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MERCURY CONTAMINATION STUDY FOR FLIGHT SYSTEM SAFETY

Final Report

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Prepared by

C. S. Gorzynski, Jr. and J. N. Maycock

October 1972

JPL CONTRACT NO. 953519

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

Corporate Research and Development Laboratory/RIAS
1450 South Rolling Road
Baltimore, Maryland 21227

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ABSTRACT

The effects and prevention of possible mercury pollution resulting from the failure of solar electric propulsion spacecraft using mercury propellant have been studied for all phases of the system operation from tankage loading to post-launch trajectory injection. During pre-flight operations and initial SRM flight mode there is little danger of mercury pollution if proper safety precautions are taken and if established industrial and laboratory procedures for handling mercury are used. Any spillage on the loading, mating, transportation, or launch pad areas is obvious and can be removed by vacuum cleaning and chemical fixing. Mercury spilled on Cape Kennedy ground soil will be chemically complexed and retained by the sandstone subsoil. A cover layer of sand or gravel on spilled mercury which has settled to the bottom of a water body adjacent to the system operation will control and eliminate the formation of toxic organic mercurials. Mercury released into the earth's atmosphere through leakage or a fireball will be diffused to such low concