. It is noted that the temperature measurement shown in figure D-2 would indicate that fluid 1 came in contact with the temperature sensor at time t_4.

There are several factors which can provide potential sources of error in the specification of energy addition limitations. These are potential errors in the pressure data, the initial conditions, the thermodynamic properties of oxygen, the calculated characteristics of fluid 2 and in the assumed temperature profile of fluid 1. There is a distinct possibility of at least one fan motor running in the time interval between t_0 and t_1 (ref. D-3). Considering all of these potential sources of error, it is estimated that the energy addition limitations shown in figure D-8 should have an error band of ${}^{+6}_{-0}$ Btu for all times shown. Also as noted previously, energy potentially lost to heating the structure has not been included.

MASS LOSS EFFECTS

The energy addition rates associated with the two thermodynamically limiting processes and the two energy distribution limits are shown in figure D-9. At the times t_2 and t_5, there are rapid drops in the rate of energy addition. The calculations to this point have neglected mass loss above the level of a nominal usage rate; however, a rapid change in energy addition could be explained by a mass loss. If the energy addition rates are extrapolated as shown in figure D-9, the maximum resulting mass-loss-rate requirement can be obtained from an energy balance. The maximum mass loss rates for times t_2 and t_5 are shown in figures D-10 and D-11 for the two limiting thermodynamic processes. It is noted for the isentropic energy addition case that the required flow rates are significantly less than the calculated capability of the vent valve, whereas, for the constant density case, the required flow rates are comparable to the calculated capability of the vent valve. In addition, if the gas flowing out of the tank is at a higher temperature than the bulk fluid, the mass-loss rates required to cause the pressure transients at these times would be reduced because of the higher energy content of this hot venting gas. This would require combustion occurring in the vicinity of the tank exit at time t_5. There is no known reason for the vent valve to open at time t_2.

CONCLUSIONS

Thermodynamic limitations on the net energy added to the cryogenic oxygen in the Apollo 13 number 2 tank have been established under the constraints of the measured pressures and temperatures, and tank volume, and the oxygen mass. The calculations include nominal mass usage, nomial heat leak, and the work the fluid performs on the tank. These limits are above the available electrical energy and are below the potential energy released by a combustion of all the available Teflon in the tank. Consideration of possible distributions of energy within the tank and the combustion characteristics of Teflon has led to an extremely narrow limitation on the net energy added to the oxygen. Including an estimate of potential error, the energy required to raise the oxygen pressure to a peak of 1008 psi was between 23.5 and 38.5 Btu. This does not include energy which may have been lost to heating the structure of components in the tank. The pressure drop after peak pressure is consistent with opening of the vent valve for the narrow limitations on energy addition.

GENERAL POINTS AS RESULT OF THERMODYNAMIC STUDIES

In the initial organization of this investigation it was decided that a completely independent evaluation of thermodynamic aspects of reactions in the Apollo high-pressure fluid systems would be of considerable value. Arthur D. Little, Inc., was provided with only basic guidelines and general information on the Apollo high-pressure fluid systems for this independent assessment. The results of these investigations are given in Appendixes D to G.

In general, high-pressure and zero-gravity effects were found to be of greater importance than the particular thermodynamic state of the fluid. Although all of the high-pressure fluid systems were investigated, considerably more experience and information were found for high-pressure oxygen. Basically, pure oxygen and a container are incompatible, and, in the opinion of Arthur D. Little, Inc., the hazards of pure oxygen traditionally have been underestimated by designers. There is a rather extensive history of unanticipated reactions in pure oxygen systems which fall generally in the category of thermal initiation (although there is some history of pressure surge initiations). Additional significant findings are as follows.

1. Generally, isothermal fluids do not have mechanisms for spontaneous redistribution of energy into catastrophic modes; however, nonisothermal fluids are potentially much more dangerous.

2. Spacecraft accelerations do not pose a significant hazard to the high-pressure fluid systems.

3. The ignition temperature of potential reactions generally varies as the inverse of the pressure squared.

4. The combination of aluminum and Teflon in oxygen is extremely hazardous.

5. Teflon is incompatible with pure hydrogen.

6. Stable performance of the cryogenic oxygen systems requires mixing of the fluid.

7. It is conceptually possible to measure density by the use of a suspended sphere in the fluid. The effective mass of the sphere for the natural frequency of oscillation includes a virtual-mass term which is related uniquely to the displaced fluid density.

8. Cryogenic fluids can be mixed by the use of a suspended diaphragm driven by an isolated solenoid.

9. In the handling and storage of liquid oxygen, it is recommended that storage tanks be warmed periodically to eliminate contaminants, and that liquid be withdrawn from storage through a molecular sieve filler prior to filling spacecraft.

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D-1. Stewart, Richard B.: The Thermodynamic Properties of Oxygen. Ph. D. Thesis, Univ. of Iowa, June 1966.

D-2. Weber, L. A.: Thermodynamic and Related Properties of Oxygen from the Triple Point to 300K at Pressures to 330 Atmospheres. Supplement A (British Units), NDS Report 9710A, Aug. 29, 1968.

D-3. Apollo 13 Cryogenic Oxygen Tank 2 Anomaly Report.

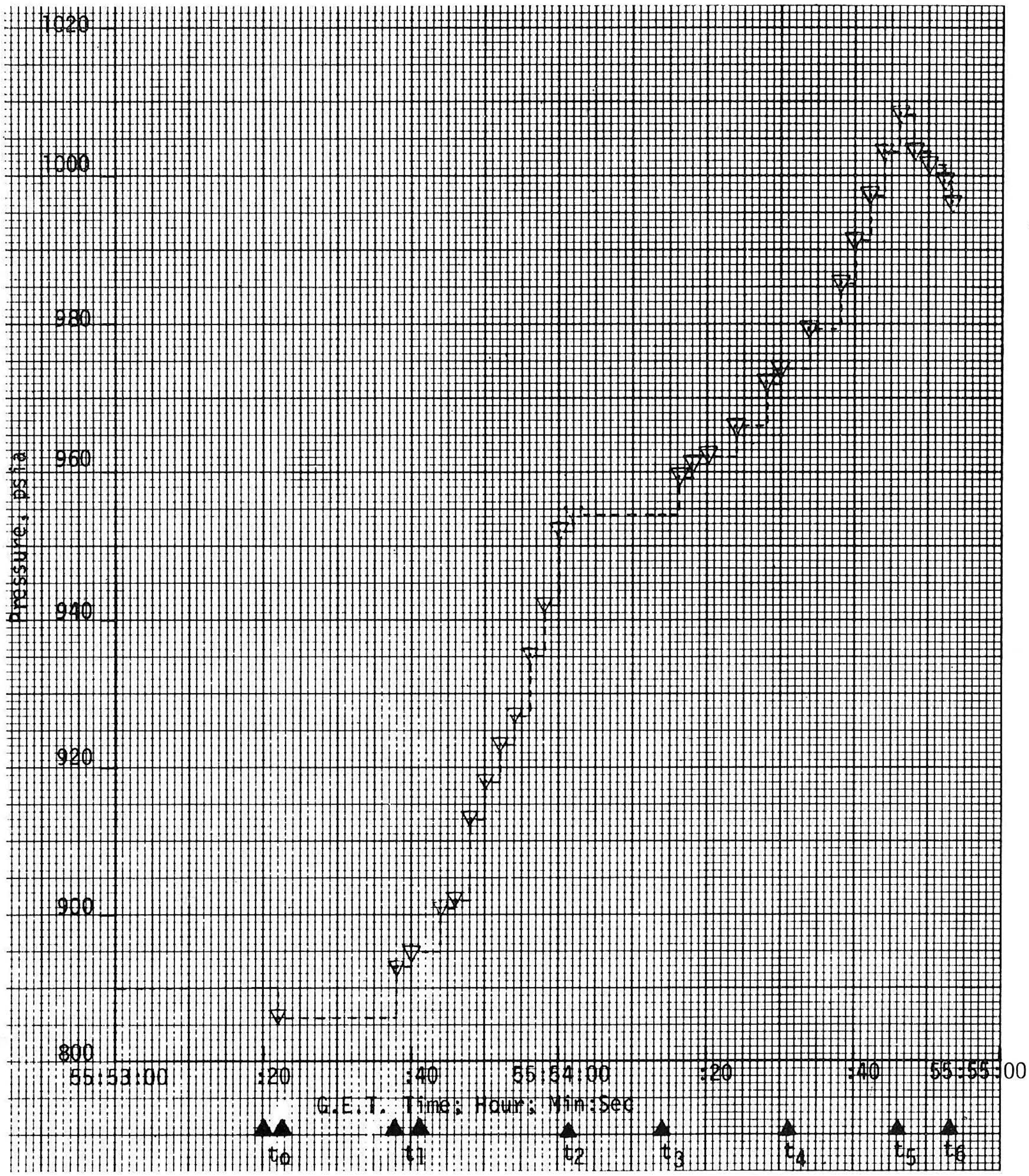

Figure D-1.- Number 2 oxygen tank pressure history.

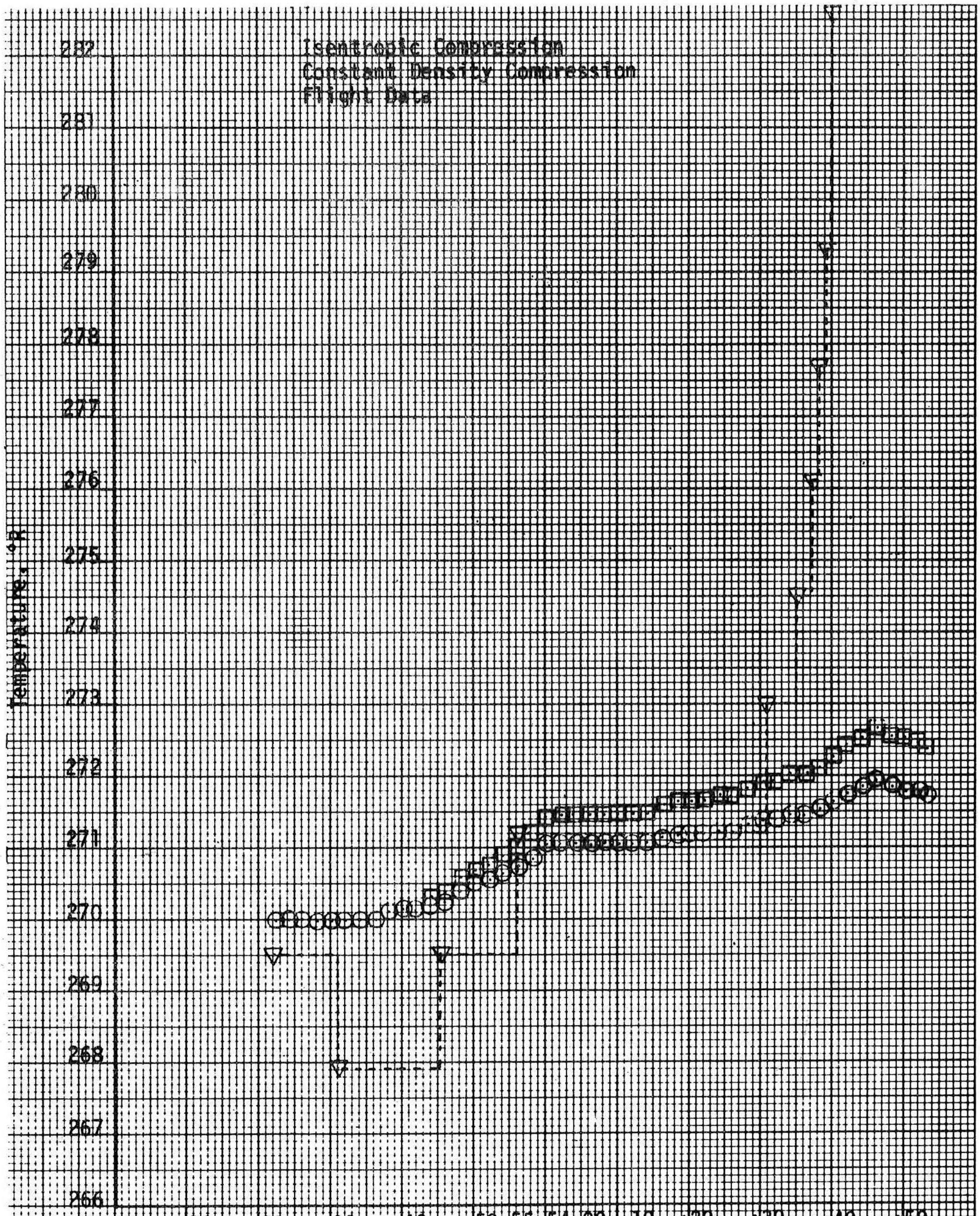

Figure D-2.- Number 2 oxygen tank temperature history.

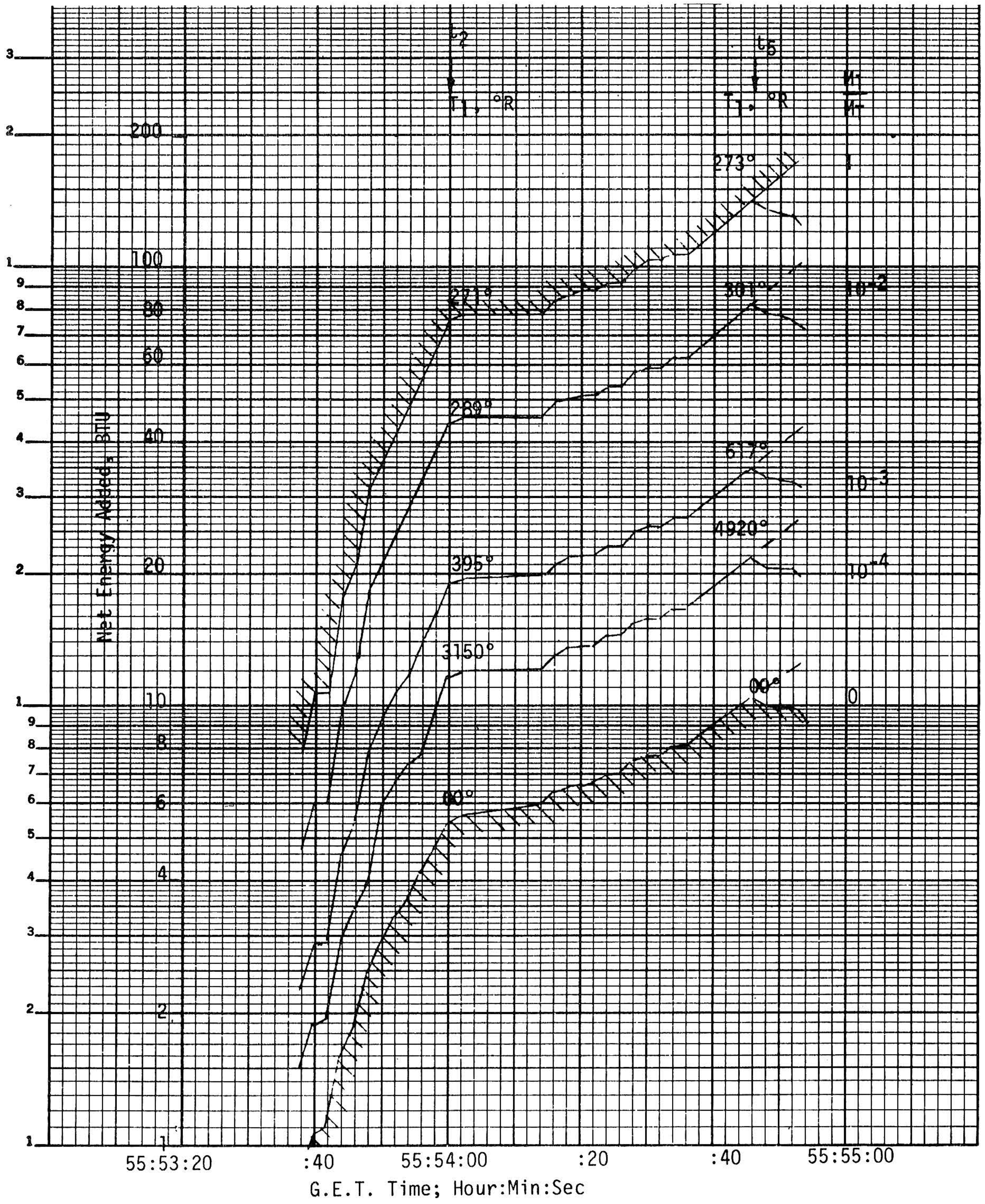

Figure D-3.- Number 2 oxygen tank energy history.

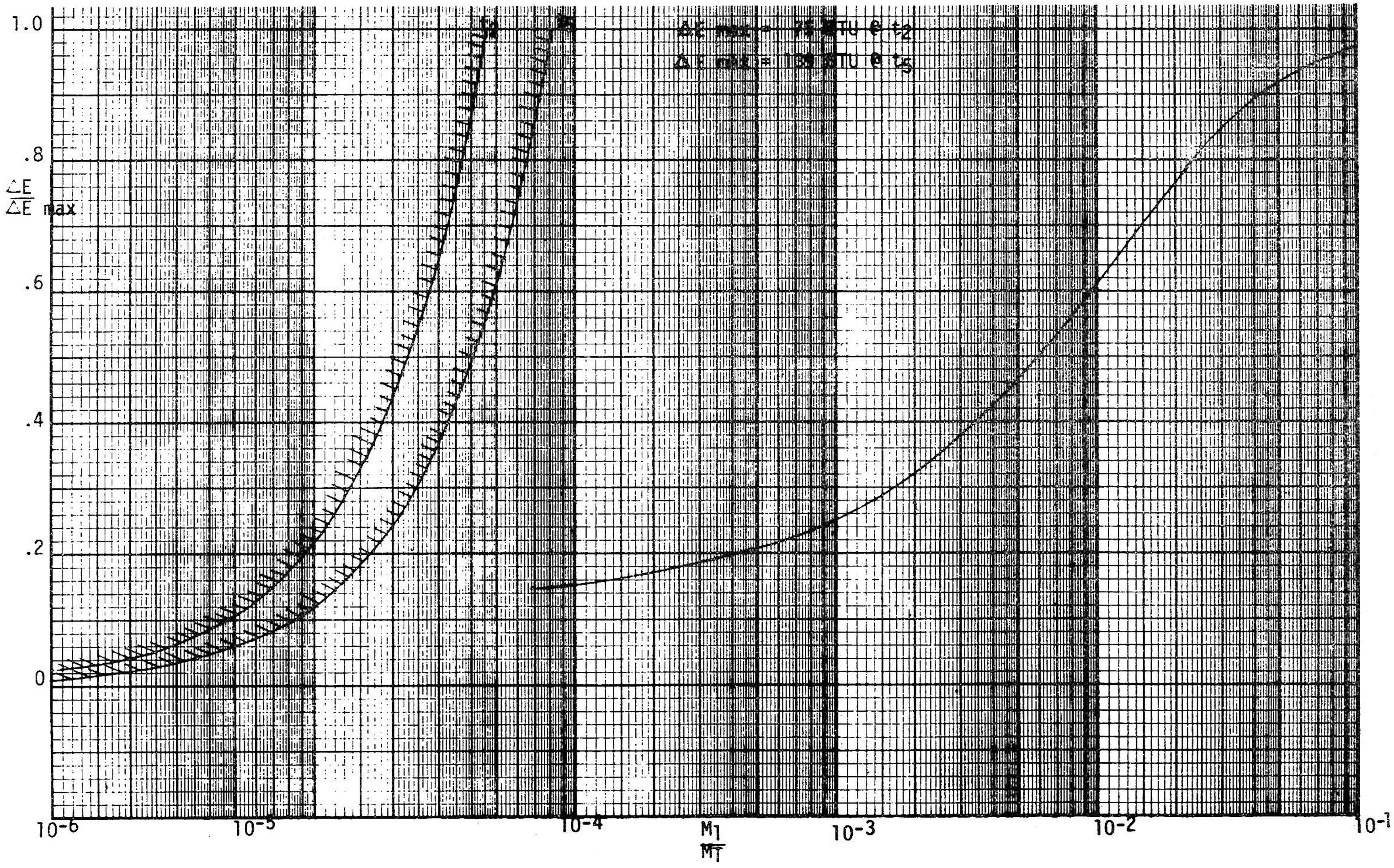

Figure D-4.- Number 2 oxygen tank energy ratio compared with mass ratio.

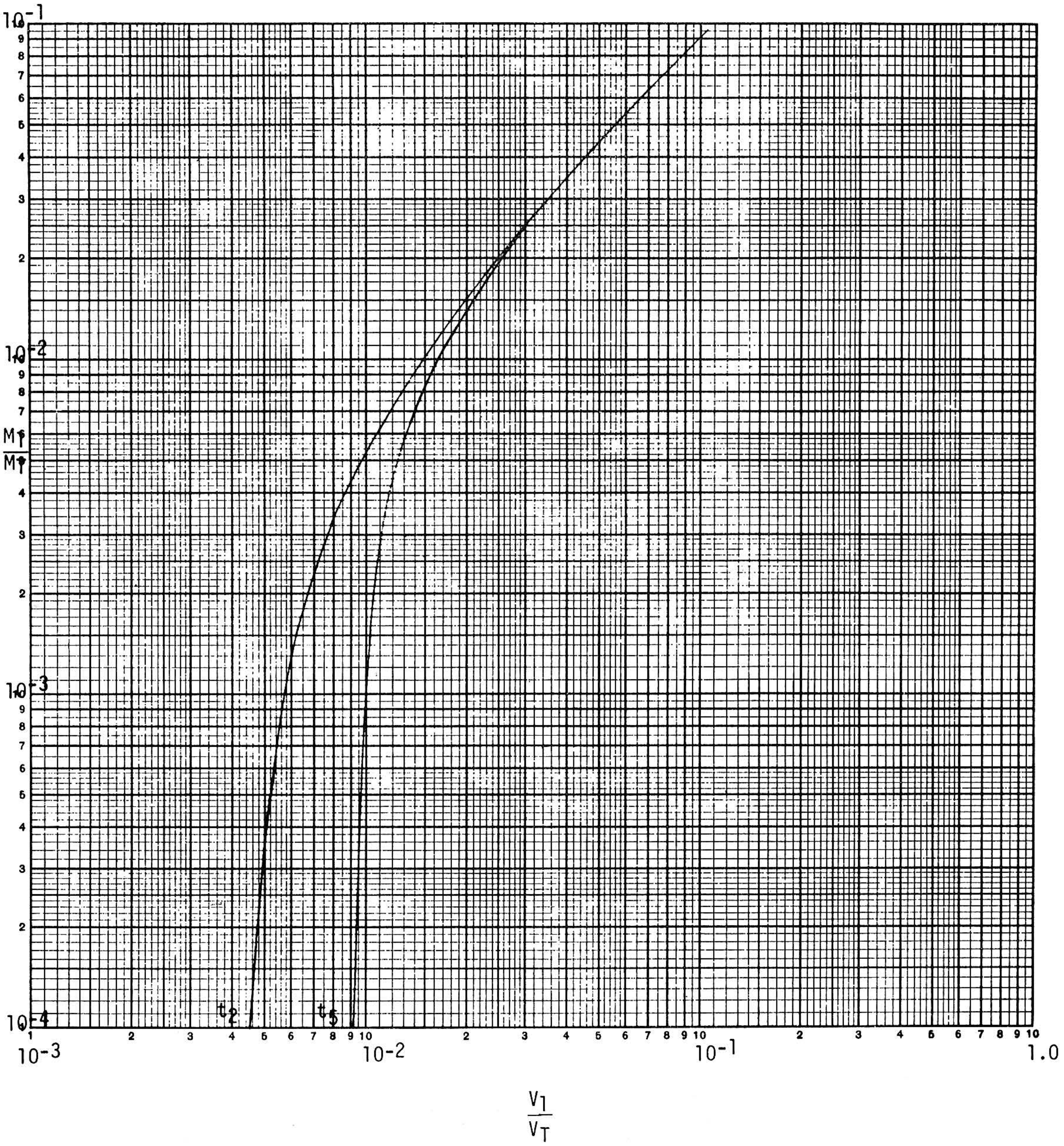

Figure D-5.- Mass ratio compared with volume ratio for times t_2 and t_5.

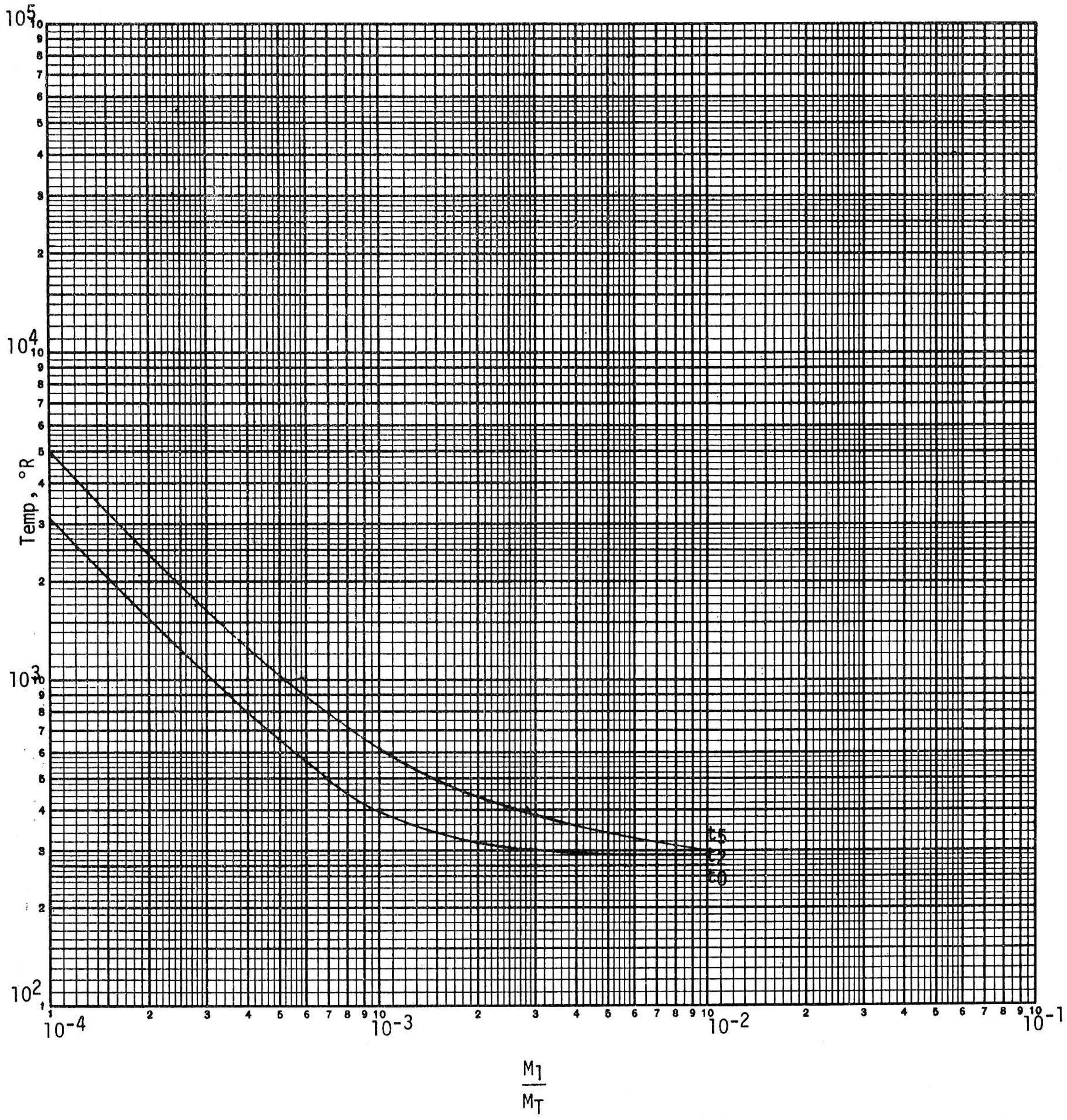

Figure D-6.- Number 2 oxygen tank hot gas average temperature compared with mass ratio for times t_0, t_2, and t_5.

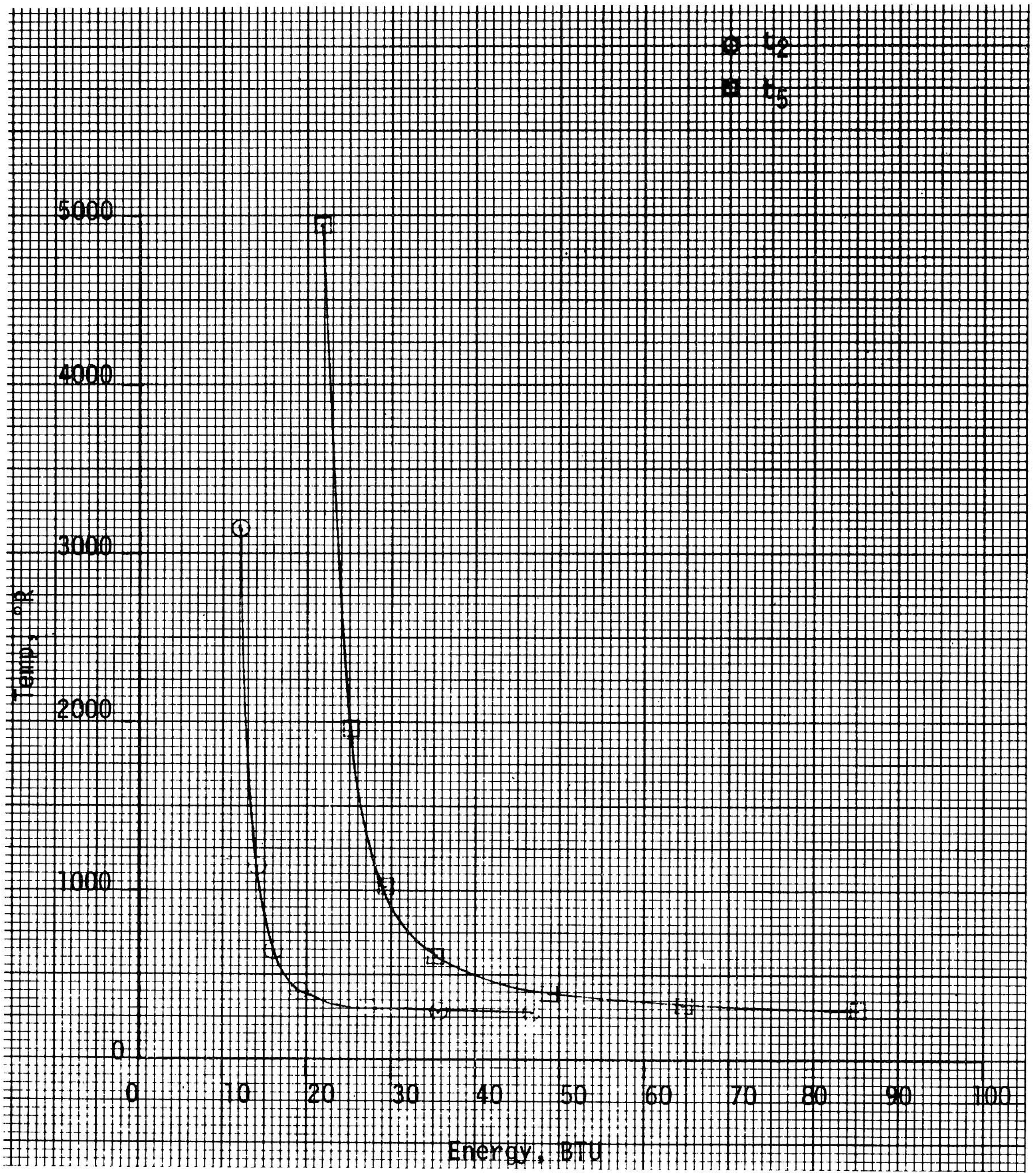

Figure D-7.- Hot-gas temperature compared with energy for times t_2 and t_5.

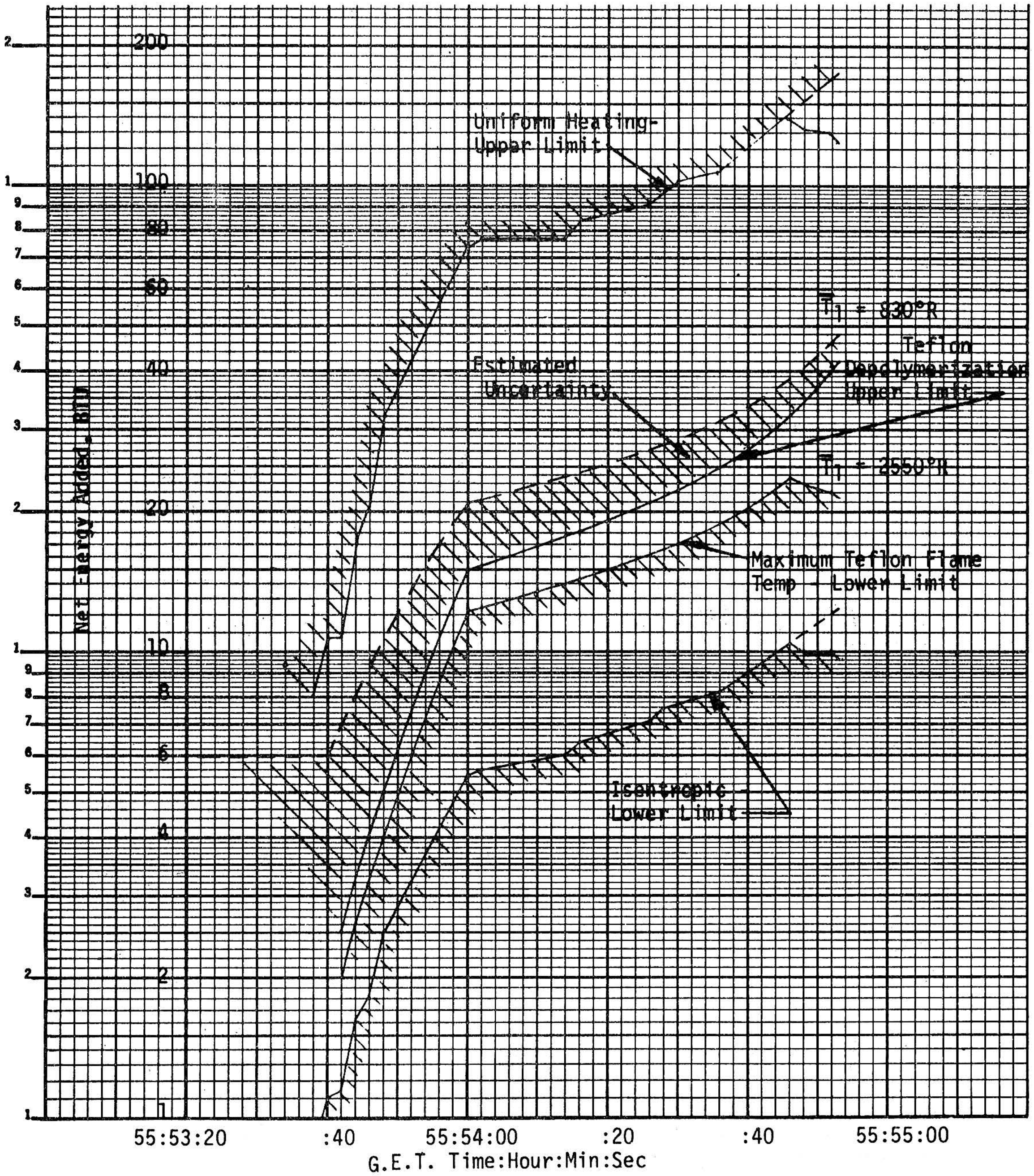

Figure D-8.- The thermodynamic limitation on the net energy addition to the number 2 oxygen tank.

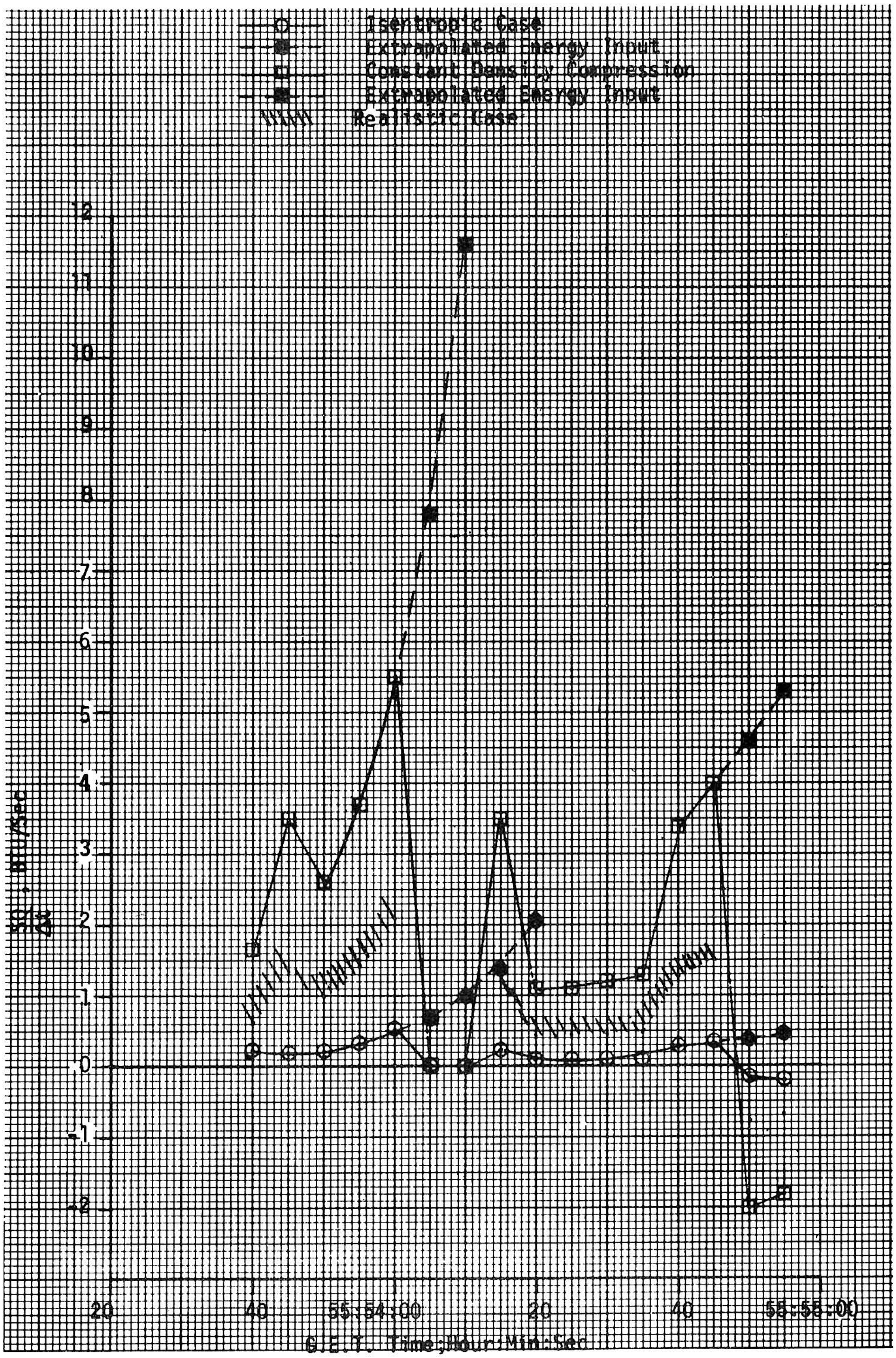

Figure D-9.- Energy-addition rate histories.

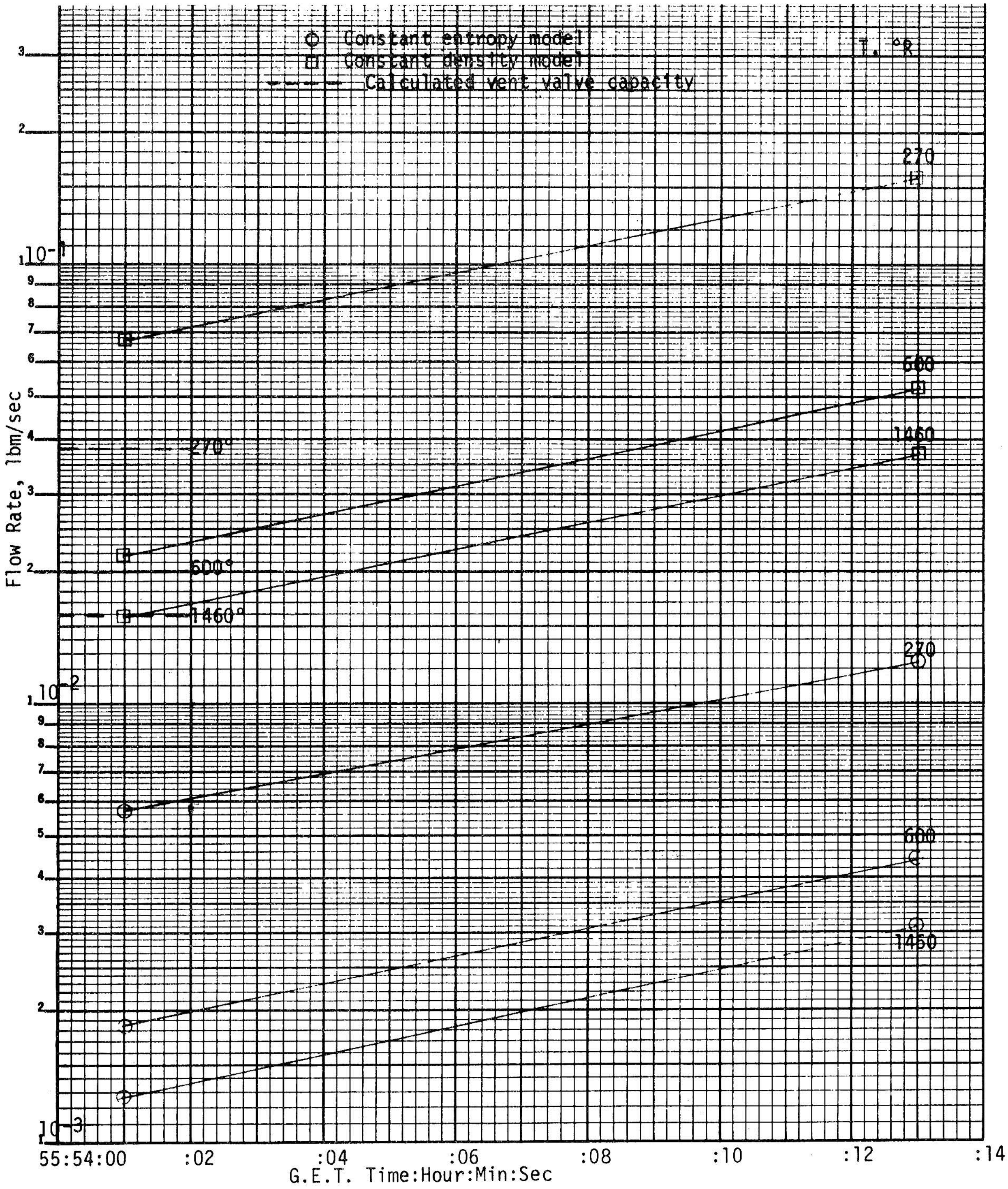

Figure D-10.- Mass-flow-rate histories at time t_2.

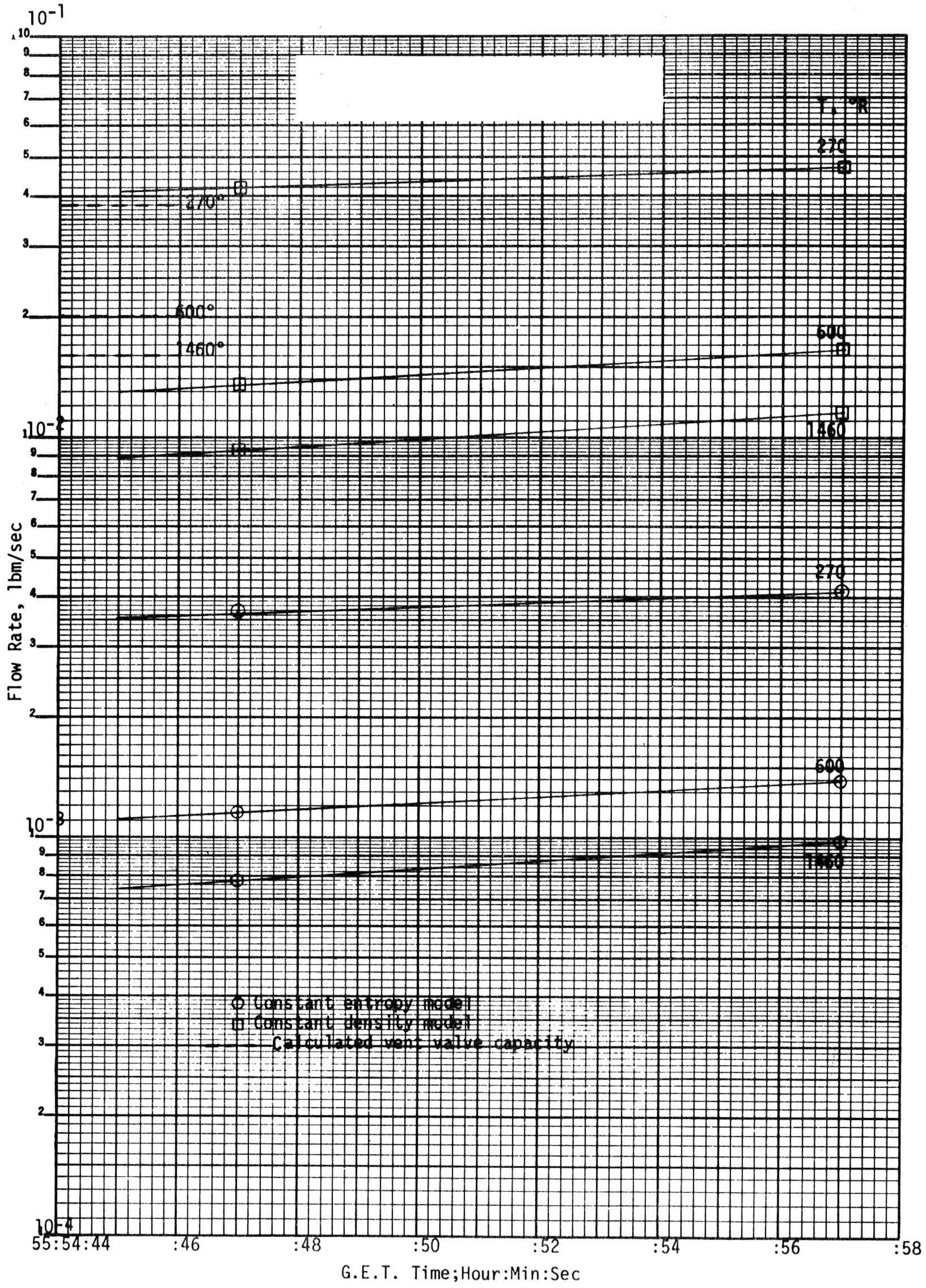

Figure D-11.- Mass-flow-rate histories at time t_5.

SECTION E — SUMMARY

SYSTEMS DESCRIPTION

Descriptive data for all tanks on the Apollo command module, service module, and lunar module have been collected, collated, and tabulated. A listing was made of tank numbers, locations, and dimensions. Construction materials, design pressures, normal operating pressures, actual operating pressures, temperatures, and fluid flow rates have been tabulated for all tanks in the spacecraft.

The oxygen tanks, hydrogen tanks, and hypergolic-propellant tanks have been examined in detail for contaminants and incompatibilities that could be potentially dangerous. Mechanisms for failure by contaminants, incompatible materials, and physical processes have been postulated for the supercritical hydrogen tank, supercritical oxygen tank, propellant tanks, and oxygen ground service equipment. The mechanisms considered are (1) brittle fracture failure (below material yield strength) caused by preexisting flaw (mode-fragmentation or leakage) and (2) tank rupture at material ultimate strength caused by pressure increase where the mode is fragmentation resulting from combustion of polymeric and metallic materials interior to the tank, from combustion of fluid impurities after segregation and concentration, and from catalytic decomposition of tank contents.

METALLURGY SURVEY

Metallurgical assessment involved consideration of inherent metallurgical characteristics of the various tank materials with respect to metal combustion, stress corrosion, and fracture-mechanics evaluation of tank integrity. Assuming the fabrication and use specifications of the tanks are not violated, and provided approved fluids and procedures associated with the tank usages are maintained, unexpected combustion of metals from impact or abrasion appears remote, and stress corrosion appears unlikely. The only instance of metallurgical incompatibility noted is in the hydrogen tanks where tin-lead solders and brass (containing zinc) and iron in the fan assemblies are of doubtful service in liquid hydrogen. These metal systems require further investigation, because it is known that lead and zinc are incompatible with liquid hydrogen, but no known data exist which can resolve the questions of the solder, brass, or iron compatibilities.

PHYSICAL CHEMISTRY SURVEY

Descriptive data on the high-pressure systems and the information obvious from the Apollo 13 accident required a physical chemistry survey of the tank systems. This survey resulted in information that is summarized as follows.

Polytetrafluoroethylene Reactivity

Safe usuage of polytetrafluoroethylene (PTFE) involves prevention of high-temperature environments (greater than 500° C (932° F) for unfilled virgin polymers and 430° C (806° F) for filled polymers) occurring within the polymer structure. Polytetrafluoroethylene is a thermodynamically reactive material and can react rapidly and destructively with a variety of materials dependent on only a few triggering mechanisms. Knowledge of the triggering mechanisms is imperative. Prevention of excessive heating on external PTFE surfaces and elimination of mechanisms for sparking, arcing, and high-pressure-induced shocking is mandatory for the safe use of PTFE in high-pressure systems.

Electrostatic Effects in High-Pressure Fluid Systems

To avoid chemical reactions caused by surface charging inside high-pressure tanks and plumbing, impurities (e.g., water as ice crystals) and high flow rates must be excluded from oxygen systems where potential combustibles such as PTFE exist. Only an experimental program can establish the magnitude of the limits of impurities and flow rates in critical systems well below those which, by experience, have not been sufficient to cause difficulties.

Polytetrafluoroethylene Degradation

Polytetrafluoroethylene is degraded for electrical and chemical service when the polymer contains inorganic chemical fillers, fibers, and coloring agents to the extent that its resistance to thermal effects may drop as much as 300° C (from 733° C to 430° C, 1351° F to 806° F). Treatment of PTFE parts with halocarbons will degrade the polymer for nitrogen tetroxide (N_2O_4) service. No hazards are expected in using PTFE components in high-pressure oxygen or N_2O_4 service provided the following conditions are maintained.

1. Unpigmented virgin polymer is used where physical conditions permit.

2. Temperatures are not permitted above 430° C (806° F).

3. Electric sparks and arcing at polymer sites cannot occur.

4. Halocarbon cleansing agents are removed completely.

Catalytic Effects

Catalytic acceleration of chemical reactions in the spacecraft pressurized containers has been reviewed, and the following areas have been identified as regions wherein significant catalytic action may occur.

Reactive degradation of fluorocarbons.- It has been noted that the reactivity of PTFE varies significantly, dependent on the fillers, coloring dyes, and contaminants that are contained in the structure. Such fillers and dyes may act catalytically to induce decomposition of the polymer. This is the case with metals which may come in intimate contact with PTFE and with particulate contaminants which can impinge the surface of the polymer. For spacecraft systems, the use of halocarbons for cleaning high-pressure PTFE parts for N_2O_4 service should be avoided because of catalytically induced reactivity.

Reaction between fluids and impurities.- Strict attention to standards of purity in the fluids and in the fluorocarbons is important to avoid unexpected catalytic effects. Rigorous application of present knowledge to purification and surface preparation would increase safety, while research into reaction mechanisms would be desirable for long range improvements.

Catalytic effects of impurities on crack propagation.- Liquid oxygen, hydrogen, and nitrogen have very low dielectric constants. They are not electrolytes and the effect of dissolved impurities is expected to be additive. The results of a recent NASA-sponsored research program point out that Ti-5Al-2.5Sn is affected adversely at ambient temperatures by the hydrogen environment. Although, obviously, the risk has been considered before the selection of this particular alloy for the hydrogen tanks, this alloy and its surface treatment should be reviewed. The hypergolics are electrolytes, and impurities in this case must be expected to act as powerful catalysts. Some research on impurity effects on the corrosivity of N_2O_4 was done and was incorporated in the specifications. The influence of impurities on corrosivity and crack propagation in the case of monomethyl hydrazine and Aerozine-50 apparently has not yet been investigated. However, each flight batch is tested with surface-flawed specimens to indicate no metalic-fluid incompatibilities.

Electron Microscope as an Engineering Tool

The extent of polymer degradation upon exposure to high-pressure-shock treatment, oxidation, catalytic influence, and hydrogenation can be followed by the use of electron microscopic techniques. Degradation induced by fillers, coloring agents, and aging can be delineated by correlating size and numbers of voids in PTFE structure with known histories of specimens of virgin composition.

Thermodynamic Restrictions on Energy Processes in Apollo 13 Oxygen Tanks

The thermodynamic limitations on the net energy added to the oxygen in the Apollo 13 number 2 tank are shown in figure D-8. The limits have been established under the constraints of the measured pressures and temperatures, the tank volume, and the oxygen mass. The calculations include nominal mass usage, nominal heat leak, and the work which the fluid performs on the tank. The ultimate limits of uniform heating and an isentropic process have been reported previously. The isentropic limit has been lowered because of increased accuracy obtained in the calculation procedures. However, this lower limit is within the accuracy of knowledge of the thermodynamic properties of supercritical oxygen. Because of the extremely low thermal conductivity of supercritical oxygen and the zero-gravity state, it is reasonable to describe the distribution of energy within the oxygen by a two-fluid model. The two-fluid model establishes very sensitive temperature distributions, which, in turn, allow a very close specification of the energy added to the oxygen. Because the ultimate limitations are well within the energy available from the PTFE combustion, the characteristics of PTFE burning have been used to establish peak-temperature limitations, and (therefore) energy addition. The lower limit is obtained by assuming that the peak temperature in the reaction zone is equal to the theoretical limiting flame temperature for a stoichiometric reaction. The upper limit is established by the constraint that the peak temperature had to be high enough to allow the PTFE to undergo depolymerization. This is only a limit to the energy added to the oxygen and does not include energy which may have gone into heating structural components of the tank. Details of this analysis are presented in the final report.

SECTION F — FINDINGS

As long as the accepted standards for fluid purity, high-pressure-container and related plumbing specifications, and qualification and acceptance testing are maintained rigidly for the Apollo spacecraft systems, a delicate balance of conditions exists which can assure flight worthiness of the structures and systems. The Apollo 4 to 12 flights indicate this overall condition.

However, as a result of this investigation, there have come to light some findings relative to reaction processes in the high-pressure systems which appear significant to increased safety of manned space flight. These findings are tabulated as follows.

1. Particulate contaminants in the fluid system (ice crystals from moisture contamination) are hazardous because they can induce catalytic effects and shock fatigue in polymers exposed in high-pressure systems.

2. Analysis of liquid aliquots from liquids yields a more accurate result than analysis of gaseous aliquots from liquids or gaseous aliquots from gases taken from above a liquid.

3. Polytetrafluoroethylene (PTFE) polymers are combustible in high-pressure oxygen systems, and the reaction process is dependent upon a triggering mechanism which can be an electrical wiring anomaly, a static-charge buildup, or shock impact at high flow rates.

4. Polytetrafluoroethylene polymers may be a fuel for reactions with high-pressure hydrogen by a process of hydrogenation, and this reaction would be dependent on a triggering mechanism (electrical or high-pressure shock treatment).

5. Polytetrafluoroethylene polymers are found to be degraded substantially in their chemical, electrical, and thermal resistance properties when the polymer is filled or is color coded.

6. Polytetrafluoroethylene polymers which are filled should not be subjected to a thermal environment exceeding 430° C (806° F).

7. Halocarbon fluids are found to degrade PTFE polymers for chemical and shock impact resistance, and for nitrogen tetroxide (N_2O_4) service.

8. Electron microscopy studies of virgin PTFE polymer and filled PTFE polymer components are a plausible tool for delineating high-pressure-induced incipient-failure modes for spacecraft parts.

9. High purity levels for hydrogen are important for spacecraft service. However, a certain low level of impurities (e.g., 100 ppm oxygen) in hydrogen is necessary to prevent crack growth in titanium tanks for hydrogen service.

10. Tin-lead solder is found to be incompatible for liquid-oxygen service under impact conditions.

11. Hydrazine in aqueous solution is found to desensitize metal surfaces used in hydrazine service.

12. Electrical discharge through PTFE polymer will induce high-energy reactivity of the polymer in supercritical oxygen and reactivity occurs at liquid nitrogen temperature.

13. The influence of impurities in monomethyl hydrazine and Aerozine-50 on corrosivity and crack propagation in titanium alloys is found to be unknown, but no adverse effects from these impurities in spacecraft tanks have been experienced and each batch of fluids is tested prior to flight for compatibility.

14. Thermodynamic limitations on net energy additions to supercritical fluids are found to be very small.

15. Polytetrafluoroethylene is found to have a tendency to swell in N_2O_4; possible effects of this property have not been assessed.

16. Isothermal high pressure fluids cannot redistribute energy catastrophically; non-isothermal fluids may do so.

17. Stable performance of cryogenic supercritical oxygen systems requires stirring of some nature.

18. Ignition temperatures of potential reactions vary as the inverse of the pressure squared.

19. Spacecraft accelerations pose no hazards to high pressure systems.

SECTION G — ACKNOWLEDGMENTS

The members of Panel 7 are indebted to the following individuals for their help.

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Panel 7

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APPENDIX A

COMMAND AND SERVICE MODULE FLUIDS ON SPACECRAFT 109

APPENDIX A

COMMAND AND SERVICE MODULE FLUIDS ON SPACECRAFT 109

The matrix presented in table A-I is the sample analysis data on fluids used on Spacecraft (SC) 109. The data were compiled from SC records, analysis reports, and reviews of ground support equipment (GSE) records by cognizant GSE engineering personnel.

The waiver written on the electrical power system (EPS) hydrogen was the result of the selected impurities analysis. The specification calls for a maximum not to exceed 9.0 ppm by volume. The analysis as made was

Nitrogen	$\leq$ 2 ppm
Methane	$\leq$ 1 ppm
Water	= 6.5 ppm
Total	= 9.5 ppm

The total selected impurities expressed to two significant numbers exceeded the allowable amount, but the combined nitrogen-methane analysis was known to be less than 3 ppm. Under the circumstances it was reasonable to accept the analysis and write a waiver on the material. The same analysis and procedure was used for both liquid and gaseous hydrogen because the same source is used for both.

This circumstance points out a weakness in the quality control (QC) of cryogenic liquids. At the present time, the analysis of a cryogenic liquid is not a liquid analysis. The sample for analysis is obtained in the liquid form according to the applicable NASA specification. However, the actual analysis is made on gases taken from above the analytical sample. As a result, each analysis reported is on a material that has had one additional purification step.

The additional purification step is the distillation of the liquid analytical sample to the gaseous state which is actually sampled. The process will always yield a purer sample for two reasons. First, fractional distillation yields a purer gas phase because high boiling impurities are concentrated in the remaining liquid. Second, nonvolatile impurities remain in the liquid phase and do not enter the gas phase. Thus the analysis will show fewer impurities, and an impure liquid could apparently meet specification requirements.

TABLE A-I.- SAMPLE ANALYSIS DATA

Fluid	Specification	Filter size, microns	Sample type	Sample Results	Remarks/waiver no.
Electrical Power System					
H_2	MSFC-SPEC-356A	15	Chemical	Failed	Samples 60-6162 and 60-6163/Waiver 109-PO-014
GH_2	MSFC-SPEC-356A	10	Particle and Chemical	Failed	Same as above
O_2	MSFC-SPEC-399A	15	Chemical	Passed	—
Environmental Control System					
O_2	MSFC-SPEC-399A	25	Chemical	Passed	
Reaction Control System					
MMH[a]	MIL-P-27404	15	Chemical	Passed	
N_2O_4	MSC-PPD-2B	15	Chemical	Passed	
Service Propulsion System					
N_2O_4	MSC-PPD-2B	15	Chemical Particle	Passed	
N_2	MSFC-SPEC-234A	15	Chemical	Passed	
Aerozine-50	MIL-P-27402A	15	Chemical	Passed	

[a] MMH = monomethylhydrazine.

APPENDIX B

CONTAMINANTS DETECTED AND IDENTIFIED IN GROUND SUPPORT EQUIPMENT

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CONTAMINANTS DETECTED AND IDENTIFIED IN GROUND SUPPORT EQUIPMENT

In each documented case of contamination found in plumbing equipment leading to the command and service module (CSM), there have been one or more materials present that were capable of causing pressure buildup as a result of instability in liquid oxygen (LO_2). Instability in this case is judged on the results of the Army Ballistic Missile Agency (ABMA) Impact Sensitivity Test (ref. B-1), Oxygen Bomb Test (ref. B-2), and Promoted Ignition Test (ref. B-3).

The products of the possible reactions are condensable at liquid oxygen temperature, but the reactions are exothermic. The liberation of heat during localized reaction between the contaminants and liquid oxygen will cause pressure buildup caused by vaporization of oxygen and products of the reaction around the hot spot.

In addition to the postulated reactions (table B-I) which can occur in the metallic state, additional reactions can occur with the other metals if they are present as metal salts. Metal halides are particularly sensitive to oxidation in liquid oxygen.

Table B-I lists location of the contaminant and when it was detected, identification of the contaminant, and reactions that can occur between the contaminants and the liquid oxygen of the system. The contaminants listed were separated by filters from the fluid that filled the vehicle tanks because the particle size was too large to pass the mesh size of the filter. However, all of the contaminants could enter the spacecraft tanks in the smaller particle size.

Table B-II lists the generalized results of liquid oxygen compatibility tests for materials related to those found as contaminants in this system. Compatibility tests have not been run on all materials and certainly not on all material combinations, but they are complete enough to make an estimate of the hazards involved with particular contaminants in contact with liquid or gaseous oxygen.

The Army Ballistic Missile Agency (ABMA) Liquid Oxygen Impact Sensitivity Test (ref. B-1) is based on the fact that many materials react when impacted in contact with liquid oxygen. The material may do the following:

1. Detonate

2. Give off flashes of light

3. Show evidence of burning (oxidative decomposition)

4. Become discolored

The above are the only criteria for failure of the Liquid Oxygen Impact Sensitivity Test.

The test procedure involves dropping a standard plummet of known weight, 20 ± 0.05 pounds (9.4 kg), from known heights up to 43.3 ± 0.2 inches (1.1 meters) under nearly frictionless conditions.

MSFC-SPEC-106B (ref. B-4) states that the material shall be subjected to 20 successive tests at 72 foot-pounds (10 kilogram-meters) using equipment and procedures described in the specification. No reaction must occur during 20 successive tests at the 72-foot-pound level of test before a material can be accepted for use. If more than one reaction occurs in 20 tests, the material is rejected. If one reaction occurs during the 20 tests, the material is subjected to an additional 40 tests. If any reaction occurs during the 40 tests, the material is rejected.

As a general rule, organic materials (plastics and polymers) are extremely sensitive to impact in liquid oxygen. Exceptions are the perfluoronated carbon compounds such as Kel-F, Krytox, FEP Teflon, and TFE Teflon. However, Teflon samples contaminated with extraneous materials, and even fingerprints, have failed the ABMA tests. There were two recorded cases where pigmented or treated Teflon did not pass the test (ref. B-2, pp. 35, 36).

With a few exceptions most metals are satisfactory for use with liquid oxygen. However, the state of division and surface coating play a decisive role in metal reactivity. For example, aluminum fabricated in test sheets or hardware passes the test satisfactorily. The lack of reactivity can be traced to the hard, dense, tightly held aluminum oxide coating that protects the pure aluminum metal underneath. When the Al_2O_3 coating is abraided or removed, oxygen reacts violently with the fresh aluminum surface.

The results obtained in the ABMA tester are the reactivities of clean, uncontaminated materials, and they do not generally reflect reactivities of impure, contaminated, or finely divided samples except in very few cases. Most operators caution against any type of contamination in the tester. Adherence to the highest cleanliness standard is required in order to obtain reproducible results, which is another way of saying impurities and contamination on otherwise insensitive materials will increase their sensitivity to reaction in liquid oxygen.

The Oxygen Bomb Test (ref. B-5) is used to determine the spontaneous ignition temperature of organic materials in 2000-psi oxygen. A specimen of the test material is heated in the bomb in a 2000-psi atmosphere of oxygen until spontaneous ignition of the sample occurs or until the temperature reaches 500° C, whichever occurs first. This is considered an excellent rating test for thread lubricants, thread sealants, and fluorocarbon plastics. The effect of oxygen pressure on spontaneous ignition temperature can be determined by comparing tests at different oxygen pressures.

The Promoted Ignition Test (ref. B-5) is designed to determine the resistance to ignition and the amount of burning after ignition of the more resistant metals. The test is made by subjecting the metal specimen to the energy released when a promoter material (neoprene is commonly used) is subjected to its spontaneous ignition temperature in oxygen. The test has considerable flexibility because the weights of both metal and promoter can be varied as can metal specimen configuration.

Reactions were postulated in table B-I whenever that type of material was impact tested and found to be unsatisfactory, or whenever it was tested by other means and reaction occurred at a comparatively low temperature. Thus, the reaction equations in table B-I are based on results tabulated in table B-II.

REFERENCES

B-1. Lucas, W. R.; and Riehl, W. A.: An Instrument for the Determination of Impact Sensitivity of Materials in Contact with Liquid Oxygen. ASTM Bull. No. 244, Feb. 1960.

B-2. Key, C. F.: Compatibility of Materials with Liquid Oxygen, III. NASA TM X-53533, 1966.

B-3. Key, C. F.: Compatibility of Materials with Liquid Oxygen, IV. NASA TM X-53733, 1968.

B-4. Anon: NASA Specification for Testing Compatibility of Materials for Liquid Oxygen Systems. MSFC-SPEC-106B, 1966.

B-5. Nihart, G. N.; and Smith, C. P.: Compatibility of Materials with 7500-psi Oxygen. AMRL-TDR-64-76, Union Carbide Corp., Linde Div., Oct. 1964.

B-6. Key, C. F.: Compatibility of Materials with Liquid Oxygen. NASA TM X-53052, 1964.

B-7. Key, C. F.; and Riehl, W. A.: Compatibility of Materials with Liquid Oxygen. NASA TM X-985, 1964.

TABLE B-I.- CONTAMINANTS DETECTED IN GROUND SUPPORT EQUIPMENT AT KENNEDY SPACE CENTER

CAR[a]	EI[b]	Name	Date	CSM	Where detected	Remarks	Contaminants	Reactions possible
61219	S14-132	LC39-FDS	3-21-69	106	ME273-0038 -0010 (1) of 1 (2) of 2	Both fill disconnects contaminated	Fe-major Cr-minor Ni-minor Zn-minor Ti-minor S-minor Mn-minor Mo-minor	$2S^\circ + 3O_2 \longrightarrow 2SO_3$ + Heat $Fe^\circ + O_2 \longrightarrow Fe_2O_3$ + Heat $Cr^\circ + O_2 \longrightarrow Cr_2O_3$ + Heat
61701	S14-132	LC39-FDS	3-24-70	109	15241-637 Filter of 2	Particle size generally below 500µ Glass beads in filter pads Cryotec on filter (Cryotec is an epoxy patch component)	Fe-major Al, Cr-light major Ni-heavy minor Fe_3O_4, Fe_2O_3, FeO, Austinite, Ti, Si-minor Mg, Mn-light minor Glass beads Cryotec	$CF_3(CF_2)_x - CF_3 + O_2 \longrightarrow XCOF_2$ $COF_2 + O_2 \longrightarrow F_2O + CO_2$ + Heat $Fe^\circ + O_2 \longrightarrow 2Fe_2O_3$ + Heat $Al^\circ + O_2 \longrightarrow 2Al_2O_3$ + Heat $Mg^\circ + O \longrightarrow MgO$ + Heat $Al^\circ + Mg^0 + Fe_2O_3 \longrightarrow Al_2O_3 + MgO + FeO$ + Heat Glass beads can abrade passivated Al surface (Al_2O_3) and expose fresh metal surface. The clean surface can then react explosively with LO. Epoxy + $O_2 \longrightarrow CO_2 + H_2O$ + Heat
61041	S14-088	MSOB-FDS	10-30-69	104	ME273-0038 -0001 POD of 2	1/4 inch sliver from O-ring	Buna-N rubber	Buna-N rubber + $O_2 \longrightarrow$ $XCO_2 + XH_2O$ + Heat

[a] CAR (Corrective Action Request).

[b] EI (End Item).

TABLE B-I.- CONTAMINANTS DETECTED IN GROUND SUPPORT EQUIPMENT AT KENNEDY SPACE CENTER - Concluded

CAR[a]	EI[b]	Name	Date	CSM	Where detected	Remarks	Contaminants	Reactions possible
A122583	S14-082	DOW-FDS	5-01-69	110	ME273-0038 -0003	7 particles >100µ (0 allowable)	Fe-major Cr-minor Ni-light minor Cu,Pt-trace Ag-trace Acetate fiber	Acetate fiber + $O_2 \longrightarrow CO_2 + H_2O$ + Heat $Fe^{\circ} + O_2 \longrightarrow Fe_2O_3$ + Heat $Cr^{\circ} + O_2 \longrightarrow Cr_2O_3$ $Pb^{\circ} + O_2 \longrightarrow PbO$
61123	S14-088	MSOB-FDS	12-19-68	104	ME273-0038 -0003 POD-HVI		Au-major Ag-major Austenite-minor Fe,Si,Cu-minor	$2Fe^{\circ} + 3O_2 \longrightarrow xFe_2O_3$ + Heat
6-725	S14-041	LC34-FDS	9-23-68	101	ME273-0038 -0001 POD-OF	Considerable contamination visually verified.	No analysis	Unknown
61162	S14-132	LC39-FDS	2-21-69	104	ME273-0038 -0003 POD-HF_2		Fe-major Cr-heavy minor Fe_2O_3-light minor Iron oxide-minor Ni,Mo-minor Butyl rubber	Butyl rubber + $O_2 \longrightarrow$ $CO_2 + H_2O$ = Heat $Fe^{\circ} + O_2 \longrightarrow Fe_2O_3$ + Heat

[a] CAR (Corrective Action Request).

[b] EI (End Item).

TABLE B-II.- CONTAMINANT MATERIALS — OXYGEN COMPATIBILITY

[References B-2, B-3, B-5, B-6, and B-7]

Materials	ABMA impact test (a)	Oxygen bomb test ignition temperature (2×10^3 psi O_2)	Promoted ignition test temperature (2×10^3 psi O_2)
Iron, fabricated	S		
Iron, powder	U		
Chromium	-		
Nickel	S		304° C (Monel)
Titanium	U		
Sulfur	U		
Manganese	-		
Molybdenum	-		
Aluminum, fabricated	S		
Aluminum, powder	U		
Teflon, virgin	S	469° C	
Teflon, contaminated	U		
Silicon	-		
Silica (glass beads)	-		
Epoxy (Cryotec)	U		
Buna-N Rubber	U	200° C	
Lead	U		
Silver, pure and hard alloy	S		349° C
Silver, soft	U		
Cellulose acetate (fiber)	U		
Gold	S		369° C
Butyl Rubber	U	200° C	

[a] Rating code: U = Unsatisfactory
- = Testable but no information
S = Satisfactory
Blank = No information

APPENDIX C

HARDWARE ANALYSIS OF P/N 15241-637

APPENDIX C

HARDWARE ANALYSIS OF P/N 15241-637

Test Report TR-220 furnished information about hardware analysis of Wintec filter assembly P/N 15241-637, S/N 001. This filter assembly was in use during the apparent system malfunction during the unloading of a liquid oxygen tank on Apollo 13. This unit was also used for servicing the Apollo 12. Wintec filter assembly P/N 15241-637, S/N 001, is welded into a Consolidated Precision Corp. vacuum jacket assembly, P/N 05475, S/N 1120.

Examination of the hardware after differential pressure tests of the element disclosed three contaminants.

1. Three glass beads found collected on the filter from the effluent flowing from the spacecraft (flow direction "B" nut to bayonet)

2. A quantity of lubricant on two of the filter pads, from the same liquid as in item 1

3. One fiber (65 by 500 microns, approximate dimensions)

The glass beads per se cannot cause pressure buildup or adverse reactions. However, they are capable of abrading inert or passivated surfaces. When the protective oxide coatings are removed, fresh reactive metal surface is exposed, and in the case of the oxygen tank, the reaction can be rapid, with the liberation of substantial amounts of heat (exothermic reaction) (ref. C-1).

The aluminum alloys in the supercritical oxygen tank are listed by alloy type and amount present. Five aluminum components inside the oxygen tank have been identified by alloy type and also a fifth identified aluminum part. If any of these could be abraded to start a reaction, the smallest amount of heat liberated, assuming complete reaction, would be 312 Btu. This energy release is sufficient to cause a pressure buildup in the tank.

The colorless lubricant was not identified in TR-220, but a portion was saved for infrared analysis. The analysis proved the lubricant to be Krytox 240 AC grease, which is a relatively new fluorocarbon grease that offers acceptable resistance to liquid oxygen sensitivity tests. This lubricant was apparently present as a result of excessive lubrication during filter assembly connection prior to tank pumpdown. The presence of the lubricant is undesirable because lubricants can vary in composition as a result of manufacturing procedures. Any given batch of lubricant should be accepted for use in a liquid oxygen environment only after that batch has been tested and found satisfactory.

The fiber was not identified, and its composition is unknown. Organic fibers as a class should not be brought in contact with liquid oxygen, as judged by the 10 kg-m impact-sensitivity test. Generally, inorganic fibers are acceptable, but they offer abrasion problems rather than inherent reactivity. Thus, a fiber collected at this point represents a potential hazard, because it indicates the possible presence of other fibers in the tank.

REFERENCE

C-1. Riehl, W. A.; and Nunnelley, J. R.: Investigation of LOX Filter Explosion. Rept. IN-M-S&M-M-61-4. Aug. 17, 1961.

TABLE C-I.- ALUMINUM ALLOYS IN THE SUPERCRITICAL OXYGEN TANK

Aluminum material	Weight available, oz	Ratio of reaction product and heat of reaction, Btu/Mole	Heat released, Btu
2024 Al	4	Al_2O_3, 1545	6 500
3003 AL	.5	Al_2O_3, 1545	803
1100 Al	.2	Al_2O_3, 138	321
Al	8	Al_2O_3, 1545	12 848
6061 Al	2	Al_2O_3, 1545	3 250
2117 Al	3	Al_2O_3, 1545	4 900

APPENDIX D

The Possibility of a Catastrophic Pressure Fluctuation in a Near-Critical-Point Fluid

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APPENDIX D

THE POSSIBILITY OF A CATASTROPHIC PRESSURE FLUCTUATION IN A NEAR-CRITICAL-POINT FLUID

The question has been raised as to whether a pressure fluctuation large enough to rupture the container could occur in a contained supercritical gas because of some form of excess energy storage or instability associated with the peculiar properties of gases near their critical points. To answer this question, the following four possibilities will be examined.

1. Spontaneous fluctuations about the equilibrium state of the gas

2. Fluctuations caused by a nonequilibrium state of the gas resulting from the operation of withdrawing some gas from the tank

3. Fluctuations induced by acceleration during launch or maneuvers

4. Fluctuations caused by a combination of acceleration and a nonequilibrium state of the gas.

SPONTANEOUS FLUCTUATIONS

It is well known that local fluctuations in the density of a gas occur near the critical point. The nonuniform density produces the phenomenon of critical point opalescence, in which the gas acts like a pigment and scatters light strongly. Opalescence proves that the density of the gas is nonuniform, at least on the scale of the wavelength of visible light. The cause of the relatively large density fluctuations is the high compressibility of the gas near the critical point. If we consider the fluctuations in the gas as a superposition of the normal modes of sound waves in the container, then we must allot an average energy of $\frac{1}{2}$ kT per mode. Under conditions of high compressibility, the mode amplitude corresponding to this energy is high also.

However, the question of importance here is whether a fluctuation is possible on a large enough scale to break the wall of the tank. Because the tanks have a safety margin of several hundred psi in excess of their operating pressure and because this excess pressure would have to be sustained for an appreciable time to rupture the wall, the spontaneous fluctuation would have to take the form of a low-frequency standing wave in the gas with a pressure amplitude of several hundred psi. Because the oxygen and hydrogen tanks are well insulated thermally (and therefore have a fixed total internal energy E), such a fluctuation would involve spontaneous conversion of a sizable fraction of the random thermal energy E into coordinated energy. This means that the entropy of the gas would spontaneously decrease by a large amount in defiance of the second law of thermodynamics. Therefore, it is concluded that no such fluctuation is even remotely possible.

FLUCTUATIONS CAUSED BY A NONEQUILIBRIUM STATE OF THE GAS

A nonequilibrium state of the gas in the container can produce coordinated (as opposed to random) motion of the gas. The situation will be considered that exists in an oxygen tank immediately after operation of the heater to drive some gas to a fuel cell. Let m_0 be the original mass of gas in the tank, at pressure p_0 and temperature T_0, and let the mass of gas removed be fm_0. Assume that the mass $(1 - f)m_0$ remaining in the tank consists of a portion m_1 still at pressure p_0 and temperature T_0, and a portion m_2 surrounding the heater that has been heated to a higher temperature T_2 but still is at the original pressure p_0. Let V_0, V_1, and V_2 be the specific volumes of the masses m_0, m_1, and m_2, respectively. Then, from conservation of mass and volume

$$m_1 + m_2 = (1 - f)m_0 \qquad \text{(D-1)}$$

$$m_1V_0 + m_2V_2 = m_0V_0 \qquad \text{(D-2)}$$

from which can be obtained

$$\frac{V_2}{V_0} = \frac{1 + f\,\dfrac{m_1}{m_2}}{1 - f} \qquad \text{(D-3)}$$

It will be assumed that the fraction of gas removed from the tank is f = 1/50, and that the fraction of the remaining gas that is expanded by the heater is $m_2/m_1 = 1/50$. Then, equation (D-3) gives

$$\frac{V_2}{V_0} = 2.00 \qquad \text{(D-4)}$$

At the start of the mission, the specific volume of the oxygen is $V_0 = 1.0\ \text{cm}^3/\text{g}$. Therefore, from equation (D-4), $V_2 = 2.00\ \text{cm}^3/\text{g}$. Taking the tank pressure as $p_0 = 60$ atmospheres, then, from the equation of state chart for oxygen, it is found that the temperatures in the two regions of the tank are $T_0 = -153^\circ$ C and $T_2 = -114^\circ$ C. Ordinarily, the stirrer will mix the gas and bring it to a common temperature. However, it will be supposed that this step is not carried out; therefore, it is asked: how much coordinated energy could be extracted from this nonequilibrium state of the gas by any conceivable process? The answer is that the maximum amount of coordinated energy is what one would get from an ideal heat engine operating between the temperatures T_2 and T_0.

The maximum energy W is related to the heat Q that flows from the warmer to colder gas by the Carnot efficiency of the heat engine. Thus

$$W \simeq \frac{1}{2}\left(\frac{T_2 \quad T_0}{T_2}\right)Q \qquad \text{(D-5)}$$

where the factor of 1/2 arises because, as the cycle proceeds, the temperature difference across which the engine operates does not stay constant but decreases from $T_2 - T_1$ to zero.

The value of Q can be taken as approximately equal to the heat that flows from the warmer to the cooler portions of the gas when the gas is merely stirred until the temperature becomes uniform. To determine Q, first the final equilibrium temperature and pressure of the gas must be calculated. To do this, the conservation equations for energy and mass are used.

$$m_1E_1 + m_2E_2 = \left(m_1 + m_2\right)E \tag{D-6}$$

$$m_1V_0 + m_2V_2 = \left(m_1 + m_2\right)V \tag{D-7}$$

The enthalpy equations are used also.

$$H_1 = E_1 + p_0V_1 \tag{D-8}$$

$$H_2 = E_2 + p_0V_2 \tag{D-9}$$

$$H = E + pV \tag{D-10}$$

From these five equations it may be shown that

$$H - pV = \frac{m_1}{m_1 + m_2}\left(H_1 - p_0V_0\right) + \frac{m_2}{m_1 + m_2}\left(H_2 - p_0V_2\right) \tag{D-11}$$

$$V = \frac{m_1}{m_1 + m_2}V_0 + \frac{m_2}{m_1 + m_2}V_2 = \frac{V_0}{1 - f} \tag{D-12}$$

All quantities on the right-hand sides of equations (D-11) and (D-12) are either known or determinable from the p, H chart of the equation of state of the oxygen. Therefore, equation (D-12) immediately gives V; then, equation (D-11) becomes a straight line on the p, H chart. Therefore, H and p are determined by the point where this line intersects the value of V given in equation (D-12). The value of T can then be read off from the isotherms. On carrying out this procedure, the following data are found for the initial and final states of the gas in the tank.

Region 1	Region 2	Final state
$V = 1.00 \text{ cm}^3/\text{g}$	$V_2 = 2.00 \text{ cm}^3/\text{g}$	$V = 1.02 \text{ cm}^3/\text{g}$
$T_1 = 120^\circ \text{ K}$	$T_2 = 159^\circ \text{ K}$	$T = 121^\circ \text{ K}$
$p_0 = 60 \text{ atm}$	$p_0 = 60 \text{ atm}$	$p = 28 \text{ atm}$
$= 6.0 \text{ joule/cm}^3$	$= 6.0 \text{ joule/cm}^3$	$= 2.8 \text{ joule/cm}^3$
$H_1 = 13 \text{ cal/g}$	$H_2 = 39 \text{ cal/g}$	$H = 13 \text{ cal/g}$
$= 52 \text{ joule/g}$	$= 156 \text{ joule/g}$	$= 52 \text{ joule/g}$
$m_1 = 1.2 \times 10^5 \text{ g}$	$m_2 = 2.4 \times 10^3 \text{ g}$	$m = 1.2 \times 10^5 \text{ g}$

The heat that flows from region 2 to region 1 is approximately

$$\begin{aligned} Q &= m_2 \left[\left(H_2 - p_0 V_2\right) - (H - pV) + \left(\frac{p_0 + p}{2}\right) \left(V_2 - V\right) \right] \\ &= 2.4 \times 10^5 \text{ joule} \qquad \text{(D-13)} \end{aligned}$$

The Carnot efficiency is

$$\frac{1}{2} \, \frac{T_2 - T_1}{T_2} = \frac{1}{8} \qquad \text{(D-14)}$$

Therefore, from equation (D-5), the maximum possible coordinated energy that can be generated is $W = 3 \times 10^4$ joule.

First, it will be assumed that this energy appears in the form of a standing sound wave in the tank. The relation between the pressure amplitude Δp of such a wave and the energy is

$$\Delta p = \frac{2c}{V}\sqrt{\frac{W}{m}} \qquad \text{(D-15)}$$

where c, the speed of sound in the gas, is given by

$$c = \left(\frac{\partial p}{\partial \rho}\right)_s = -V^2\left(\frac{\partial p}{\partial V}\right)_s \qquad \text{(D-16)}$$

For the final state conditions just given, c is approximately 2×10^4 cm/sec. Then, equation (D-15) gives $\Delta p = 6.4 \times 10^7$ dyne/cm^2 = 64 atm.

Owing to the part of the internal energy converted to wave energy, the static pressure in the gas falls below the value of 28 atm resulting from mixing. The new thermal internal energy is

$$(H - pV) - \frac{W}{m} = 49 \text{ joule/g} - 0.25 \text{ joule/g}$$

which indicates that the static pressure actually is lowered by an insignificant amount. It is remarkable that such a small fraction of the internal energy, when converted to wave energy, can produce a wave pressure amplitude that is even larger than the static pressure.

The total peak pressure on the wall is the sum of Δp and the static value of 28 atm which is 92 atm or 1500 psi. However, it is to be noted that because the wave pressure amplitude is larger than the static pressure, the assumption of sinusoidal waves in a linear medium, on which equation (D-15) is based, is rather approximate. However, the analysis does show that the potential energy represented by the temperature gradient in the tank is great enough to produce dangerous oscillating pressures if an efficient mechanism exists for converting part of the nonequilibrium thermal energy to wave energy.

Another type of coordinated motion consists of mass circulation of the gas in the tank. If the available thermal energy W is converted into mechanical energy of this kind, the velocity u of the gas is given by

$$\frac{1}{2} mu^2 = W \tag{D-17}$$

and the incremental pressure on the wall is

$$\Delta p = \rho u^2 = 2\rho \frac{W}{m} \tag{D-18}$$

On taking $W = 3 \times 10^4$ joule, $m = 1.2 \times 10^5$ g, and $\rho = 1 g/cm^3$ as before, $\Delta p = 75$ psi. Therefore, generation of the maximum possible circulatory motion, which is a more likely form of motion than compressional waves, does not produce a dangerous pressure increase.

A certain way to avoid any pressure increase caused by mechanical motion of the gas is to maintain efficient stirring at all times to prevent any temperature gradients from arising.

FLUCTUATIONS CAUSED BY ACCELERATION

Acceleration of the spacecraft causes gradients of pressure, density, and temperature in the gas tanks. A steady acceleration $\underline{a}$ in the x-direction produces a pressure gradient given by the force-balance equation

$$\frac{\partial p}{\partial x} = -a\rho \tag{D-19}$$

where ρ is the gas density. To get an equation in terms of ρ alone, the expression for the speed of sound is used.

$$\left(\frac{\partial p}{\partial \rho}\right)_s = c^2 \tag{D-20}$$

From equations (D-19) and (D-20), equation (D-21) is obtained.

$$\frac{\partial \rho}{\partial x} = - \frac{a}{c^2} \rho \qquad \text{(D-21)}$$

Therefore, the difference in density across the diameter D of the tank is

$$\Delta\rho = \frac{aD\rho}{c^2} \qquad \text{(D-22)}$$

From equation (D-19), the difference in pressure across the tank is

$$\Delta p = aD\rho \qquad \text{(D-23)}$$

For the case of oxygen, it is assumed that $\rho = 1$ g/cm^3, $p =$ 60 atm, $c = 2 \times 10^4$ cm/sec, $D = 60$ cm. Then, for an acceleration $a = 5g = 5 \times 10^3$ cm/sec^2

$$\Delta\rho = 8 \times 10^{-4} \text{g/cm}^3$$

$$\Delta p = 5 \text{ psi}$$

Therefore, the incremental pressure on the wall is negligible. When the acceleration ends, the static distribution of density and pressure turns into a compressional wave that has a maximum pressure amplitude of only 5 psi.

It is worth noting from equation (D-22) that because c approaches zero at the critical point, $\Delta\rho$ becomes large under near-critical conditions. However, it is seen from equation (D-23) that Δp remains small at the critical point. Therefore, it is concluded that accelerations cause no direct hazard.

FLUCTUATIONS CAUSED BY COMBINATION OF NONEQUILIBRIUM STATE AND ACCELERATION

Although acceleration alone causes very little static or dynamic excess pressure, the question arises whether it can provide an efficient mechanism for conversion of nonequilibrium thermal energy as discussed in the second section of this appendix.

The same nonequilibrium state as in the second section in which there is a warmer mass of 2.4×10^3 g and density 0.5 g/cm^3 and a cooler mass of 1.2×10^5 g and density 1.0 g/cm^3. Under these conditions, the maximum change in potential energy would occur if the 2.4×10^3 g of warmer gas exchanged places across a diameter of the spherical tank with a mass of 4.8×10^3 g of colder gas of the same volume. If the spacecraft acceleration is 5×10^3 cm/sec^2 and the diameter of the sphere is 60 cm, the amount of potential energy converted into kinetic energy is 2.4×10^3 g $\times$ 5×10^3 cm/sec^2 $\times$ 60 cm = 72 joules. In this calculation, the effect of expansion and contraction of the displaced masses has been neglected because the density difference caused by the acceleration is much less than that caused by the temperature difference (as seen in the previous section).

The energy of 72 joules appears in the form of circulatory motion of the gas, and, by equation (D-18), produces an excess pressure of only 0.2 psi. It is concluded that acceleration does not enhance significantly the pressure excess resulting from a nonequilibrium state of the gas.

COMMENTS ON GROUND TESTING OF APOLLO 13

Introduction

During one of the briefings at NASA, Houston, we learned that one of the heaters in No. 2 oxygen tank had remained in continuous operation during a three hour period in the preflight checkout. This memorandum purports to examine the heating of the lead wires that would result from this event.

We make the simplifying assumption that radial flow of heat away from the tube which carried the lead wires would be negligible in the evacuated and insulated dome. We assume that flow of heat takes place only along the wires and the enclosing tube. We assume that the electrical terminal was at 20° C and that the temperature of the tube rises through a maximum and declines again to 20° C about 70 cm from the connector and attains the temperature of the oxygen where the tube enters the tank. The tube was assumed to be 20-mil stainless steel of 0.5-inch diameter.

Because the resistance of the lead wires varies with temperature, it is necessary to analyze this problem by an iterative process. First, the temperature distribution is established for the case of constant resistance. This distribution is then substituted in the differential equation which is solved for a new distribution. The form of the equations is such that this can be repeated.

Numerical Data

We find a thermal conductance $KA = 0.125$ W-cm/°K. This is composed of the following.

Heater leads	0.0783
Tube	0.0202
Temperature-sensor leads	0.0102
Quantity probe leads	0.0082
Motor leads	0.0082

Each heater yields 417 watts from 65 volts. This implies a current of 6.4 amps in each lead. We assume only one heater remained on and we neglect all other heating of leads. At 20° C the resistance of #20 AWG copper is 10.15 ohms per 100 feet. We find the I^2R heating for the four heater leads is $q_o = 5.5 \times 10^{-2}$ W/cm at 20° C. For copper wire the coefficient of resistance is 0.004 per °C. The thermal conductivity does not vary significantly over the temperature range of interest.

Constant-Resistance Case

The heat-flow equation is

$$KA \frac{d_2T}{dx^2} = -q_m$$

where q_m is some mean heating rate to be established. If the origin is taken midway between the two points 70 cm apart at which the temperature is assumed to be $T_o = 20°$ C, then this equation integrates to

$$KA\left(T - T_o\right) = \frac{q_m}{2}\left(X^2 - x^2\right) \tag{D-24}$$

Variable-Resistance Case

The actual heat-flow equation is

$$KA \frac{d_2T}{dx^2} = -q \tag{D-25}$$

where

$$q = q_o[1 + \alpha(T - T_o)] \tag{D-26}$$

In this we substitute for $(T - T_o)$ from the solution for the constant-resistance case and obtain

$$KA \frac{d_2T}{dx^2} = -q_o \left[1 + \frac{\alpha q_m}{2KA} \left(X^2 - x^2 \right) \right] \qquad \text{(D-27)}$$

$$= -q^* \left[1 - \beta x^2 \right] \qquad \text{(D-28)}$$

where

$$q^* = q_o \left[1 + \frac{\alpha q_m X^2}{2KA} \right] \qquad \text{(D-29)}$$

and

$$\beta = \frac{\alpha q_m}{2KA + \alpha q_m X^2} \qquad \text{(D-30)}$$

Equation (D-28) integrates to

$$KA\left(T - T_o\right) = \frac{q^*}{2} \left(X^2 - x^2 \right) - q^* \frac{\beta}{12} \left(X^4 - x^4 \right) \qquad \text{(D-31)}$$

We require that q_m be chosen so as to present the correct total wattage. This requires

$$q_m X = \int_o^X q_o [1 + \alpha(T - T_o)]\, dx \qquad \text{(D-32)}$$

wherein we substitute for $(T - T_o)$ from equation (D-24) and obtain

$$q_m X = q_o X + \frac{\alpha q_o q_m X^3}{3KA} \tag{D-33}$$

whence

$$\frac{q_o}{q_m} = 1 - \frac{\alpha q_o X^2}{3KA} \tag{D-34}$$

Numerical Results

On substitution of the numerical quantities in the formulae just mentioned we obtain

(a) from equation (D-34)

$$\frac{5.5 \times 10^{-2}}{q_m} = 1 - \frac{0.004 \times 5.5 \times 10^{-2} \times 35^2}{3 \times 0.125} = 0.596$$

whence

$$q_m = 9.23 \times 10^{-2}$$

(b) from equation (D-29)

$$q^* = 5.5 \times 10^{-2} \left(1 + \frac{0.004 \times 9.23 \times 10^{-2} \times 35^2}{2 \times 0.125}\right)$$

$$= 1.57 \times 10^{-1}$$

(c) from equation (D-30)

$$\beta = \frac{0.004 \times 9.23 \times 10^{-2}}{2 \times 0.125 + 0.004 \times 9.23 \times 10^{-2} \times 35^2}$$

$$= 5.26 \times 10^{-4}$$

(d) from equation (D-31)

$$0.125(T - T_o) = \frac{1.57 \times 10^{-1}}{2}\left(X^2 - x^2\right) - \frac{1.57 \times 10^{-1} \times 5.26 \times 10^{-4}}{12}\left(X^4 - x^4\right)$$

$$(T - T_o) = 0.628\left(X^2 - x^2\right) - 5.5 \times 10^{-5}\cdot\left(X^4 - x^4\right)$$

From this we conclude

$$\left(T_{max} - T_o\right) = 0.628 \times 35^2 - 5.5 \times 10^{-5} \times 35^4$$

$$= 768 - 82.5$$

$$= 686^\circ \text{ C}$$

This is to be compared with

$$\left(T_{max} - T_o\right) = \frac{9.23 \times 10^{-2} \times 35^2}{2 \times 0.125} = 565^\circ \text{ C}$$

obtained on the assumption that the resistance of the wire was independent of temperature.

Pressure Blowoff

If 834 watts of heating persisted over a period of 3 hours, then there would have been a pressure blowoff unless enthalpy was removed from the tank by gas flow.

ON THE BEHAVIOR OF SUPERCRITICAL GASES

Introduction

The behavior of supercritical gases has been explored in considerable detail. In the case of the supercritical tanks of Apollo, no unusual behavior of engineering importance can result from the phenomena which are observed only in the immediate vicinity of the critical point. In the highly densified state, major departures from the ideal gas law result in some surprising behavior which is understandable from the thermodynamic data and the Van der Waals equation of state. Some of the unusual features which can be understood from a careful examination of the thermodynamics will be examined.

The Critical State

At the critical point the fluid undergoes a transition from the gaseous state where the molecules behave as independent particles to the liquid state in which substantial order prevails. The liquid state consists of a close-packed aggregate of molecular clusters in which each molecular cluster may contain some 10^8 molecules in greater order than prevails in a gas. At the critical point the liquid attains its maximum permissible temperature — at any greater temperature the ordered structure of the molecular cluster cannot be realized regardless of how great a pressure is applied and regardless of what increased densification is achieved.

Thus, at the critical point the transition between gaseous and liquid state entails a small change of entropy associated with the formation or dissolution of the molecular clusters. Thus, at the critical point a finite Tds occurs without change of temperature; this implies that both C_p and C_v will become infinite at the critical point.

Experiments to investigate the appearance and dissolution of molecular clusters must be carried out very slowly; temperature changes at the rate of 0.01° K per hour do not lead to reversible results. A brief summary of behavior in the vicinity of the critical point is found in "Molecular Theory of Gases and Liquids" by Hirschfelder, Curtiss, and Bird.

ENERGY ASSOCIATED WITH TRANSITIONS IN THE CRITICAL REGION

The fact that C_p and C_v become infinite at the critical point does not imply that large amounts of energy are associated with transitions in the vicinity of the critical point. The important consideration in this respect is the value of the integrals

$$\int C_v \, dT \qquad \text{or} \qquad \int C_p \, dT$$

in a narrow temperature range in the vicinity of the critical point. In an associated essay, it is shown that these integrals are finite and relatively small (appreciably less than 1 cal/g) from which it is clear that there can be no mechanism for the release of significant amounts of energy by any unusual phenomenon in the vicinity of the critical point. One should attribute the singularity of C_p and C_v at the critical point to the vestige of the latent heat of vaporization as the difference between liquid and gas phase becomes vanishingly small.

Velocity of Sound in the Vicinity of the Critical Point

The velocity of sound C_o at zero frequency satisfies

$$C_o{}^2 = -V^2 \left(\frac{\partial P}{\partial V}\right)_s$$

One may establish readily that

$$C_o{}^2 = V^2 \left[\left(\frac{\partial P}{\partial T}\right)_V^2 \cdot \frac{T}{C_v} + \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial P}{\partial T}\right)_V\right]$$

In the vicinity of the critical point $\left(\frac{\partial T}{\partial V}\right)_P = 0$, and this reduces to

$$C_o{}^2 = \frac{V^2 T}{C_v} \left(\frac{\partial p}{\partial T}\right)_V^2$$

In the gas phase immediately above the critical point, C_o is finite, having a value of approximately 210 m/sec. In the immediate vicinity of the critical point, the singularity in C_v implies that C_o should vanish.

Experiments on sound propagation in the vicinity of the critical point are very difficult to perform. The adiabatic assumption (zero frequency) requires that heat not flow from condensation to rarifaction during the propagation of the sound. As the velocity of propagation declines, the wavelength $\lambda = C/f$ becomes increasingly long. The "zero-frequency" condition will be satisfied only provided that a quarter wavelength is small compared to the dimension of a molecular cluster. Any disturbance produced by the propagation of the sound wave is likely to displace the system from its critical state and will result in an increase in sound velocity. If the velocity of sound fluctuates, the medium will be highly dispersive. The fact that substantial differences in density can result from infinitesimal pressure fluctuations also accounts for the anomalous attenuation of acoustic waves in the vicinity of the critical point.

ON THE NEED FOR STIRRING IN SUPERCRITICAL TANKS

The need for stirring the contents of tanks containing fluids in supercritical states can be demonstrated most convincingly from the following argument. Consider the tank filled with supercritical fluid in a state characterized by P_1V_1. Now imagine a fraction β of the mass to be heated without mixing, and let this serve to expel at constant pressure P_1 a fraction α of the mass in the state characterized by P_1V_1. For each gram initially within the tank, one will have in the unmixed state a mass $(1 - \alpha - \beta)$ in a state characterized by P_1V_1 and a mass β in a state characterized by P_1V_2 where

$$V_2 = \frac{\alpha + \beta}{\beta} V_1$$

Let us now cease the heating, close the vent, and mix the contents. The mixing of the contents is equivalent to placing the tank in thermal isolation and separating the two states in the tank with a thermally conducting barrier which moves so as to maintain zero pressure gradient across the barrier. As thermal equilibrium is established, one will find at each infinitesimal step the internal energy of one region will change in accordance with

$$dE_1 = dQ_1 - pdV_1$$

while that of the other region will change in accordance with

$$dE_2 = dQ_2 - pdV_2$$

But $dQ_1 = -dQ_2$, because this is the heat flow through the barrier, and $dV_1 = -dV_2$ because the barrier moves in a tank of constant total volume. Thus, $dE_1 + dE_2 = 0$ at all infinitesimal steps in the process. Thus, the total internal energy is conserved as the fluid is stirred, a consequence which stems clearly from the fact that the tank does not interact with its surroundings.

The total internal energy before mixing is given by

$$\frac{1}{1 - \alpha} \left[\left(1 - \alpha - \beta\right)\left(H_1 - P_1V_1\right) + \beta\left(H_2 - P_1V_2\right)\right] = \left\{\left(H_1 - P_1V_1\right) + \frac{\beta}{(1 - \alpha)}\left[\left(H_2 - H_1\right) - P_1\left(V_2 - V_1\right)\right]\right\}$$

(The factor $1/(1 - \alpha)$ is required to normalize to unit mass.) This is also the internal energy of the uniformly mixed fluids.

Consider now the case of $\alpha = \beta = 0.02$; we use 2 percent of the mass, expelling this by heating 2 percent of the mass without stirring. Then we mix the fluids. We examine the effects on the pressure assuming $V_1 = 1.0$ cc/g and $P_1 = 60$ atmospheres (900 psi).

In this case $V_2 = \frac{\alpha \quad \beta}{\beta} V_1 = 2.0$ cc/g, whence, $P_1(V_2 - V_1) =$ 1.41 cal/g. We compute a total free energy, before and after mixing of

$$E = 12.93 - 1.41 + \frac{0.02}{0.98}\left[(39.42 - 12.93) - 1.41\right] = 12.03 \text{ cal/g}$$

(Here the enthalpies are read from the Enthalpy/Log-of-Pressure plot.)

One seeks to establish the state after mixing. To do this, one must assume a pressure, calculate H_3 enter the chart at $V_3 = \frac{1.0}{0.98} = 1.02$ and determine the pressure. By an iterative process, one finds that the consistent P_3 is approximately 28 atmospheres or 420 psi.

One may readily verify that this is consistent because $P_3V_3 = \frac{27}{60} \times \frac{1}{0.98} \times 1.41 = 0.67$ cal/mole. Thus $H_3 = 12.03 \times 0.67 = 12.70$ and $V_3 = 1.02$. Corresponding to these values of H_3 and V_3, we find $P_3 = 28$ atmospheres.

Operational Significance

If the fluid were not stirred in use, then, when rocket thrust is used, convection will occur in the fluid. This can lead to partial mixing and the associated loss of pressure. If the convection carries the heated gas to the exit port and consumption of oxygen continues during the thrust phase, the source of pressurization may be burned in the fuel cells. Either of these events could lead to electrical failure in a thrust phase. The situation becomes more serious if α is larger than 0.02. Thus, one is led to the inescapable conclusion that temperature equalization is essential to assume reliable fuel-cell performance.

Physical Explanation of the Phenomenon

When the gas is at a high density corresponding to $V_1 = 1.0$ cc/g, the Van der Waals forces play a very significant role in maintaining the density. When the temperature is uniform throughout the fluid, the increase of specific volume requires an expenditure of work to increase the mean molecular distance against the strong Van der Waals forces. These forces fall off as $\frac{1}{V^2}$; thus, when $V_1 = 1.00$ changes to $V_3 = 1.02$, the Van der Waals force falls by only 4 percent. By contrast, when the small region of mass fraction $\beta = 0.02$ is expanded from $V_1 = 1.00$ to $V_2 = 2.00$, the Van der Waals forces will have fallen to 25 percent of their initial value. Clearly, less work will be expended against the Van der Waals forces when the same volume increase is achieved by expanding a lesser mass by a greater fraction than by expanding the total mass by a lesser fraction.

An approximate quantitative understanding of the energy deficit that can result from local heating and subsequent mixing instead of uniform heating can be gained through a study of the Van der Waals equation.

$$\left(p_e + \frac{a}{V^2}\right)(V - b) = RT \tag{D-35}$$

Where the subscript e is the externally observable pressure. The constants a and b are evaluated at the critical point

$$a = 3V_c^{\ 2}p_c \qquad b = \frac{V_c}{3}$$

where the subscripts c refer to the critical point.

For oxygen one obtains

$$a = 19.9 \text{ cal/cm}^3 \tag{D-36a}$$

$$b = 0.785 \text{ cm}^3\text{/g} \tag{D-36b}$$

One may regard the Van der Waals equation as

$$(p_e + p_v) = \frac{RT}{(V - b)}$$

where p_e is the observable pressure that the gas exerts on the outside world and p_v is an equivalent "Van der Waals pressure," which tends to reduce the volume of the fluid because of dipole-dipole forces which fall off as the inverse sixth power of the center-to-center separation.

We consider a process in which p_e is maintained constant as the gas is heated. Then

$$p_e = \frac{RT}{(V - b)} - \frac{a}{V^2}$$

and we require that changes in temperature and volume be such as to satisfy $dp_e = 0$; i.e., we require

$$\frac{R\,dT}{(V-b)} - \frac{RT\,dV}{(V-b)^2} + \frac{2a\,dV}{V^2} = 0$$

whence

$$dT = dV\left[\frac{T}{(V-b)} - \frac{2a(V-b)}{RV^3}\right] \qquad \text{(D-37)}$$

For any thermodynamic process we require

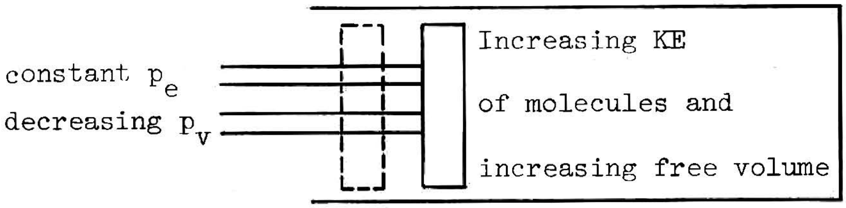
$$dQ = p_e\,dV + dE \qquad \text{(D-38)}$$

where $p_e\,dV$ is the work the gas does on its surroundings and dE is the increase in internal energy. In the ideal gas dE is a function of temperature only, and is equal to 1/2 kT per degree of freedom. In the Van der Waals gas we have departures from ideal behavior. We visualize the process of expansion at constant external pressure as being one in which the addition of heat does three things.

1. It increases the kinetic energy of the molecules with an energy of 1/2 $k\Delta T$ per degree of freedom

2. It does work $p_e\Delta v$ on the external world

3. It expands the gas against the confining Van der Waals forces; this work is $p_v\Delta v$



Under these assumptions, equation (D-38) becomes

$$dQ = p_e \, dV + \left[\frac{5}{2} RdT + p_v \, dV\right]$$

In this we substitute for dT from equation (D-37) and obtain

$$dQ = p_e \, dV + \left[\frac{5}{2} \frac{RT}{(V - b)} - \frac{5a(v - b)}{V^3} + \frac{a}{V^2}\right] dV$$

And for the first term in the bracket we substitute from equation (D-35) to obtain

$$dQ = p_e \, dV = \left[\frac{5}{2} (p_e + \frac{a}{V^2}) - \frac{5a}{V^2} + \frac{5ab}{V^3} + \frac{a}{V^2}\right] dV$$

$$= p_e \, dV + \left[\frac{5}{2} p_e - \frac{3}{2} \frac{a}{V^2} + \frac{5ab}{V^3}\right] dV \qquad \text{(D-39)}$$

It is instructive to write equation (D-39) as

$$dQ = p_e \, dV + \left[\frac{5}{2} p_e + \left(\frac{5}{3} \frac{V_c}{V} - \frac{3}{2}\right) \frac{a}{V^2}\right] dV$$

from which it is clear that so long as V is less than $\frac{10}{9}$ Vc the heat requirement to produce expansion at constant pressure will be greater than that for an ideal gas. For V greater than $\frac{10}{9}$ Vc, this situation will be reversed. Clearly for a given volume expansion less energy will be required if a lesser mass is expanded to a greater specific volume.

Equation (D-39) integrates at once to

$$Q = p_e(V_2 - V_1) + \left[\frac{5}{2} p_e(V_2 - V_1) + \frac{3a}{2}\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - \frac{5ab}{2}\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right)\right] \tag{D-40}$$

Here, the first term in the bracket is simply the increase in kinetic energy of the ideal gas.

We now compute the difference, caused by nonideal behavior, between the amount of heat required to heat the entire mass uniformly to achieve a 2-percent expansion and that required to double the volume of 2 percent of the mass leaving the remainder of the gas at the initial temperature and specific volume. In each case we allow expansion to occur so as to maintain constant p_e. We begin with

$$V_1 = 1.00 \text{ cm}^3/\text{g}.$$

We substitute for a and b from equations (D-36(a)) and (D-36(b)) and find that for each gram contained this difference is

$$\begin{aligned} &- 29.8[1.00 - 0.98] + 39.0[1.00 - 0.96] \\ &+ 0.596[1 - 0.50] - 0.780[1.00 - 0.25] \\ &= 0.975 \text{ cal/g} \end{aligned}$$

Enthalpy-pressure charts are available for oxygen. For hydrogen, nitrogen, and helium, the charts are in the entropy-temperature format. In the high-density supercritical region it is not possible to estimate the pressure drop with any precision. However, we see no reason to assume that stirring will not be equally important in the case of the hydrogen tanks.

The question of using heaters without simultaneous mixing raises a number of serious questions. One relates to the rate at which the heat will be conducted away from the source of heat. In this regard the dominant term for the flow of heat away from an instantaneous line source is

$$\mathrm{Exp}\ (-r^2/4Kt)$$

where K is the diffusivity. As a means of estimating the order of magnitude of K, we note that at STP for air $K = 0.187\ \mathrm{cm}^2/\mathrm{sec}$. In the diffusivity $K = K/c$, we find K the conductivity of the gas is independent of pressure; the specific heat c is independent of the density. We refer to the enthalpy-pressure chart and correct for density p only and conclude that at 0° C and 900 psi

$$K = 0.187 \times \frac{11}{630} = 3.3 \times 10^{-3}\ \mathrm{cm}^2/\mathrm{sec}$$

At lower temperatures, K will tend to be even lower at 900 psi. On setting $t = 3600$ seconds (i.e., 1 hour) we find that the temperature rise will be $1/e$ of the axial rise at a radius $r = 7$ cm. The conclusion is that if one does not stir hot gas will accumulate around the heater.

Consider the consequences of failure to mix. As heat flows away from the heater its effectiveness in maintaining pressurization falls off. One can imagine a situation half way through the mission in which half the oxygen has been used and in which the bulk of the tank is characterized by a specific volume of 2 cm^3/g. If local heating of 2 percent of the volume is then used to expel 12 percent of the remaining volume (equivalent to 6 percent of the initial contents) over a period of a few hours, the temperature of the gas around the heater will be approximately +20° C.

If the thrusters are now used, the gases will move convectively in such a direction as to bring this oxygen at 900 psi and 20° C into direct contact with the Teflon in the dome. This would be a very dangerous event, and there is no assurance that even hotter oxygen might not be encountered in practice (if 8 percent rather than 6 percent of the original filling were expelled in this fashion, the temperature of the hot oxygen bubble would be about 100° C).

It is certain that any attempt to dispense with mixing would be to court disaster. The more thorough and continuous the mixing can be, the more stable performance one can expect.

An Absolute-Density Gage

At Arthur D. Little, Inc., we have explored rather thoroughly the feasibility of measuring fluid density by a technique which is independent of gravitational effects. The principle invoked in these studies is to note that when a sphere is vibrated in a fluid it behaves as though its inertial mass is equal to its own mass plus exactly half of the mass of the fluid it displaces.

The excitation of the system is done by means of a servocontrolled frequency which forces the ball to oscillate in a resonant state where resonance is defined, not in terms of the amplitude maximum but rather in terms of having zero phase difference between the oscillating motion and the driving force. For this condition the density of the fluid is uniquely and sensitively related to the resonant frequency and the resonant frequency is independent of the viscous forces.

We have studied both transverse and torsionally-driven oscillations as candidate density gages. Both approaches can lead to satisfactory instruments.

Should this matter of a density gage which is independent of gravity be of interest to NASA we will be happy to provide further details.

Experiments to investigate the appearance and dissolution of molecular clusters must be carried out very slowly; temperature changes at the rate of 0.01° K per hour do not lead to reversible results. A brief summary of behavior in the vicinity of the critical point is found in "Molecular Theory of Gases and Liquids" by Hirschfelder, Curtiss, and Bird.

THE MINIMUM ENERGY REQUIRED TO IGNITE A COMBUSTIBLE GAS MIXTURE IN ZERO GRAVITY

In view of the possibility of combustible mixtures, such as oxygen and Teflon vapor, it is of some interest to know what minimum energy must be supplied to such a mixture, for example in the form of a spark, to cause ignition. This memorandum is based on ideas contributed by Dr. W. E. Gordon of Pennsylvania State College in a telephone conversation on May 20, 1970.

Two conditions are necessary for ignition: the energy supplied must raise the temperature of a volume of the mixture above the ignition temperature, and the heated volume must exceed a certain critical size.

The critical volume V must have a radius comparable with the thickness of the flame front η_o that develops after ignition. Thus,

$$V = \frac{4\pi}{3} \eta_o^3 \tag{D-41}$$

The reason for this requirement is that if the heated volume were smaller, the additional heat developed by the reacting gases would flow away so quickly from the hot spot by conduction that the rate of heat loss would be larger than the rate of heat generation and a propagating flame would not develop.

The magnitude of the flame front thickness η_o is such that the forward heat flow by conduction into the cold unreacted gas at temperature T_o is just enough to raise its temperature to the flame temperature T_f, i.e.,

$$K\left(\frac{T_f - T_o}{\eta_o}\right) = C\rho v_f\left(T_f - T_o\right) \tag{D-42}$$

where v_f is the flame velocity, and K, C, ρ are the conductivity, specific heat, and density of the unreacted gas. Therefore,

$$\eta_o = \frac{K}{C\rho V} \qquad \text{(D-43)}$$

The flame velocity v_f depends on the rate of heat generation in the reaction and on the thermal mass of the gas.

The energy E_i needed for ignition is the energy to raise the temperature of the volume V from T_o to T_f.

$$E_i = C\rho V\left(T_f - T_o\right) \qquad \text{(D-44)}$$

From equations (D-41) and (D-42), this becomes

$$E_i = \frac{4\pi}{3} \frac{K^3\left(T_f - T_o\right)}{C^2\rho^2 v_f^3} \qquad \text{(D-45)}$$

Since the quantities T_f, v_f, K, and C vary only slowly with pressure p and ρ varies directly with pressure, we see that

$$E_i \propto \frac{1}{p^2} \qquad \text{(D-46)}$$

This relation shows that at 60 atmospheres pressure the energy needed to initiate a flame in a combustible mixture is a factor of 3600 less than at 1 atmosphere.

The $1/p^2$ law derived here agrees with experimental data on ignition by sparks reported by Lewis and von Elbe, Combustion, Flames, and Explosions of Gases (Academic Press, Inc., New York, 1961) p. 328, at the low end of their pressure range, where the conditions should approximate those of zero gravity because buoyant forces are relatively less important at low pressures.

ON THE MYTH OF LARGE ENERGY STORAGE AND RELEASE AT THE CRITICAL POINT

The purpose of this memorandum is to dispel the myth that fluids at or near their critical points can store tremendous amounts of energy that can be released explosively by means of a suitable trigger. This belief seems to have arisen from such critical-point phenomena as opalescence, zero velocity of sound, infinite specific heat, and hysteresis.

In discussing this question, we must distinguish clearly between equilibrium and nonequilibrium states of the fluid. The case of nonequilibrium states is discussed in the memorandum entitled "The Possibility of a Catastrophic Pressure Fluctuation in a Near Critical Point Fluid."

An equilibrium state is one that has a single well-defined temperature and maximum entropy for the given value of the internal energy. Spatial fluctuations of thermodynamic variables, such as density, take place as the fluid changes from one to another of the vast number of states having the same energy.

Fluctuations of density are relatively large, both in magnitude and in cell size because the compressibility $(\partial V/\partial p)_T/V$ is infinite at the critical point; i.e., the critical isotherm is horizontal at this point on the p, V diagram.

The infinite compressibility means that if a movable piston is inserted in a vessel containing gas at the critical point so as to separate the gas into two regions, the piston can be moved a small distance with zero force. The result is that the density of the gas is increased in one region and decreased in the other, but the total internal energy of the system is unchanged and the temperatures and pressures in the two regions are unchanged. However, the internal energy in the compressed gas is increased and that of the expanded gas decreased by the same amount. This is essentially the process that occurs spontaneously in a gas at the critical point but in a multitude of cells. The situation can be described as one of neutral equilibrium in which displacements call for no application of force, and from which one cannot extract useful energy. In fact, the change in free energy ΔF in each cell of the system is zero because $\Delta F = V\Delta p - S\Delta T$ and Δp, ΔT are both zero along the critical isotherm at the critical point.

A mechanical system of two equal weights suspended on a frictionless pulley is a close analogy to the critical point system with two compartments and a piston. The weights can be moved up and down without effort, but the gravitational potential difference between the weights cannot be converted into work.

The various configurations of cells of differing density and specific internal energy but essentially the same pressure and temperature can be called quasi-static states of the gas at the critical point. These quasi-static states all have the same total internal energy and change slowly from one to another because of the condition of neutral equilibrium of the system in which there is no driving force. This circumstance accounts for the hysteresis effects that are observed near the critical point.

We have been discussing effects that arise from small displacements along the critical isotherm on the p, V diagram. We now consider whether large amounts of energy can be absorbed or released in small displacements from the critical points at right angles to the critical isotherm, i.e., along the constant volume line passing through the critical point. The quantity of interest here is C_v the specific heat at constant volume. Measurements by Bagatskii, Voronel', and Gusak (Soviet Physics JETP 16, No. 2, pp. 517-518, Feb. 1963) for argon show that C_v is infinite at the critical point, which might lead one to think that infinite energy storage is possible at the critical point. What matters however is not C_v itself, but the area under the C_v compared with T curve, which gives the increment in internal energy. On determining the area under the graph of the C_v spike, published by the Russian authors, from 1° C below the critical point up to the critical point, we find that the change in internal energy of argon is $\Delta E = 0.09$ cal/g. From the critical point to 1° C above it, we find $\Delta E = 0.04$ cal/g. These values show that although C_v is infinite at the critical point the energy differences involved in heating the fluid through the critical point are quite negligible.

TEMPERATURE CORRECTION OF QUANTITY GAGE AND PRESSURE PULSE ON INITIATING STIRRING

It is not possible, with the limited amount of information available to us, to account in a quantitative way for the required 15° addition to the measured temperature in determining the content of the tank from the quantity gage under zero-g conditions. However, it would appear that this may be a very real effect attributable to heat leakage along the quantity probe. As the oxygen supply becomes depleted, the heaters will be turned on at more frequent intervals; thus, there will be a shorter time for the temperature to build up between successive periods of mixing. This will tend to compensate for the fall in heat capacity of the fluid contained in the probe. Any heat leakage along the probe will also tend to raise the temperature recorded by the thermistor, because, in the absence of convection, local temperature rise can be appreciable.

The fact that the pressure exhibits a sharp drop of the order of 12 psi each time the stirring motors are turned on is compatible with the hypothesis that local heating occurs within the bulk of the liquid.

One could perform a fairly accurate check on this hypothesis by examining the recorded temperature which produces the 900 psi pressurization at various stages of depletion during the flight. Early in the consumption when the specific volume is 1.2 cc/g, an error of 10° K in the temperature would imply an erroneous specific volume of 1.44 cc/g.

APPENDIX E

Chemistry and Thermochemistry of Fluids in the Critical and Supercritical Regions

prepared for

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by

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ARTHUR D. LITTLE, INC.
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Table of Contents

CHEMISTRY AND THERMOCHEMISTRY OF FLUIDS IN THE CRITICAL AND SUPERCRITICAL REGIONS

I. INTRODUCTION

The purpose of this memorandum is to consider the possible effects of space-related conditions on the hazardous behavior of fluids carried aboard the Apollo and LM spacecraft. Special regard is given to chemical behavior as it may be modified by critical or supercritical conditions, by zero-gravity, or by combinations of hazardous materials. This scope corresponds to Part B of the task outline contained in the letter of May 12 from R. C. Ried, Deputy Director, Panel 7, to E. S. Shanley.

The bulk of this discussion covers the behavior of the supercritical oxygen storage system. The nitrogen tetroxide, Aerozine-50, and monomethyl hydrazine systems are not near the critical point, although some of the remarks about behavior in zero gravity may apply also to these materials. Hydrogen is considered with reference to possible combustion reactions with Teflon. Helium, nitrogen, and water are considered inert for the purpose of this discussion.

In addition to various members of the Arthur D. Little, Inc., staff, we are grateful to Professor William E. Gordon of Pennsylvania State University, Professor George B. Kistiakowsky of Harvard, and Professor Regio Pelloux of M.I.T. for their contributions and discussion.

II. SUMMARY

We find that the major hazards of these systems are associated with potential chemical reactions in the oxygen system and possibly also in the hydrogen system. In the oxygen system, both the Teflon insulation and many of the metals used are potential fuels; only an ignition source of sufficient energy is required to start combustion. In the hydrogen system, the Teflon insulation is thermodynamically unstable with respect to hydrogen fluoride and carbon. The monomer of Teflon, C_2F_4, is known to burn with hydrogen.

The fact that these fluids are near critical conditions poses no special hazard peculiar to these conditions. Both the high pressure and the gravity-free environment, however, probably will increase the ease of ignition of Teflon in these environments. In addition, there is evidence to indicate that Teflon may be a particularly efficient source of ignition for aluminum and other metals, because the decomposition products of Teflon tend to remove the protective oxide from these metals. Several mechanisms exist for rapid flame propagation even in a gravity-free environment.

We recommend that both fuels and potential sources of ignition be removed as far as possible from these fluid systems. If these hazards are retained, testing should be done in a gravity-free environment, and with the particular combinations of material (especially Teflon with metals) used in the spacecraft systems.

III. EFFECTS OF CRITICAL OR NEAR CRITICAL CONDITIONS ON CHEMICAL REACTIONS

Since the effects observed in the critical region of oxygen (and other fluids) are a function of relatively weak intermolecular or van der Waals forces, no direct effects of criticality are to be expected on its chemical reactivity, which involves much more energetic primary chemical bonds. We have obtained no indications of any such effect either from the literature or from discussion with a number of qualified physical chemists.

One possible physical effect which we have considered is the very large coefficient of thermal expansion of a gas in the critical region. It has been suggested that, in a gravity-free environment, this expansion may tend to create forced convection or increased mixing which would increase the combustion rate in the critical region. It should be noted, however, that in this same region the specific heat of the gas also becomes very large(1), so that a given heat input will produce only a small increase in temperature. Thus, the two effects tend to cancel and no markedly different combustion behavior is to be expected in the critical region even in the absence of gravity.

IV. EFFECTS OF HIGH-PRESSURE ON ACTIVATION ENERGY

As is well known, pressure will shift the equilibrium of a chemical reaction during which a volume change takes place. Also, pressure can change the effective concentration of a gaseous reactant, and thus alter its reaction rate. There is little information, however, about possible effects of pressure on the activation energy itself. Bridgman(2) cites studies of the effect of pressures up to about 500 atm. on the hydrolysis of esters in aqueous acid. Increases of about 20% in reaction rate are observed at these pressures but this is largely attributable to increased ionization of the acid under pressure. If any change in activation energy takes place at these pressures, the effect must be very small. To the extent that oxygen can be considered analogous with these systems, no appreciable effect on activation energy is to be expected, since we are dealing only with pressures of the order to 70 atmospheres.

Molecular oxygen is known to dimerize to the molecule O_4 under high pressure. The suggestion has been put forth that this molecule may dissociate into ozone and atomic oxygen, both of which are vigorous oxidizing agents. Sidgwick(3), however, points out that the heat of dimerization is only 0.13 kcal/mole and must be due to some kind of van der Waals force. Under these conditions, we consider a dissociation into the highly energetic species ozone and atomic oxygen to be extremely unlikely. Sidgwick points out that O_4 has no more oxidizing power than ordinary diatomic oxygen.

V. EFFECTS OF SPACECRAFT CONDITIONS ON EASE OF IGNITION

A. GENERAL

In this section, we consider possible special effects which spacecraft conditions may have on ignition processes in fluid storage systems. The possibility of ignition implies that these systems are chemically unstable and the oxygen system is undoubtedly the greatest hazard in this respect. The oxygen system is considered in detail in sections B and C below.

It should be also noted, however, that Teflon is chemically unstable with respect to HF and carbon in the presence of hydrogen. The data of Duus(4) permit us to estimate that the heat evolution will be 80.5 kcal per C_2F_4 unit for hydrogenation of this polymer. Duus also observed that a mixture of C_2F_4 (monomer) and hydrogen could be ignited by a hot carbon rod, and that the subsequent reaction was complete enough to provide the basis for calorimetric measurements. In the case of the monomer, the heat evolved is somewhat larger, amounting to about 128.8 kcal per mole of C_2F_4. These figures indicate that Teflon polymer must be considered as a potential fuel in a hydrogen environment.

With regard to possible ignition conditions, it should be noted that the Teflon-covered nickel wires may have a catalytic effect on the ignition since nickel is a well known hydrogenation catalyst. It is possible, for example, to visualize a sequence of events in which such a wire becomes overheated by a short circuit and pyrolyzes some of the Teflon jacket into tetrafluoroethylene monomer, which becomes ignited in the presence of the hot nickel surface. As discussed in section B below, a gravity-free environment may facilitate the ignition process. Once the ignition has taken place, it is expected that the combustion may spread along the wires with a large release of energy.

We recommend that this potential hazard be evaluated.

B. IGNITION OF TEFLON IN OXYGEN

In this and the following section, we take the point of view that the most likely sequence of combustion events in the oxygen system is the direct ignition of the Teflon components followed by the spread of the combustion to the metallic components. This is not to say that we consider the direct ignition of the metals an impossibility, but only that, other things being equal, the metals will require higher temperatures and more energy for ignition.

The major factors contributing to the ignition of Teflon in the spacecraft oxygen system are probably the high pressure and the absence of gravity. As stated above, the fact that the oxygen is near its critical point is not expected to have any direct effect on its chemical reactivity. Some data for the ignition of Teflon in oxygen at various pressures are available; the evidence for a possible gravity effect on ignition is indirect and is inferred by analogy to other systems.

The effect of increasing pressure in reducing the minimum ignition energy of gaseous mixtures is well known. For such systems the minimum instantaneous ignition energy varies as $1/p^2$(5)*. For the ignition of solids in high pressure oxygen the ignition energy is usually not measured. The ignition temperature may reach a plateau as pressure is increased.

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* See Appendix for further discussion of the ignition energy.

Guter(6) has measured the ignition temperature of Teflon (TFE) in slowly flowing oxygen at atmospheric pressure. At 520°C, he observed no ignition; at 530°C, ignition took place in 60 to 70 seconds, and at 550°C, ignition took place in about 30 seconds. Nihart and Smith(7) observed an ignition temperature of 469°C in oxygen at 2650 PSI and of 474°C at 7870 PSI. Marzani(8) found an ignition temperature of 462°C in oxygen at 4025 PSI. These data indicate that TFE probably attains its minimum ignition of around 460-470°C in the pressure region between atmospheric and 2000 PSI. Marzani considers the ignition process to take place in the gas phase as a result of the reaction of oxygen with gaseous pyrolysis products from the polymer.

An effect of gravitational field on the apparent ignition temperature of a gas mixture is to be inferred from a consideration of the nature of the ignition process. If we consider a small volume of gas (the ignition volume) containing an ignition source (for example a hot wire), we may write a heat balance over this volume in the following form:

$$Q_s + Q_r + Q_\ell$$

where Q_s is the heat added from the ignition source, Q_r is the heat generated by chemical reaction in the ignition volume, and Q_ℓ is the heat loss, which will occur mainly by convection of the heated gas. Q_r will, of course, be a strong function of temperature, and when the temperature becomes high enough so that Q_s plus Q_r can overcome the heat loss, the gas will ignite.

The important point to note here is that both Q_r and Q_ℓ are affected by convection, but that the effects are in opposite directions. Q_r may be increased by a moderate amount of convection since fresh reactants are brought to the reaction zone. Q_ℓ always represents a loss of heat and will be brought to a minimum in the absence of a gravitational field.

The effect of convection on ignition temperature has been studied by Guest(9) using a mixture of natural gas and air. He finds that the use of baffles or downward gas currents (which tend to oppose natural convection) around a heated bar will lower the apparent ignition temperature, sometimes by several hundred degrees centigrade. Under spacecraft conditions, especially with cold, high-density oxygen, we believe that convective effects will be even more important than at normal atmospheric pressure. For this reason, any test program which fails to take account of zero-gravity effects will probably be entirely inadequate.

C. IGNITION OF METALS BY FLUOROCARBONS

Because of its large heat of combustion, we consider aluminum to be potentially one of the most dangerous materials used in the spacecraft oxygen system. Because of its protective layer of high-melting oxide, however, aluminum is usually very difficult to ignite in an oxygen environment. For example, von Grosse and Conway(10) report an ignition temperature greater than 1000°C for aluminum in air. In the presence of carbon, however, the ignition and combustion of aluminum is facilitated because the carbon tends to reduce the refractory oxide layer. The same is true of the presence of fluorides since fluorine compounds tend to flux the refractory layer of Al_2O_3. It is notable that the melting point of Al_2O_3 is 2015°C vs 1040°C for AlF_3. Teflon, containing both fluorine and carbon, should therefore be an efficient ignition source for aluminum as well as for other metals.

We have demonstrated that this is in fact the case by a simple laboratory experiment using a natural-gas fed Bunsen burner as the ignition source. If the Bunsen flame is held against a small pile of aluminum powder on a firebrick for several minutes, the surface of the pile becomes red hot but no ignition takes place. If the experiment is repeated with aluminum containing a little powdered Teflon, however, the pile ignites with a bright flash in 5 to 10 seconds. We therefore consider that Teflon in the proximity of aluminum and other metals is a particularly dangerous source of ignition.

VI. EFFECT OF SPACECRAFT CONDITIONS ON REACTION RATE AND FLAME PROPAGATION

We have found no data on the combustion of fuels with oxygen in the vicinity of its critical point. The reverse case, namely the burning of oil drops above and below the critical point in high-pressure air, has been studied by Faeth et al.(11) under gravity-free conditions in a freely-falling chamber. These authors find that the droplet lifetime decreases monotonically with pressure up to the critical pressure. Above this point the droplet lifetime increased roughly in proportion to the cube root of the pressure. It is not obvious that this case applies to the spacecraft conditions, but the data at least indicate that no unusual or unpredictable phenomena occur in the critical region.

The absence of gravity is probably the greatest factor in determining combustion behavior in the spacecraft oxygen system. It is now generally recognized(12, 13) that combustion is retarded in the absence of gravity due to lack of convective mixing. In the supercritical oxygen system, however, there are several factors operating which tend to accelerate the combustion despite the lack of gravity. The first of these factors is the high pressure and density of the oxygen. Because of this, only a small motion of the fluid will be required to bring in enough oxygen to support combustion. Such motion could be produced, for example, by the stirring mechanisms in the container or by small local accelerations due to ignition.

The second factor is that extended surfaces, such as paper, string, or insulated wire, can continue to propagate combustion because the flame front moves along the surface into a region where the oxidizer is not depleted.

The third factor is that if combustion takes place in a partially enclosed space, such as a tube with one end closed, the expanding fluid can produce forced convection currents which will be highly effective in fanning the combustion.

We conclude that the gravity-free environment is no reliable defense against violent combustion in these systems.

VII. TEST METHODS FOR POTENTIALLY FLAMMABLE MATERIALS IN HIGH-PRESSURE FLUIDS

As stated above, we consider the current test procedures to be inadequate in several respects for predicting the hazards in spacecraft fluid systems. In particular, we recommend the following tests.

1. The ignition of Teflon in supercritical oxygen should be studied in a gravity free environment. As stated in section V above, there are reasons for believing that the absence of gravity will render ignition much easier under these conditions. Tests should be made of the effects of heavy currents or simulated short circuits on Teflon insulated wires, and of the effects of sparking such as might be caused by the grounding of a wire with faulty insulation.
2. The same type of tests should be conducted in supercritical hydrogen to determine if Teflon will ignite and support combustion under these conditions.
3. Tests should be conducted with the same combinations of materials as are used in the spacecraft system. We consider the proximity of Teflon to aluminum and other metals to be particularly hazardous. The ignition of metals by burning Teflon in oxygen should be studied. In hydrogen, there appears to be little hazard of metal ignition.

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APPENDIX

THE MINIMUM ENERGY REQUIRED TO IGNITE A COMBUSTIBLE GAS MIXTURE IN ZERO GRAVITY

(The following derivation was communicated via telephone by Dr. William E. Gordon. Because of the pressure of time, Dr. Gordon has not had the opportunity of reviewing this manuscript.)

In view of the possible formation of combustible mixtures, such as oxygen and Teflon vapor in the spacecraft, it is of some interest to know what minimum energy must be supplied to such a mixture, for example, in the form of a spark, to cause ignition.

Two conditions are necessary for ignition--the energy supplied must raise the temperature of a volume of the mixture above the ignition temperature and the heated volume must exceed a certain critical size.

The critical volume v must have a radius comparable with the thickness of the flame front η_o that develops after ignition. Thus

$$V = \frac{4\pi}{3} \eta_o^3 \qquad (1)$$

The reason for this requirement is that if the heated volume were smaller, the additional heat developed by the reacting gases would flow away so quickly from the hot spot by conducting that the rate of heat loss would be larger than the rate of heat generation and a propagating flame would not develop.

The magnitude of the flame front thickness η_o is such that the forward heat flow by conduction into the cold unreacted gas at temperature T_o is just enough to raise its temperature to the flame temperature T_f, i.e.,

$$K \left(\frac{T_f - T_o}{\eta_o} \right) = C \rho v_f (T_f - T_o) \qquad (2)$$

where v_f is the flame velocity, and K, C, ρ are the conductivity, specific heat, and density of the unreacted gas. Therefore,

$$\eta_o = \frac{K}{C \rho v_f} \tag{3}$$

The flame velocity v_f depends on the rate of heat generation in the reaction and on the thermal mass of the gas.

The energy E_i needed for ignition is the energy to raise the temperature of the volume V from T_o to T_f:

$$E_i = C \rho V(T_f - T_o) \tag{4}$$

From (1) and (2) this becomes

$$E_i = \frac{4\pi}{3} \frac{K^3(T_f - T_o)}{C^2 \rho^2 v_f^3} \tag{5}$$

Since the quantities T_f, v_f, K, and C vary only slowly with pressure p and ρ varies directly with pressure, we see that

$$E_i \propto \frac{1}{p^2} \tag{6}$$

This relation shows that at 60 atmospheres pressure the energy needed to initiate a flame in a combustible mixture is a factor of 3600 less than at 1 atmosphere.

The $1/p^2$ law derived here agrees with experimental data on ignition by sparks reported by Lewis and von Elbe, Combustion, Flames and Explosions of Gases (Academic Press, Inc., New York, 1961) p. 328, at the low end of their pressure range where the conditions should approximate those of zero gravity since buoyant forces are relatively less important at low pressures.

APPENDIX F

An Assessment of the Hazardous Aspects of Storage and Handling of Oxidizers and Fuels used in Apollo and LM Systems

prepared for

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APPENDIX F

AN ASSESSMENT OF THE HAZARDOUS ASPECTS OF STORAGE AND HANDLING OF OXIDIZERS AND FUELS USED IN APOLLO AND LM SYSTEMS

I. INTRODUCTION

This is a review of the materials carried in the Apollo and LM vehicles with regard to hazards from inadvertent reaction. It corresponds with Part C of the task outline contained in the May 12 letter from R. C. Ried, Deputy Director, Panel 7, to E. S. Shanley.

This discussion covers oxygen, nitrogen tetroxide, hydrogen, Aerozine-50 and monomethyl hydrazine. The treatment is based on normal chemical considerations without regard for any special properties of critical state materials, the effects of zero gravity, or other space-related phenomena.

Helium, nitrogen, and water also carried on these vehicles are non-reactive and of no concern for the purpose of this discussion.

II. SUMMARY

Consideration of the materials carried on Apollo and LM indicates that the significant chemical hazards are posed by oxygen and the hydrazines.

The hazards of oxygen although widely known are frequently underestimated. Oxygen is vigorously reactive with almost all materials of construction including its own containers and piping systems.

In the ultimate, safety rests solely in the ability to eliminate all possible sources of ignition. Inclusion of electrical wiring in high-pressure oxygen systems is an example of extremely hazardous design. Two hydrazine compositions are carried in Apollo and LM: Aerozine-50 and monomethyl hydrazine. These materials have a good record of safety in use. Nevertheless, each is highly unstable by itself. Calculated heat of decomposition of Aerozine-50 liquid to the most stable gaseous products is about 1450 BTU per pound. The value for monomethyl hydrazine is almost the same. In the thermochemical sense these materials are less stable than ammonium nitrate, 100% hydrogen peroxide, or nitromethane. Our study thus far leaves open the possibility that the hydrazines may be capable of violent decomposition through the effects of some as-yet unknown initiating mechanism.

III. OXIDANTS

A. GENERAL

Chemical hazards, aside from toxicity, are related to uncontrolled release of energy. It is a common observation that oxidants are more frequently involved in accidental energy release than are fuels and reducing agents. This circumstance results from the fact that many oxidizing agents contain stored chemical energy which is subject to rapid release under some conditions. Beyond this, oxidizing agents are reactive or potentially reactive with many structural materials.

Virtually all metals, organic compounds, polymers and plastics are subject to oxidation accompanied by more or less substantial energy release. Accordingly, a system composed of an oxidizing agent and its container is usually thermochemically unstable and subject to spontaneous reaction. At the present state of the art, it is not possible to build tanks, gauges, and piping systems of unoxidizable materials such as glass or ceramics. Recourse must be had to selection of materials which are relatively difficult to ignite and which react least vigorously with the oxidant. Beyond this, means are adapted to eliminate ignition sources. Given this sort of evolution, oxidizing agents are handled with relative safety. However, the history is generously sprinkled with accidents of greater or less severity. It is salutory to bear in mind that every metallic or plastic container filled with an oxidant is an energetic reaction system in a meta-stable condition. Each such system is capable of more or less rapid energy release accompanied by destruction of the container if a suitable ignition source is provided.

It is not possible to specify exactly the nature or magnitude of a suitable ignition source. Ease of ignition is not an intrinsic property but depends on state of sub-division, presence of foreign materials, and on other circumstances. For example, structural metals generally burn in oxygen only after heating to relatively high temperature. However, iron, lead, nickel, and many other metals ignite spontaneously in air if sufficiently finely divided. Foreign materials frequently exert a profound effect on the rate of oxidation reactions. Metals and metal oxides frequently increase the rate of reaction between oxidants and combustible matter and can lead to spontaneous reaction at room temperature.

We have found little information on the effect of foreign materials acting as catalysts for the oxidation of metals. However, it is prudent to assume that such effects may exist. Accordingly, one should design containers for oxidizers in a way that facilitates rigorous cleaning. Further, the number and variety of materials exposed to the oxidant should be held to an absolute minimum, since the possibility of unanticipated cooperative reactions can not be ruled out.

B. OXYGEN

The literature on oxygen hazards is very extensive and not reassuring. Oxygen handling systems are plagued by accidental fires. Most of these occur in the gas as opposed to the liquid. The combustion process frequently involves the materials of construction of the handling system. Organic contaminants in trace amounts are frequently cited as intermediate, easily ignited fuel which served as a sort of kindling.

Table 1 contains information on the heat of reaction of oxygen with various materials, together with other information. In general, materials with low heats of combustion are to be preferred to those with higher heat release. Materials with high ignition temperatures are at least somewhat safer from accidental ignition. Materials which melt before reaching ignition temperature are considered safer than materials which hold their shape and position until ignition occurs. Ignition

TABLE 1

Oxidation Properties of Some Common Materials

Material	Oxidation Product	Heat Released BTU/lb. of Material Burned	Ignition* Temp.°F	M.P. °F
Aluminum	Al_2O_3	12,650	>1830**	1220
Copper	CuO	1,100	1982***	1982
Iron	Fe_2O_3	3,200	1710	2885
Nickel	NiO	1,800	--	2642
Lead	PbO	450	1600	620
Palladium	PdO	167	--	2822
Platinum	PtO	81	--	3254
Tin	SnO_2	2,110	1590	448
Titanium	TiO_2	8,200	1130	3272
Silver	Ag_2O	115		1742
Zinc	ZnO	2,280	1650	786
Teflon	$CO_2 + CF_4$	1,980	985	
Hydrogen	H_2O (g)	52,000	1085	
Fuel Oil	$H_2O(g) + CO_2$	18,000	500 (approx)	
Coal	CO_2	14,000	500 (approx)	

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* Data for metals mostly taken from von Grosse, Ind. Eng. Chem., 50, 663(1958). Values are somewhat variable.

**Variable figures are reported for aluminum.

***An oxygen at 1 atm. Graves, W.E., Iron and Steel Engr., 988 (Jan., 1965).

temperature, as noted above, is highly dependent on state of subdivision, purity, and presence of foreign materials. The values quoted in Table 1 are for relatively pure, massive material.

Oxygen systems are actually designed on the basis of empirical information and experience. However, history indicates that designers continually underestimate the hazards of oxygen. Perhaps familiarity and non-toxicity lead easily to relaxation of vigilance. Also, oxygen and combustible materials frequently exhibit no signs of reaction at all until some initiation is provided. Once started, the reaction often proves to be violent and destructive. In this connection it is necessary to continually stress the vulnerability of organic materials in oxygen. Organic compositions almost without exception are subject to spontaneous reaction with oxygen. Ignition temperature may be low or moderate. Small quantities of organic matter have frequently served to initiate reaction between oxygen and structural elements. It is worth noting that even poly(tetrafluoroethylene) one of the most chemically inert of organic compositions, burns rather readily in oxygen and releases as much heat as many metals.

High oxygen pressure lowers the ignition temperature of many materials. Outbreak of fire is infrequent in completely static systems. The initiation process is usually associated with some change, such as first pressurization of a pipe or vessel, pressure surge leading to adiabatic compression and high temperature in the gas phase, high velocity impact due to particulates in the gas stream, static discharge or inadvertent external heating. C. H. Reynales (2) has cited eight more or less well-established causes of accidental fires in oxygen equipment of which the above are typical.

There is no dependable standard procedure for testing materials in oxygen. Rather, it is necessary to devise tests which simulate normal use conditions and also the worst anticipated conditions. To the extent possible, whole configurations should be tested, since it is not possible to anticipate all of the interactions that may occur. In thinking about test methods, it is useful to bear in mind that most initiation is ultimately thermal in nature. Thermal excitation can be provided in various ways as by adiabatic compression, a shock wave, an electric spark or short circuit, and so on. The rate of temperature rise and the amount of initiating energy delivered are the most important distinbuishing factors.

The Apollo EPS oxygen system inevitably involves most of the usual hazards of high pressure oxygen systems. Much of the system is cold, which provides a certain amount of protection against local hot spots. Important increases in safety margin will depend upon the following changes:

- Rigorous limitation of the amount and variety of material exposed to high pressure oxygen.
- Exclusion of possible sources of high temprature in the high pressure oxygen system. Electrical power wiring in an oxygen container is an extreme example of hazardous design.

- Exclusion of relatively easily ignitable materials, such as Teflon, other polymers or plastics, and all other organic materials. All such materials may serve as starter fuels whose ignition may lead to combustion of the oxygen-containing structure itself.
- Careful attention to the design of reducing valves, shut-off systems, pop-off valves, and the like, to minimize the possibility of pressure surges and other mechanical effects which may lead to high temperature.

C. NITROGEN TETROXIDE

Nitrogen tetroxide, N_2O_4, is a thermochemically stable material; therefore, it has no potential for spontaneous decomposition. Spontaneous fires or violent reaction can result on mixing or contact between nitrogen tetroxide and combustible materials. Inadvertent mixing with hydrazine-type fuel would of course lead to spontaneous violent reaction. Spillage on combustible insulating material or other organic matter can lead to high fire risk.

Trace quantities of organic material are far less dangerous in N_2O_4 than in oxygen. Most lubricants, many polymers, and other organic materials likely to be found as contaminants are soluble in N_2O_4 and therefore experience dilution and dispersion in contact with this oxidizer. Further, most organic materials are oxidized or nitrated more or less rapidly on contact with N_2O_4 leading to an automatic cleaning process. By contrast, organic material can accumulate in oxygen systems, only to react violently upon some later initiation.

Nitrogen tetroxide in a metal container constitutes a thermochemically unstable system. However, common materials of construction such as stainless steel, plain steel, nickel and aluminum alloys do not seem to be subject to fast reaction with N_2O_4, even under adverse conditions. We have found no record of accidents involving rapid reaction of structural metals with this oxidant. The Apollo N_2O_4 tank is of a titanium alloy. Titanium is known to have excellent corrosion resistance to N_2O_4 and to nitric acid. It is highly probable that titanium is not subject to fast reaction with this oxidant, although we have not found documentation on this point.

The relatively low hazard potential implied above is borne out by many years of essentially incident-free experience with nitrogen tetroxide. Aside from mechanical failure of the tank or handling system, the nitrogen tetroxide poses no special safety problem in the Apollo system.

IV. FUELS

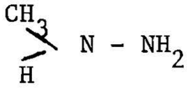
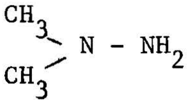
Most fuels are not capable of spontaneous decomposition. Thus hydrogen gas, hydrocarbons, and most combustible materials liberate heat only through reaction with oxygen or some other oxidizing agent. Further, such materials are not subject to reaction with common materials of construction. Tanks containing ordinary fuels including hydrogen are accordingly relatively free of chemical hazard. Fire risk of greater or less degree arises of course if leaks occur. Other than this and the usual mechanical hazards of pressure vessels, fuel tanks in general and the Apollo hydrogen tanks in particular are relatively free from chemical hazard.

The hydrazine family of fuels is exceptional in the fact that they contain a substantial amount of stored chemical energy. Table 2 below contains information. Decomposition to the elements results in substantial energy release, as indicated by positive values for heat of formation and free energy of formation.

It is likely that all of these materials decompose spontaneously to yield ammonia and/or ammonia derivatives, rather than the elements. Below are listed the energetically most favorable decomposition reactions together with estimates of heat yield.

TABLE 2

Properties of Hydrazine and Hydrazine Derivatives

Composition	Formula	Heat of Formation* of the Liquid From its Elements		Free Energy of* Formation of the Liquid from its Elements	
		K Cal/g mol	BTU/lb.	K Cal/g mol	BTU/lb.
Hydrazine	N_2H_4	+ 12.0	+ 675	+ 38.0	+ 2135
Monomethyl hydrazine	 $\genfrac{}{}{0pt}{}{CH_3}{H}\!\!>N - NH_2$	+ 12.7	+ 496	--	--
Dimethyl hydrazine UDMH	 $\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!\!>N - NH_2$	+ 12.74	+ 381	--	--
Aerozine 50	50% N_2H_4 50% UDMH	+ 12.25	+ 527.6	--	--

---

*Positive sign indicates absorption of energy on formation of the compound.

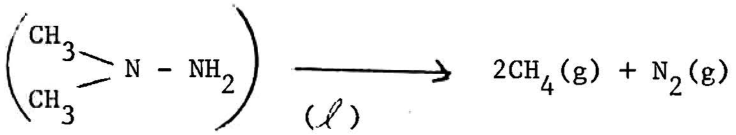
Hydrazine

$$3N_2H_4(\ell) \longrightarrow 4NH_3(g) + N_2(g)$$

$$\left.\begin{array}{l}\Delta H = -\ 837\ \text{Cal/g}\\ \qquad\ -\ 1445\ \text{BTU/lb.}\end{array}\right\}\ \text{of hydrazine decomposed}$$

$$\left.\begin{array}{l}\Delta F = -\ 1310\ \text{Cal/g}\\ \qquad\ -\ 2260\ \text{BTU/lb.}\end{array}\right\}\ \text{of hydrazine decomposed}$$

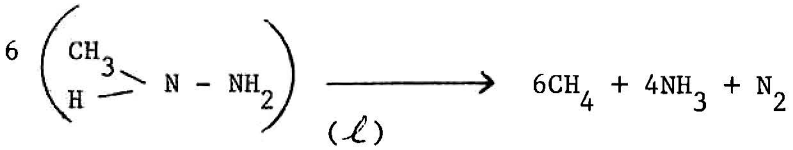
Dimethyl hydrazine



$$\left(\begin{array}{l}CH_3\\CH_3\end{array}\!\!>N-NH_2\right)_{(\ell)} \longrightarrow 2CH_4(g) + N_2(g)$$

$$\left.\begin{array}{l}\Delta H = -\ 810\ \text{Cal/g}\\ \qquad\ -\ 1460\ \text{BTU/lb.}\end{array}\right\}\ \text{Of UDMH decomposed}$$

Monomethyl hydrazine



$$6\left(\begin{array}{l}CH_3\\H\end{array}\!\!>N-NH_2\right)_{(\ell)} \longrightarrow 6CH_4 + 4NH_3 + N_2$$

$$\left.\begin{array}{l}\Delta H = -\ 823\ \text{Cal/g}\\ \qquad\ -\ 1480\ \text{BTU/lb.}\end{array}\right\}\ \text{of monomethyl hydrazine decomposed}$$

The reactions written are the most energetically favorable ones. Actual decomposition may not follow the suggested paths. Nevertheless, materials with such substantial possible heats of decomposition (and at least in the case of hydrazine, free energy of decomposition) must be viewed with some concern, regardless of the results of empirical testing.
For example, TNT releases about 1000 cal/g on explosion. Solid ammonium nitrate has a calculated heat of decomposition of about 355 cal/g to yield gaseous products. Hydrogen peroxide 100% yields about 370 cal/g on decomposition to gaseous products. Nitromethane yields a calculated heat of decomposition of about 630 cal/g. All of these materials can be brought to detonation, although some of them require strenuous initiation. All have been involved in highly destructive accidents.

It may be possible to develop additional understanding of hydrazine-family compounds by calculation of entropy changes in the explosion state. For example, it appears that explosion may fail to occur in some energy-rich materials because the entropy of the products in the explosion state would be less than that of the original compound. The entropy effect in question can occur only at extreme pressures and therefore pertains only to condensed-phase materials. The known detonability of hydrazine vapor is compatible with this idea but not diagnostic. The vapor would be expected to be considerably more sensitive than the liquid because the heat added in vaporization is large, i.e., 10.7 K cal/g mol (600 BTU/lb.).

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It would be possible to explore the entropy concept only through a considerable computation program.

We have not been able to search the hydrazine literature with great thoroughness. However, information on handling the hydrazines is based on a relatively limited number of original studies and a great deal of successful handling experience. This does not preclude the possibility that some unexpected initiation mechanism could exist for these highly unstable materials.

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APPENDIX G

COMMENTS ON SUPERCRITICAL OXYGEN TANK WIRING CONDUIT

prepared for

National Aeronautics and Space Administration
Manned Spacecraft Center
Houston, Texas 77058

by

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May 14, 1970

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Technical Memorandum

Supercritical Oxygen Tank Thermal Protection System Hazard

prepared for

National Aeronautics and Space Administration
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by

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22 May 1970

C-72563

APPENDIX G

During our visit to MSC on 28 and 29 April we attended on-going meetings of the Spacecraft Incident Investigation Committee in Building 25, Room 320. A duplicate of the service module supercritical oxygen tank was located in this conference area for us to look at. The domed portion of the vacuum vessel was removed to permit viewing of the opening into the interior of the tank and the components that were located in the dome space. We took particular note of the wiring conduit which contained the power leads for the fan motors and heaters and the instrument leads for the thermostats, compacitant gauge and thermistor temperature sensor. These leads feed through the vacuum shell in a hermetic seal which then pass into the oxygen vessel through a 1/2-inch (approximately) diameter tubing formed into a 10-inch coil with approximately 3 turns. The interior of the conduit is open to pressurized oxygen to the point of the hermetic seal. The conduit appears to be supported only at its ends where it is attached to the vacuum shell and to the oxygen inner-vessel. There appear to be no mechanical supports of this conduit at intermediate locations. We were told that the dome area of the vacuum vessel is filled with "chopped aluminized mylar" [probably tinsel] which may have filled the spaces around the coil.

One possible explanation for the power short is that the insulation on the power wires could have become abraded due to vibration of the conduit. We can conceive that the conduit, responding to the launch environment, can cause the rubbing of the power leads against one another with a subsequent loss of electrical insulation. This rubbing action could be enhanced if the conduit wires were installed under strain. The close proximity of any two power leads with reduced thickness of insulation can lead to a power short.

We feel that there are a number of unanswered questions about the conduit system. Its natural frequency, and deflections, for example, should be determined both by analysis and/or experiment. It is not known what dampening effect the mylar insulation located in the dome has on this conduit when the service module is subjected to the mechanical vibrations experienced at launch. Further, it is important to study the method of assembling the leads into the conduit, as the procedures may have introduced strains into these wires which could cause or increase insulation wear. These conditions could then have led to the situation where an initiation source of sufficient energy, produced by shorting of the power leads, ignited the surrounding teflon and then resulted in catastrophic failure of the oxygen storage vessel.

COMPATIBILITY TESTING OF MATERIALS FOR SPACECRAFT

Technical Memorandum

by

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May 20, 1970

C-72563

COMPATIBILITY TESTING OF MATERIALS FOR SPACECRAFT

Materials used in a spacecraft are currently being selected from an approved list. Materials in this list had undergone testing according to standard tests developed by or for NASA. These tests are basically related to the flammability of the material[1] and/or its compatability[2] with the gases and liquids to which it will be exposed. We feel that the tests were designed essentially for the purpose of selecting materials for use in the manned section of the spacecraft where the pressure is relatively low and oxygen is the only gas which is of concern. It is possible that materials passing these tests have been selected and used under different environmental conditions in other parts of the spacecraft and where they could present a hazardous situation. For example, an insulation which may be adequate for use in pure oxygen at 1 atm may be too flammable to use at high pressures in an oxygen storage tank. A metal which may be compatible with liquid oxygen by the standard drop-weight test at 1 atm, may fail a similar test performed in gaseous oxygen at 60 atm. We believe that the material/environment/test interrelationship should be examined more carefully in order to arrive at a better testing program, the results of which will serve as a more reliable basis for the selection of materials for use aboard spacecraft in the future.

Examination of all likely causes of accidents aboard the spacecraft should lead to a number of tests which will simulate possible hazardous situations and environments. Examples:

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1. For example, NASA, MSC, SN-P-003, "Procedures and Requirements for the Flammability and Off-gassing Evaluation of Spacecraft Nonmetallic Materials", January 15, 1968.

2. For example, NASA-MSFC-SPEC-106B, "Testing Compatibility of Materials for Liquid Oxygen Systems".

1. Two materials may be individually compatible with the environment, but taken together, they may no longer be acceptable (e.g., aluminum powder is difficult to ignite in air. Mixed with teflon powder, it becomes a dangerous squib). Teflon-insulated nickel and copper wires should thus be tested under the environment to which they will be exposed. Since shorting due to mechanical erosion is possible, the wires employed in the oxygen tank should have been tested by shorting in O_2 at 900 psi while carrying representative loads.

2. The jet of gas, liquid or aerosol emerging at sonic velocity from a crack or pinhole in the wall of a high pressure tank and impinging upon insulation or other adjacent objects may cause enough heating and erosion at the stagnation point for ignition to occur. A compatibility test could be easily designed for checking the effect of impingement of high velocity gas and liquid jets on materials.

3. Wire bundles are widely used in spacecraft. Since ignition temperatures of materials are generally lowered in oxygen atmospheres and especially at high pressures, and because of the absence of natural convection (cooling) currents in zero-gravity, it is quite possible for the internal temperatures of a bundle to rise to dangerous levels due to heat accumulation.

   A theoretical solution of the temperature profile in a realistic wire bundle is not easily attainable because of the complexity of the wire and load distribution. In general, all previous work has been limited to <u>homogeneous</u> bundles consisting of similar wires carrying similar loads.

We believe that the thermal behavior of actual wire bundles should be examined more carefully, particularly in reference to the distribution of high-load carrying wires. As an interim remedy to a possible cause of an accident aboard spacecraft, high-load carrying wires should be separated as far as possible and placed on the outside of the bundle. Tests should be designed to ascertain that no dangerous heat accumulation will occur in a wire bundle when each wire is allowed to carry the maximum possible electric load.

4. In going through the list of materials used in the oxygen tank, we noted a number of materials which are listed by NASA as noncompatible with liquid oxygen (e.g., Solder Tin-lead 60:40), yet being used in supercritical oxygen at 900 psi. It seems reasonable to assume that materials which are unacceptable for use in liquid oxygen at atmospheric pressure will also be unacceptable (if not more so) in 900 psi gaseous oxygen. Other materials which are satisfactory in liquid oxygen may prove unacceptable for use with 900 psi oxygen gas. We believe that the presence of such materials in the tank, even though they are employed in small amounts and in stationary equipment, constitutes a hazard. The compatibility test should be extended to cover oxygen at the high pressures to which the material is to be exposed.

Background

It is our understanding that the supercritical oxygen storage vessels in the service module are thermally protected with multilayer insulation. This insulation is in the vacuum space between the inner and outer shells and is used to support the inner vessel in the outer one. It consists of alternate layers of aluminum foil and glass paper spacer under a compressive load of the order of 1 psi. The spacer is impregnated with a silicone binder to stabilize the fibers in the mechanical environments. In the evacuated dome at the top of the vessel, where the piping and wiring conduits pass through the vessel walls, thermal insulation is provided in the form of gold coated Kapton and aluminized mylar. The aluminized mylar is wrapped around the wiring conduit. The gold coated Kapton in strips 1 inch wide is woven among the piping and is used to fill the open spaces between the inner and outer vessel walls.

Discussion

In another technical memorandum(1) we have made an analytical study of the possible temperature conditions which could arise from the leakage of oxygen into the insulation space and its subsequent pressurization. The results indicate that temperature of the order of 1100°F are possible. It is a well-known fact that most organic materials ignite at temperatures between 400 and 500°F in air and that this ignition temperature is lowered as the total pressure and partial pressure of oxygen are raised. While there is little data on the ignition temperature and burning behavior of the organic and silicone materials found in the insulation space of the oxygen tanks, we believe that these materials should be treated as hazardous until their benign nature can be demonstrated.

For many years, the U.S. Air Force and the U.S. Navy have had standard specifications for liquid oxygen storage tanks for use at bases and on shipboard. A significant feature of these specifications is the requirement for inert, non-flammable insulation for use in the vacuum space of the storage tank. Definitive tests are delineated to prove non-flammability of the insulation in a pure oxygen atmosphere in the presence of a hot wire or spark.

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(1) J.C. Burke, Analysis of Thermodynamic Temperature Rise Resulting from Pressurization of Insulation Space by High Pressure Oxygen

We recommend that comparable tests be specified by NASA which will be a requirement of any future procurement for oxygen storage vessels. The maximum pressure obtainable in the insulation space of the vessels can be specified, and proof of the safety of the insulation should be obtained.

Alternately, we recommend that all Mylar and Kapton materials be removed from the dome area of the storage vessels. The void spaces in this region should be filled with unbonded and unlubricated, type B, glass wool fibers. Several radiation shields of aluminum or gold foil can be easily combined with the glass wool to achieve thermal conductances that are comparable to the present system. The elimination of combustible materials from the dome region, where oxygen leakage sources are probable, will greatly improve the hazardous conditions and will mitigate against catastrophic failure of the storage system.

Further we recommend the removal of silicone binder from the spacer material. We have no information concerning the manufacturing procedures and techniques used in producing and applying the multilayer insulation to the oxygen tanks. We believe, however, that it should be possible to remove the silicone binder from the glass spacer and replace it with sodium silicate with negligible loss in mechanical and thermal properties. Glass and quartz spacers are available in which the bonding of fibers is accomplished by partial sintering of the fibers. Light weight woven glass fabrics are also available for construction of an adequate spacer system.

Technical Memorandum

Analysis of Thermodynamic Temperature Rise Resulting from Pressurization of Insulation Space by High Pressure Oxygen

prepared for

National Aeronautics and Space Administration
Manned Spacecraft Center
Houston, Texas 77058

by

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ARTHUR D. LITTLE, INC.
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22 May 1970

C-72563

TABLE OF CONTENTS

I. SUMMARY AND CONCLUSIONS

We have examined the possible temperature rises associated with the pressurization of the insulation space due to leakage of high pressure oxygen from the inner vessel. The analysis herein deals only with the overall thermodynamic effects of pressurizing the insulation space. It specifically does consider the possibility of local hot spots due to the impingement of high velocity flow or due to shock waves.

In performing the analysis we considered three analytical models:

1. Expansion with complete mixing.

This is a rational model for an open tank which, in fact, has been confirmed in previous experiments involving the pressurization of the ullage space in a fuel tank. However it is likely to be non-conservative for the insulation space passage where mixing would be inhibited.

2. Piston-type isentropic compression.

This is a very conservative model in terms of the assumption of piston type compression (i.e. no mixing) and especially the assumption of adiabatic compression.

3. Piston-type compression with the compressed gas in thermal equilibrium with the insulation material.

This is a refinement of case 2 which accounts for the maximum heat transfer between the compressed gas and insulation. It is probably the most reasonable model, but since maximum heat transfer is assumed, it is not necessarily conservative.

The results show that the temperature rise in the insulation space is relatively low for model 1 (mixed expansion). The temperature ratio (final temperature over initial temperature) is equal to 1.4, independent of pressure ratio. Using an initial temperature of 300°K, and a temperature ratio of 1.4 results in a final temperature of 420°K or about 300°F.

The isentropic compression model predicts very high temperatures. In this case the temperature ratio is equal to the pressure ratio raised to the $(K-1)/K$ power. With the very high pressure ratios theoretically attainable, temperature ratios are correspondingly high. For instance if the ullage is pressurized from 1 micron to 75 psia, the pressure ratio is about 4 x 10^6 and the temperature ratio is 75. Starting at an initial temperature of 300°K the theoretical final temperature would be 22,500°K or about 40,000°F.

Model 3, (piston compression with thermal equilibrium between compressed gas and insulation) predicts temperature rises somewhat greater than model 1 but far less than predicted by the isentropic compression. This model indicates that if the insulation space were compressed to 75 psia, the maximum final temperature would be 400°F; if compressed locally to 900 psia, the final temperature would be 1100°F.

From this study, we conclude that if leakage of high pressure oxygen into the insulation space occurs, the potential exists for substantial temperature rises, possibly approaching the ignition temperature of many common insulation materials.

II. INTRODUCTION

A potential hazard in high pressure oxygen systems is the possibility that temperatures may exceed the ignition temperature of materials in the system. One mechanism for realizing a substantial and perhaps dangerous temperature is the rapid compression of a confined volume. We have knowledge of a catastrophic accident of this type which occurred some years ago in a gaseous oxygen pressurization line when sudden pressurization initiated the combustion of a nylon valve seal. We have also conducted analytical and experimental studies on the pressurization of fuel tanks where combustion was a possibility.

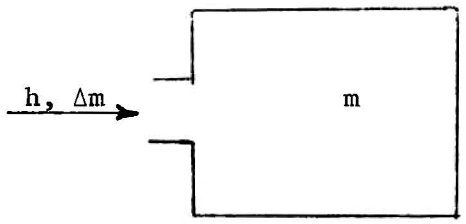
For the high pressure oxygen sphere in question, a dangerous situation may exist if the vacuum space were pressurized due to a leak from the contents of the inner vessel. Our study of the propagation of cracks in the inner sphere indicate that crack leakage is very unlikely to exist for any finite time prior to catastrophic failure of the inner vessel. However, it is possible that leakage may occur from some other source such as a leak in a fuel cell supply line. This leakage might not be catastrophic except for the temperature rise phenomena in the vacuum space which might exceed the ignition temperature of materials in the insulation space.

III. ANALYTICAL MODELS

The following models represent different physical descriptions of the pressurization of the vacuum space due to leakage of high pressure oxygen from the inner vessel.

In all of these models the conditions in the high pressure reservoir are considered constant during the pressurization. Further, we assume that the initial temperatures in the high pressure tank and the vacuum space are equal. In the analyses below, the subscript 1 denotes initial condition; subscript 2, final condition.

Model 1. Expansion With Complete Mixing



Assuming that the initial value of the mass of gas in the insulation space (m) is zero and that the entering enthalpy (h) is constant, the first law of thermodynamics results in

$$h_1 = U_2 \tag{1}$$

From the definition of enthalpy and the equation of state for a perfect gas

$$h_1 = U_1 + \frac{P_1}{\rho_1} = U_1 + RT_1 \tag{2}$$

From the above equations

$$U_2 - U_1 = C_v(T_2 - T_1) = RT_1 \tag{3}$$

Noting that $R = C_p - C_v$, (or $R/cv = k-1$), equation (3) can be written as:

$$T_2/T_1 = k \tag{4}$$

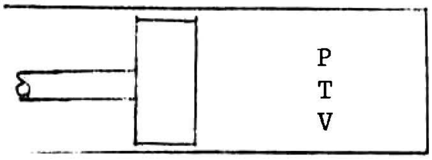
Taking the ratio of specific heats (k) as 1.4 and assuming an initial temperature of 300°K

$$T_2 = 420°K = 296°F$$

It may be noted that in the more general case where the initial mass is not zero, the temperature rise is somewhat less than predicted above.

Model 2. Isentropic Piston Compression

If we assume that the incoming gas does not mix with the gas previously in the vacuum space, we can replace this incoming gas by a piston.



If we further assume that the compressed gas does not exchange heat with the cylinder walls, the compression can be considered to be isentropic. In the isentropic case, the temperature ratio can be related to the pressure ratio or the volume ratio as follows:

$$T_2/T_1 = (P_2/P_1)^{\frac{k-1}{k}} \tag{5a}$$

$$T_2T_1 = (V_2/V_1)^{1-k} \tag{5b}$$

(The derivation of these equations, which is given in many standard texts will not be repeated here.)

The isentropic compression case leads to very high theoretical temperature ratios. For instance if the vacuum space is initially at one micron and is compressed to 75 psia

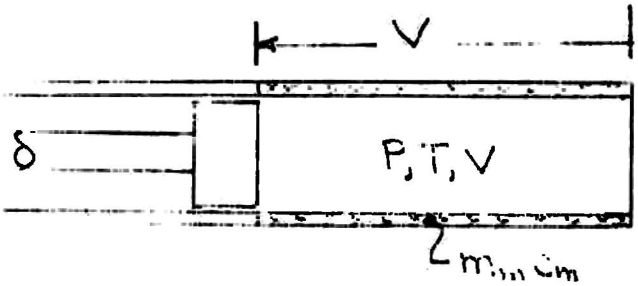
$$P_2/P_1 = \frac{75 \text{ PSIA}}{1 \text{ MICRON}} = 4 \times 10^6$$

$$T_2/T_1 = (4 \times 10^6)^{.285} = 75$$

$$T_2 = (75)(300) = 22{,}500°\text{K} = 40{,}000°\text{F}$$

Obviously we would not expect such temperatures to be real. The extreme conservation of the isentropic compression model is due both to the "no mixing" assumption and the assumption of adiabatic compression. We would expect the latter assumption to be particularly inaccurate at low initial pressures since the thermal energy per unit volume of the gas to be compressed is initially so low as to be readily dissipated by heat transfer to the insulation. For this reason we have considered the effect of insulation thermal capacitance in Model 3 below.

Model 3. Piston Compression with Thermal Equilibrium Between Compressed Gas and Insulation



In this model we assume that the compressed gas (or end gas) is in thermal equilibrium with the insulation material (or a fixed proportion thereof) surrounding the end gas. As indicated in the sketch above, we consider the insulation mass-specific heat product ($m_m C_m$) which attains thermal equilibrium with the end gas is directly proportional to end gas volume (V).

From the first law of thermodynamics:

$$- pdV = mC_v dT + m_m C_m dT \tag{6}$$

Using the equation of state for a perfect gas (pV = mRT), and noting that $R = C_p - C_v$, Equation 6 can be rewritten as:

$$\frac{dT}{T} = \left[\frac{1 - k}{1 + \frac{m_m C_m}{mC_v}} \right] \frac{dV}{V} \tag{7}$$

Prior to integrating this equation we will make the substitution:

$$\frac{m_m C_m}{mC_v} = \alpha_1 \; V/V_1$$

where

$$\alpha_1 = \left(\frac{m_m C_m}{mC_v} \right)_1$$

Integration of Equation 7 now results in:

$$T_2/T_1 = \left[\frac{V_2}{V_1} \left(\frac{\alpha_1 + 1}{\alpha_1 \; V_2/V_1 + 1} \right) \right]^{1 - k} \tag{8}$$

It may be noted that if $\alpha_1 = 0$, the above equation reduces to the isentropic compression equation previously presented as Equation 5b. It is further noted that Equation 8 can be used in conjunction with the relationship $P_2/P_1 = (T_2/T_1)(V_1/V_2)$ to determine temperature ratio as a function of pressure ratio. A plot of this type is presented in Figure 1.

In interpreting Figure 1, it is necessary to evaluate the thermal capacitance parameter (α_1). For the insulation which is used around the spherical inner vessel, we estimate that the specific heat per unit volume ($m_m C_m/V$) is about 2 Btu/ft^3°R. For an initial pressure at 1 atm and an initial temperature of 300°K, the specific heat per unit volume of oxygen is about .013 Btu/ft^3°R. Therefore, if the insulation attains complete thermal equilibrium with the end gas:

$$\alpha_1 = 150/P_1$$

where P_1 is expressed in atmospheres.

As an example of the use of Figure 1, let us assume P_1 = 75 PSIA and calculate T_2/T_1 as a function of P_1.

P_2 (PSIA)	P_1 (PSIA)	P_2/P_1	α_1	T_2/T_1
75	22	3.4	1.0	1.29
√	2.2	34	10	1.52
√	.22	340	100	1.60
√	.022	3400	1000	1.60
√	.0022	34000	10000	1.60

The results show that the temperature ratio does not continue to increase with pressure ratio as the initial pressure is progressively reduced--as was the case with isentropic compression. In this case the temperature ratio has essentially leveled off at 1.60 by the time the initial pressure drops to .22 psi. It may be remembered that the isentropic solution predicted a temperature ratio of 75 for a pressurization from 1 micron to 75 psia.

In order to quickly calculate the maximum temperature ratio corresponding to an infinite pressure ratio, but finite final pressure, it is convenient to rearrange Equation 8 using a thermal capacitance parameter defined in terms of the final state.

$$T_2/T_1 = \left(\frac{\alpha_2 + V_2/V_1}{\alpha_2 + 1}\right)^{1 - k} \tag{9}$$

where

$$\alpha_2 = \left(\frac{m_m C_m}{mC_v}\right)_2 = \alpha_1 \frac{V_2}{V_1}$$

As the pressure ratio becomes infinite (or the volume ratio approaches zero), the maximum temperature rise becomes:

$$\left(T_2/T_1\right)_{max} = \left(\frac{\alpha_2}{\alpha 2 + 1}\right)^{1 - k} \tag{10}$$

Unfortunately, α_2 depends on final temperature, so it is necessary to define yet another thermal capacitance term, evaluated at final pressure and initial temperature. (The difference in the various thermal capacitance terms is of course strictly a function of gas density, since $\alpha = m_m C_m / \rho VC_v$ and the specific heat per unit volume of the insulation $(m_m C_m/V)$ and the gas specific heat (C_v) are taken to be independent of pressure or temperature.

Therefore, $\alpha_n \sim T_n/P_n$.)

$$\alpha_{21} = \left(\frac{mC_m}{mC_v}\right)_{\text{at } P = T_2,\ T = T_1} = \alpha_2 \frac{T_1}{T_2} = \alpha_1 \frac{P_2}{P_1}$$

Making the substitution that $\alpha_2 = \alpha_{21}\ T_2/T_1$ in Equation 10 results in the relationship between T_2/T_1 and α_{21} which is plotted in Figure 2.

Using the example of a pressurization to 75 PSIA, we note that:

$$\alpha_{21} = \alpha_1 \frac{P_1}{P_2} = (1.0)\left(\frac{22}{75}\right) = .294,$$

Therefore $(T_2/T_1)_{max} = 1.6$, and $T_{2\ max} = (300)\ (.16) = 480°K = 405°F$.

If we assume that it is possible for the local pressure to rise to nearly tank pressure, then $P_2 = 900$ psi, and the results are now:

$$\alpha_{21} = (1.0)\left(\frac{22}{900}\right) = 0.245$$

Therefore $(T_2/T_1)_{max} = 2.9$ and $T_{2\ max} = (300)\ (2.9) = 870°K - 1110°F$

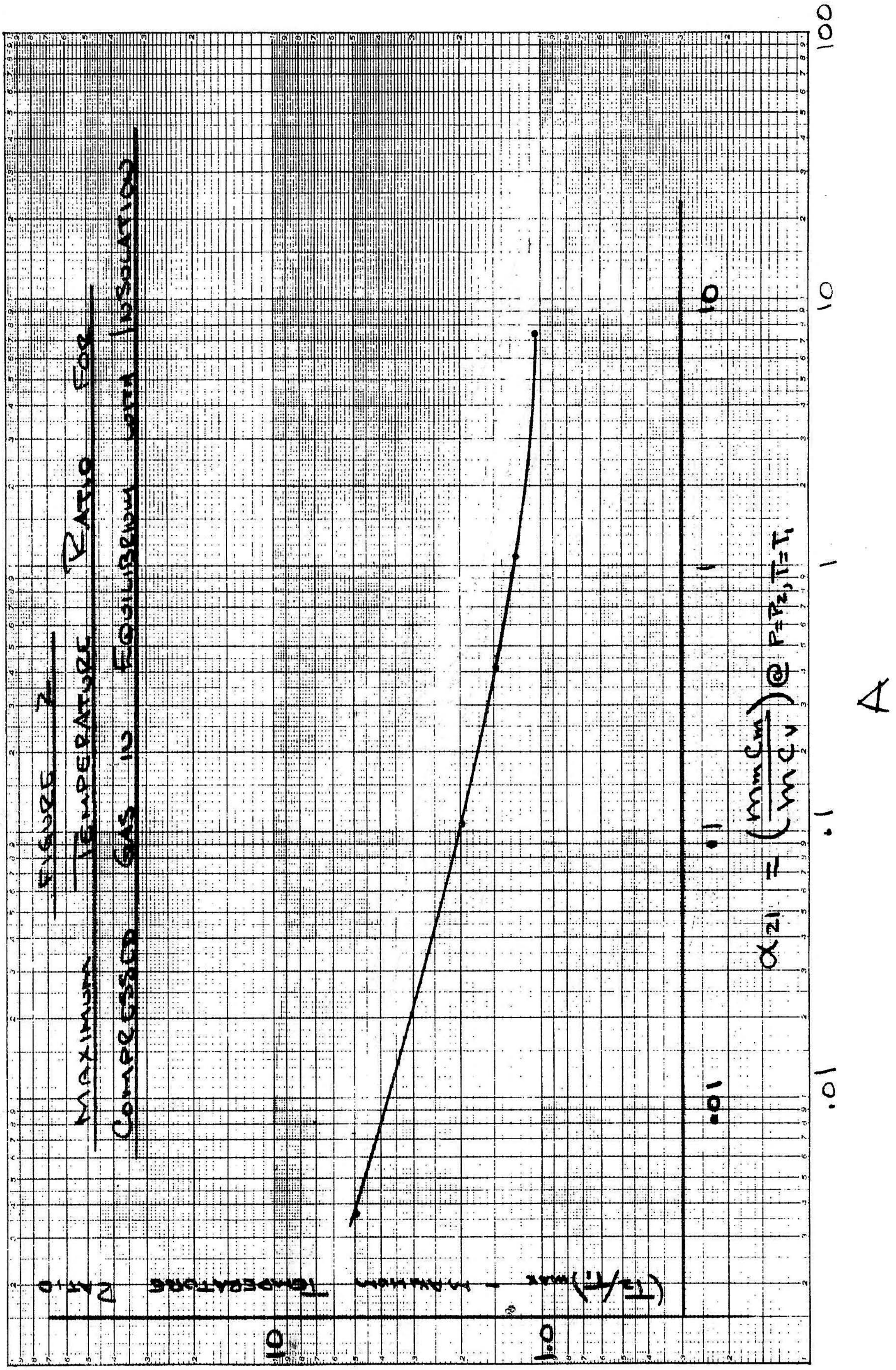


FIGURE 7
MAXIMUM TEMPERATURE RATIO FOR
COMPRESSED GAS IN EQUILIBRIUM WITH INSULATION
$(T_2/T_1)_{max}$ - MAXIMUM TEMPERATURE RATIO
10
1.0
.01
.1
1
10
100
$\alpha_{21} = \left(\frac{m_m C_m}{m C_v}\right) @ P=P_2, T=T_1$
A

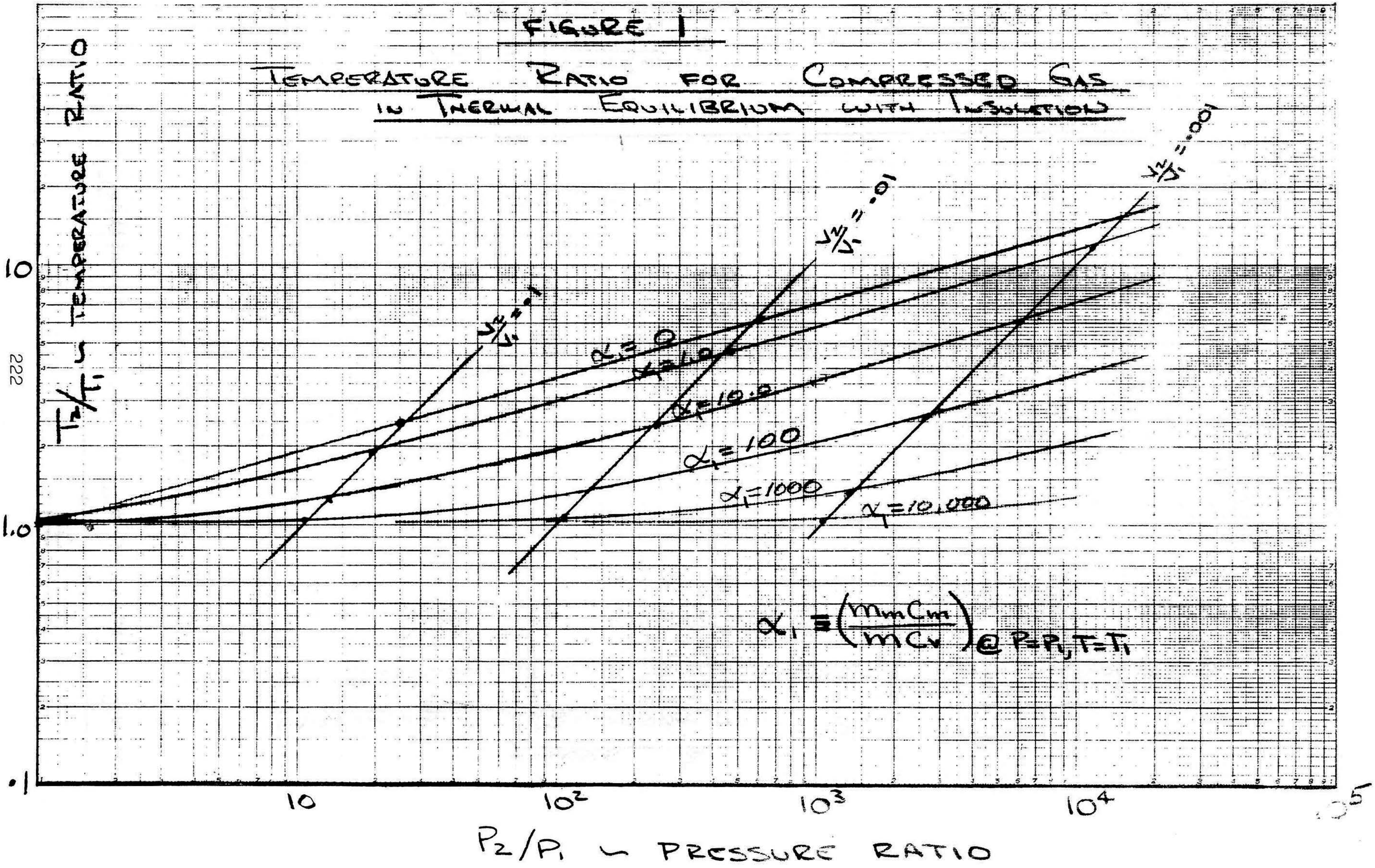


FIGURE 1

TEMPERATURE RATIO FOR COMPRESSED GAS IN THERMAL EQUILIBRIUM WITH INSULATION

$$\alpha_1 \equiv \left(\frac{m_m C_m}{m C_v}\right)_{@\,P=P_1,\,T=T_1}$$

Technical Memorandum

Possible Method for Destratification of Supercritical Fluid

Prepared for

National Aeronautics and Space Administration
Manned Spacecraft Center
Houston, Texas 77058

by

F. E. Ruccia

ARTHUR D. LITTLE, INC.
Cambridge, Massachusetts

20 May 1970

C-72563

TECHANICAL MEMORANDUM

POSSIBLE METHOD FOR
DESTRATIFICATION OF SUPERCRITICAL OXYGEN

SUMMARY

Sliding and rolling contact bearing surfaces produce hazardous conditions within the supercritical oxygen tank. Temperature equilibrium must be obtained either with a passive system, i.e. aluminum wool, or with agitators different in design from the present stirrers. Passive systems are weight sensitive. A concept for a stroking agitator without slide or ball bearings is presented. This concept has been tested in the laboratory using water as the test fluid and appears to produce the desired mixing. A method for incorporating this concept into the supercritical tanks is also suggested.

INTRODUCTION

The oxygen in the Apollo fuel cell storage vessel is temperature equilibrated to stabilize the pressure performance of the system and to prevent unwarranted losses overboard. In the current Apollo configuration, mixing is accomplished with two electric motors that spin the fluid across the tank through caged impellers. Rotating components, such as the motor armature, require bearings which can, under some circumstances, produce local high temperatures in those regions where the metal surfaces are made to move against one another. Specks of contaminants that become caught between these surfaces can produce a particularly hazardous situation. Thus, the best approach is to remove all mechanical motion from inside the storage vessel, or, as a minimum, to remove all support surfaces in which there is sliding or rolling contact.

Two methods are generally applicable for producing temperature equilibration within the fluid. The first consists in increasing the effective thermal conductivity of the fluid by the use of metal wool, i.e. copper or aluminum wool filling the tank; the second is to promote mixing of the stored fluids with an internal agitator. With regard to agitation, this action can also be produced by shaking the entire vessel and it is quite likely that operation of the Apollo spacecraft ACS produces some temperature equilibration within the stored fluids.

IMPROVEMENT OF FLUID THERMAL CONDUCTIVITY

The thermal conductivity of a fluid can be increased in any given direction by the addition of a large number of conducting wires orientated in the direction of the heat flow. The average thermal conductivity of fluid and metal is approximated with the expression:

$$\bar{K} = \bar{K}_{o_2} + K_m \frac{A_m}{A_t}$$

where:

$\bar{K}$ = Average thermal conductivity of combined system in the direction of heat flow.

$\bar{K}_{o_2}$ = Thermal conductivity of oxygen

K_m = Thermal conductivity of high conductivity material.

A_m = Cross-section area of high conductivity material.

A_t = Total cross-sectional area including both oxygen and high conductivity material.

At the high density conditions (60 atmos, 93°K), oxygen has a thermal conductivity 15×10^{-4} watt/cm°K. A ten-fold increase in this thermal conductivity is obtained with aluminum filling 0.68 per cent of the cross-sectional area of the fluid perpendicular to the direction of heat flow. Considering first order effects only, approximately 2 per cent of the liquid volume must be filled with aluminum in order to produce a ten-fold thermal conductivity increase in all directions. This would result in an additional vessel weight of approximately 16 pounds (20 per cent).

We have made no attempt here to establish temperature equilibration criteria for the stored fluid or the thermal conductivity required by the fluid to meet the criteria. Nor have we considered the hazard effects of placing large quantities of aluminum surface inside a supercritical oxygen vessel; other metals, such as copper, can be used which will produce the same effect as aluminum, but with a sacrifice in weight. The main result is that this equilibration method is weight sensitive.

EQUILIBRATION BY USE OF AGITATION

Rotating machine elements are usually supported by bearings in which there is rolling or sliding contact between surfaces. These types of bearings can be eliminated by producing machine elements that have a stroking motion, i.e., either in a linear or rotational manner. This is done by supporting and guiding the machine element action by spring elements. A typical example is a mass supported from a spring at both ends.

We have considered several concepts that produce agitation and subsequent mixing of the supercritical fluid. Among them includes a paddle supported within the vessel on an axle which is rigidly connected to the paddle and rigidly supported at its ends, such as a wire under tension. The paddle is actuated by a magnetic couple which drives the paddle through the tank wall. This drive causes the paddle to oscillate back and forth about the support. The paddle elements give a portion of the fluid a momentum which produces mixing when the momentum is transferred to the stationary fluid.

A similar device was also considered which produced mixing by a linear stroking action. Some brief laboratory tests have been performed to illustrate the concept. The results of these tests and the application of the concept are presented below.

DISC AGITATOR

A disc agitator was constructed from a plastic (polyethylene) sheet .030 inches thick into the dimensions shown in attached sketch No. 1. This disc was connected to a rod at its center. It was immersed into a water reservoir 5 inches deep with an area 15 x 20 inches. The disc rod was stroked about 1 inch at a frequency of 3 cycles per second. Ink was injected into the reservoir at various locations as a means for observing the mixing action and for establishing when complete mixing had taken place.

The peripheral segments of the disc produce a sculling action similar to that produced by a skindiver's flippers. As the disc is stroked in a given direction, the disc segments are bent backward, imparting an outward and forward motion to the fluid. This action is the essential characteristic of the agitator. For liquid oxygen service the polyethylene disc would be replaced with one of stainless steel or similar metal about .005 inches thick to obtain the same flexibility.

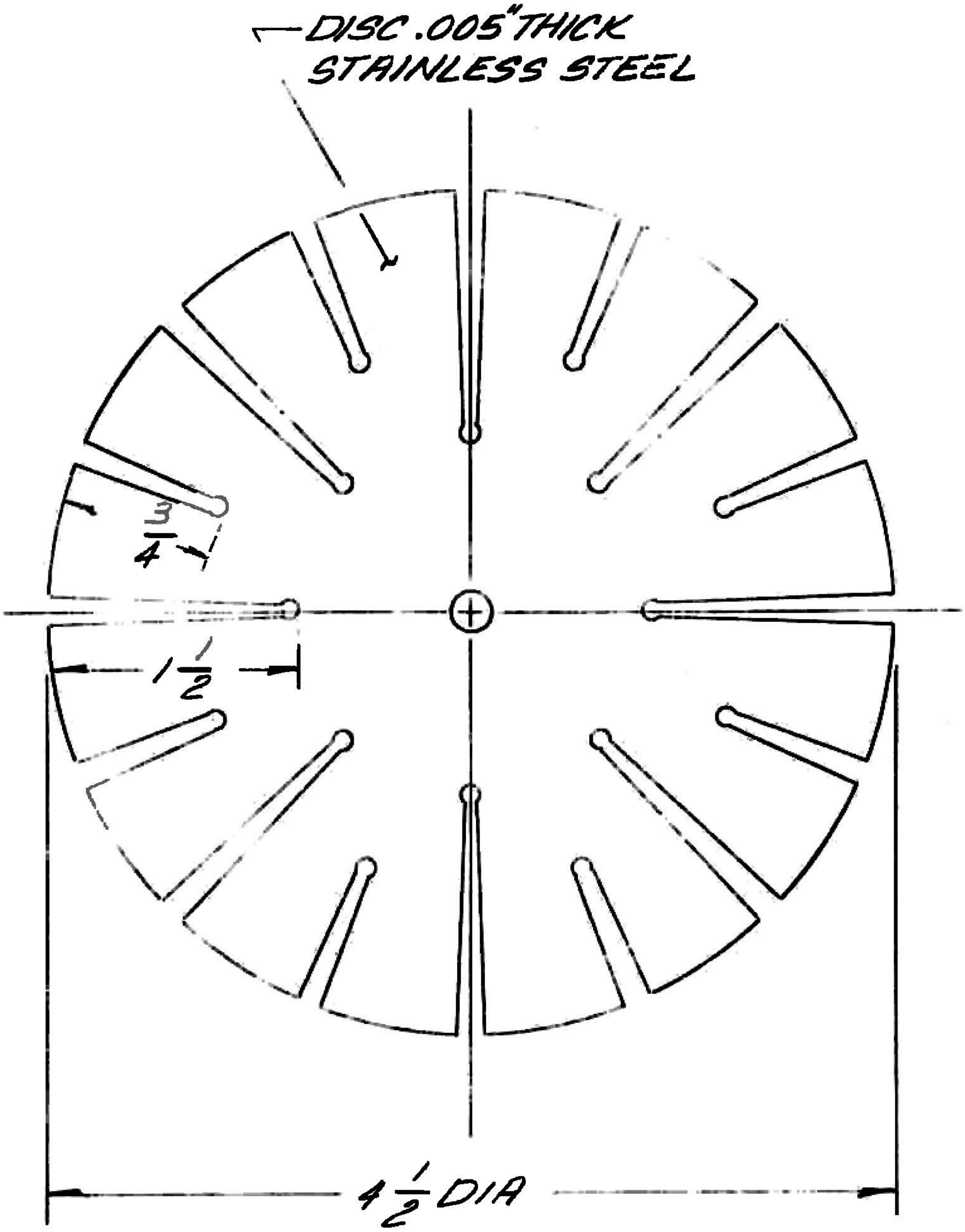
Several experiments were performed in which the ink, serving as a neutrally buoyant tracer material, was injected into the reservoir in the vicinity of the disc and several experiments were performed in which the ink was placed at several locations in the reservoir away from the disc. In both cases the reservoir became completely mixed in about 40 seconds after 120 strokes of the agitator.

A force of about 2/3 pounds was required to stroke the disc. The power expenditure was approximately 0.6 watts and the expended energy for complete mixing was 24 watt seconds. An important result of this experiment is the extraordinarily small energy required to produce complete mixing of water reservoir.

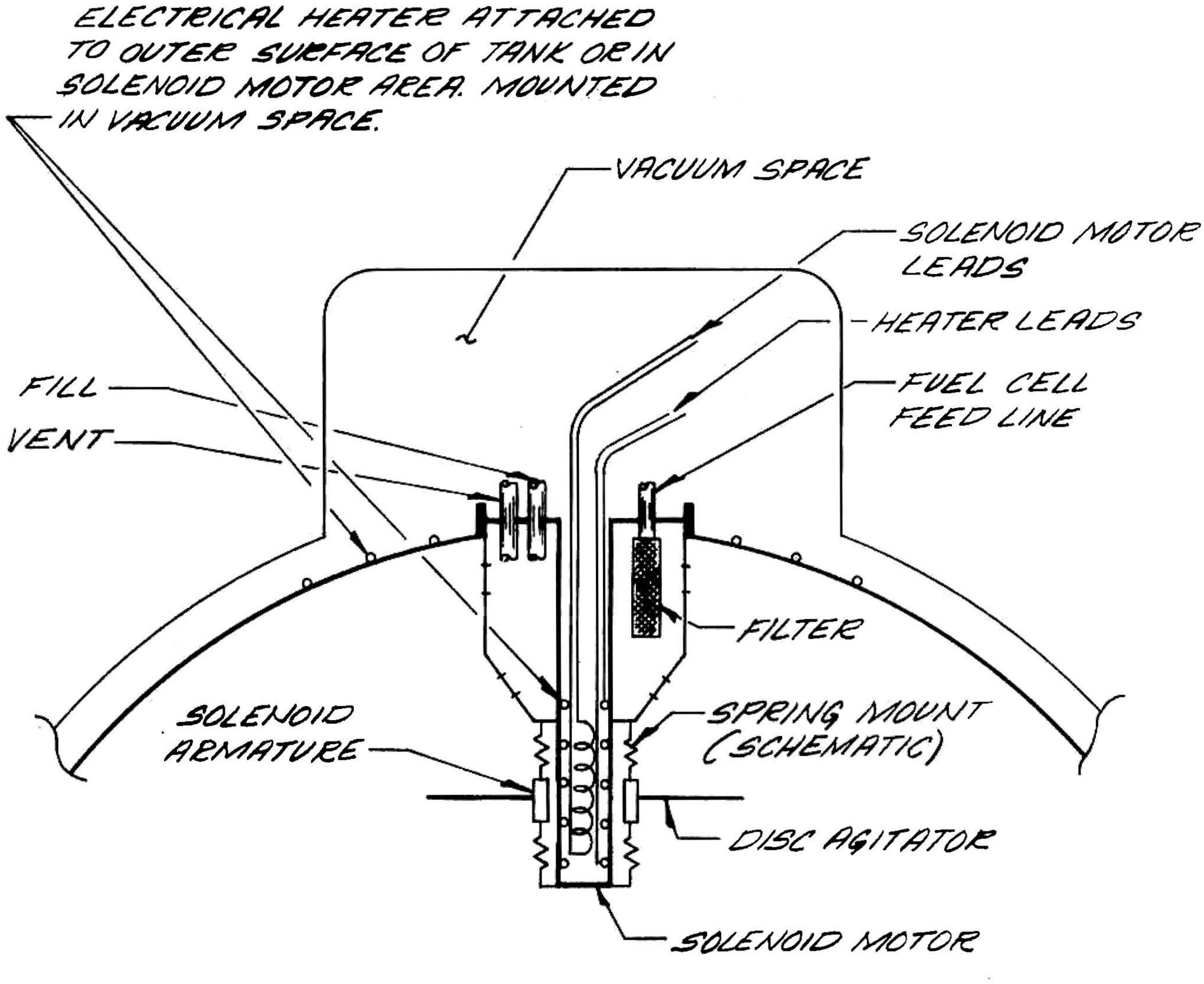
We have not made any attempt to extrapolate these results to the fuel cell oxygen and hydrogen storage systems. However, the following comments seem appropriate. While the experiment reservoir was 1/6 the volume of the oxygen storage vessel, the larger surface dimensions of the water and oxygen system are comparable. Further, the viscosity of oxygen and hydrogen are both significantly less than water and thus a given momentum will produce a longer period of mixing in these fluids than in water. The wide variations in fluid densities encountered in the storage systems may require multiple discs of different flexibility mounted on the same shaft to produce the appropriate degree of mixing at the low and high density levels. The disc agitator has the potential of acting as a density meter provided the stroke length is fixed or measured and the stroke power is accurately measured.

The application of an agitator, similar to that described above, to the supercritical oxygen tank is illustrated schematically in sketch No. 2. The disc is mounted to an armature which in turn is spring-mounted to a support at the top of the tank. Because of the flexibility of the disc, it will pass through the existing tank opening. The solenoid portion of the motor is located inside the armature in the vessel vacuum space which protrudes into the storage volume.

The heater should be located in the vicinity of the agitator, and, therefore, it is shown schematically as located at the solenoid motor (windings in vacuum space) or on the tank surface. The capacitance gauge is assumed to have been removed from the tank in the configuration shown. However, it is easy to conceive a configuration with the two combined. We believe that the weight of the agitator will be less than the weight of a single pump currently in use.



FLUID DESTRATIFICATION
DISC AGITATOR CONCEPT
SKETCH NO. 1



NOTE:
SPRING MOUNT POSITIONS ARMATURE DURING SHAKING MOTION

FLUID DESTRATIFICATION DISC AGITATOR MOTOR AND MOUNTING CONCEPT

SKETCH NO. 2

Technical Memorandum

Assessment of the Hazardous Aspect of Storage and Handling of Oxidizers and Fuels

prepared for

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by

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21 May 1970

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We understand that liquid oxygen for use on Apollo flights is purchased to specification,and may be tested for purity and contamination at the time of purchase. This liquid oxygen is then stored in a relatively large storage tank until used on demand. To the best of our knowledge, some analyses for purity are accomplished on delivery, but there are no further analyses of oxygen purity or contamination levels in the liquid.

The liquid oxygen eventually is delivered to the storage tanks in the Apollo service module for various uses. Fuel cell supplies are initially stored as "slush" oxygen, and then brought to the super-critical state by the addition of heat.

Several sources of contamination of the liquid oxygen are possible during storage and preparation for use. If we assume that liquid oxygen is stored in a relatively large tank prior to use, contamination may occur in the storage tank. Generally, large storage tanks are vented to atmosphere. Even though the tank boiloff is flowing to atmosphere through the vent line, back diffusion of contaminants does occur under the driving force of differences in partial pressure. Hydrocarbons can accumulate in the storage tank, either in solution in the liquid oxygen or as frozen, crystallized material dependent on solubility limits. A storage tank that has been in service for a relatively long time can contain a wide variety of contaminants that may initiate a later disaster. It is recommended that storage tanks be periodically emptied and warmed close to ambient temperature to evaporate any contaminants contained therein. On cooling the tank again for service, the rapid venting of oxygen will provide a helpful "flushing" mechanism.

Common practice in large liquid oxygen plants is to install a silica gel or molecular sieve filter in the liquid air line to the rectifying column. This type of filter is recommended in the withdrawal line from the storage tank to remove or adsorb any hydrocarbon accumulation that may have occurred.

Two methods generally are employed for the production of "slush" cryogens; reduction in the vapor pressure above the liquid by use of vacuum pumps; or use of external refrigeration, to produce the "slush" with the capability of maintaining a positive pressure above the liquid oxygen.

The possible hazards of the use of vacuum pumps for "slush" production are self-evident. The lower-than-ambient pressures in the oxygen vessel creates the possibility of contaminant influx from dirty lines, vacuum pumps and the surroundings in general. Acetylene, which may be present in the atmosphere from nearby welding, burning or cutting operatings, poses a particular hazard.

Should refrigeration be employed to produce the "slush", care must be taken to be sure that positive pressures above the liquid are maintained at all times to exclude contamination.

Transfer of the liquid, or "slush", into the service module tanks should be performed through positively cleaned transfer lines, into a clean storage tank.

Some evidence exists that, in a "zero G" field,the energy of ignition in a flammable-oxidizer gas mixture may follow the relationship

$$E = A\left(\frac{1}{P^2}\right)$$

where E = energy of ignition, A = a constant and P = total pressure of the mixture. Elevated pressure, therefore, can drastically reduce the energy required for ignition of a contaminant. Since the "slush" oxygen is eventually heated to its super-critical state at relatively low temperatures, it is possible that some contaminant may remain in a solid or liquid state, and in turn, contact any electrical heater or "hot-spot" (such as a warm bearing or hot metal due to friction) that can provide the energy of ignition. Little is known concerning the dispersion of one gas within another gas in the super-critical state and, therefore, we cannot predict accurately the location or concentration of any contaminant within the super-critical oxygen.

For years, it has been common practice in the cryogenic industry to evacuate tanks, transfer lines and other equipment before the introduction of hydrogen, to assure that oxygen is not contained within the system. Due to the criticality of the liquid oxygen systems aboard Apollo, it is suggested that this procedure be employed when filling the oxygen systems.

Our recommendations are as follows:

1. Be sure that the main storage tank for the liquid oxygen is periodically warmed to eliminate contaminants.

2. Withdraw the liquid from storage through a silica gel or molecular sieve filter.

3. If the "slush" oxygen is produced in a vessel external to the main storage tank, this auxiliary vessel should be connected to the service module oxygen tanks to form a completely tight system.

4. Evacuate the combined "slush" and service module systems to a pressure of 10-20 microns before introduction of liquid oxygen to the system. A well-designed liquid nitrogen cold trap should be installed between the vacuum pumps and the oxygen system to prevent back-streaming of contaminants. Any plateaus, or periods of prolonged constant pressure in the oxygen system will indicate the presence of moisture or contaminants in the system.

5. Flush the oxygen system with warm, dry oxygen gas to slightly above ambient pressure and repeat the evacuation.

6. Introduce liquid oxygen into the vessel for "slush" production. Take a sample of liquid oxygen from the main storage tank and analyze for ignitible contamination.

7. Produce the "slush" by refrigeration, rather than by use of vacuum pump, if possible.

8. Transfer the "slush" oxygen directly into the service module storage tanks by displacement with clean, dry oxygen gas.

9. Other fuels and oxidants should be handled with similar care.

Technical Memorandum

Evaluation of Some Local Thermal Effects as Potential Ignition Sources in Fluid Storage Tanks

prepared for

National Aeronautics and Space Administration
Manned Spacecraft Center
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by

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Summary

If one postulates that a leak occurs in the wall of a gas storage vessel, it is of interest to inquire whether or not there is a possibility of an autocatalytic series of events which could lead to a fire or explosion. We have, however, discussed in a separate memorandum the unlikely event of such small leaks in high-strength metal tanks which are designed on the basis of "no leak before break." For more ductile materials, however, leaks are known to occur. In fact, it is a well-known fact that in hydrogen gas cylinders, small leaks into air may ignite with no apparent source of ignition (1). This has been attributed to static charge accumulation and/or to a rise in temperature due to the negative Joule-Thomson coefficient for hydrogen.

In the following sections we consider a number of local thermal effects and conclude that none are large enough to provide probable sources of ignition in the event of storage vessel leakage.

Temperature Rises in Metal Fracture

Experimental and theoretical studies do not indicate any appreciable temperature rise occurring at the site of a fracture of a high-strength metal pressure tank. With the exception of titanium and zirconium in the presence of gaseous oxygen, no oxidation of freshly torn metal surfaces has been observed in extensive metal fracture studies (2). Thus, no ignition should be initiated solely by Inconel metal fracture in the case of oxygen storage tanks.

Viscous Dissipation of Energy in Pin-hole Leaks

It should be noted, however, that there is some viscous dissipation of energy of the exiting fluid as it flows out through the crack. Normally, such dissipative inputs are small.

In the case of gases, viscous heat generation and cooling due to free expansion are lumped together by the Joule-Thomson coefficient. It should be noted that a Joule-Thomson expansion does not always result in cooling - although this happens to be the case for the conditions encountered in the Apollo 13 service module. For liquid propellants, however, there is a possibility of heating. Brinkman(2) derived theoretically the temperature distribution in a liquid flowing in a capillary. He related three dimensionless parameters:

$$\rho = r/R$$

$$\tau = \frac{16\ \eta\ \lambda}{R^4\ (dp/dz)^2}\ \Delta T$$

$$\zeta = \frac{4\ \lambda\ \eta\ Z}{CR^4\ (dp/dz)}$$

by means of a series for which he presented graphical solutions.

r = distance from the capillary axis to the wall
R = radius of the capillary
η = viscosity
λ = thermal conductivity
ΔT = temperature rise
$\frac{dp}{dz}$ = pressure drop per unit length of capillary
Z = length of capillary
C = specific heat of the liquid per unit volume

For a capillary with an insulated wall, the maximum temperature occurs near the wall. Brinkman's calculations show that the maximum temperature rise ΔT can be given approximately by

$$\Delta T \simeq 41.2\ \frac{\lambda^{0.4}\ \eta^{0.4}\ \Delta P^{0.6}}{C^{1.4}}\ \left(\frac{Z}{R^2}\right)^{0.8}$$

For hydrazine, $\eta = .009$ poise

$C \simeq .737 \times 4.186 \times 10^7$ erg/cm^3 °C

$\lambda \simeq 1.2 \times 10^{-3} \times 4.186 \times 10^7$ erg/cm °C sec

For a pressure drop, ΔP, of 200 psi across the tank wall

$$\Delta T \simeq .297 \times 10^{-3}\ \left(\frac{Z}{R^2}\right)^{0.8}$$

For $Z = 0.15$ cm $R = .001$ cm $\Delta T = 4.1$ °C

$Z = 0.15$ cm $R = .0001$ cm $\Delta T = 63$°C

These temperature rises are not high enough to cause dissociation. It would by worthwhile, however, to examine in detail, the assumptions made by Brinkman (e.g., linear pressure drop in capillary) and validate any theoretical conclusions experimentally.

Chemical Reactions at the Site of a Fracture

If a tank under pressure contains oxygen, it may by hypothesized that at the site of a fresh break, the clean metal surface may be readily oxidized - so readily that the heat of reaction could raise the surface temperature to the ignition point.

Experimental evidence seems to rule out such a hypothesis except in the case of titanium or in unusual cases where there is also some foreign, organic fuel at the break-site. In reference to titanium, Jackson et. al. (3) state: "Under conditions of tensile rupture, a pressure of about 100 psig will initiate a violent burning reaction (in the presence of oxygen) from about -250°F up to room temperature." Titanium is also impact sensitive with liquid oxygen.

Thus, one concludes that chemical reactions are not reasonable ignition sources when a fracture occurs except for oxygen in titanium tanks. Of course, small amounts of titanium in an alloy (e.g. 2.5% Ti in Inconel-X) may be sufficient to support combustion after ignition occurs in a high pressure oxygen atmosphere (4).

Kinetic Energy of Fluid Particles Impinging on Surfaces

In a leak from a high pressure fluid vessel, it may be possible to generate liquid droplets moving at sonic velocity which could then impinge on other surfaces such as layers of insulation. In the case of oxygen, for example, total conversion of such kinetic energy to thermal energy amounts to a specific energy increase of about 6 cal/gm or about a 15°K temperature increase in the impinging liquid. Again, these energy levels are insufficient to be probable sources of ignition.

1. "Handbook of Compressed Gases," Reinhold Pub. Co., New York, (1966) p. 98-99.

2. "Heat Effects in Capillary Flow," Brinkman, H.C., *Appl. Sci. Research*, *A2*, 120-124 (1951).

3. "Reactivity of Metals with Liquid and Gaseous Oxygen," Jackson, J.D., Boyd, W.K., and Miller, P.D., Battelle Memorial Institute, DMIC Memorandum 163, January 15, 1963, WADD Tech. Report 60-258, June, 1960.

4. "Ignition Characteristics of Metals and Alloys," Dean, L.E., and Thompson, W.R., A.R.S. Journal, 917-923, July, 1961.

Technical Memorandum

Crack Propagation in Storage Vessels

prepared for

National Aeronautics and Space Administration
Manned Spacecraft Center
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by

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22 May 1970

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High strength materials are often used to minimize tankage weight in high pressure storage applications. These tanks have the characteristic of "no-leak-before-failure," that is, they are designed on a crack propagation criteria for a particular burst pressure. At burst, a catastrophic rupture occurs rather than a limited opening or leak which is a more usual failure mode for ductile materials. To preclude failure, high strength material vessels are "proofed" at a pressure chosen to eliminate any vessels having defects which could lead to failure at prolonged normal operating conditions.

In design of such a metallic pressure vessel, it is assumed that failure occurs from built-in defects when the plane strain stress intensity factor for the defects equals a critical value K_{Ic}, which is a measured property of the material for specified environments. This factor K_{Ic} establishes the maximum allowable crack length c before failure at an operating stress, σ, from the relation $K_{Ic} = \sigma c^{1/2}$. With proper design and nondestructive analysis of the vessel, any defects in the tank will not fail at the operating stress nor will they grow to a size large enough to cause failure under operating conditions.

Crack propagation rates are established experimentally and are determined as a function of applied stress intensity factor K_I and time for a slowly propagating crack in the environment to be contained. If the vessel undergoes cyclic loading, crack growth rates are determined for a cyclic stress intensity factor in this environment. From plots of such data, the time to failure of a vessel can be predicted for a given initial stress intensity factor K_{Ii}.

For many pressure vessel materials in a given environment, a threshold stress intensity K_{TH} exists, below which there is no possibility of failure since a crack will not propagate at stress intensity levels below K_{TH} or else stops growing after a short travel distance.

In either case, the design is based on no crack growth or crack propagation rates so low that any cracks surviving the proof test never grow long enough to cause catastrophic failure. In proof testing the vessel, a stress is picked which ensures that possible defects in the vessel will not cause failure at the operating stress. The proof stress eliminates the possibility of defects above a maximum K_I. (or cracks larger than $(\frac{K_{IC}}{\sigma \text{ proof}})^2$.)

The proof test should be carried out in reasonably short times. There is the danger that if the vessel is held at or near proof stresses for too long a time, slow crack propagation can occur. It is also desirable to proof test the vessel only once if possible.

We understand from contact with Mr. C.F. Tiffany of the Aerospace Systems Division of the Boeing Company that Inconel 718 does not show slow crack growth in liquid oxygen. Since the Apollo failure, Boeing has evaluated this alloy in oxygen slush and found no evidence of slow crack growth under load. A report on this finding will be presented to NASA by the Boeing Company.

Practical Consequences

a. It would appear that under these design constraints, there would be a low probability of any failure by a slow leak from the pressure vessel. No leak will occur until a crack becomes sufficiently deep for catastrophic failure to occur. Since the metal, though of high strength, is inherently brittle, one might expect considerable fragmentation if failure occurs. This fragmentation would, most probably, lead to rapid, catastrophic failure of the outer shell. The importance of any studies concentrating upon venting of gases into an insulating space is therefore diminished.

b. Since cracks propagate only under applied stress, it would appear to be important that high-strength tanks be proofed only once and under carefully controlled conditions of pressure rise, hold, and fall. Multiple proof tests can only lead to more cracks and higher crack propagation rates under proof stress conditions.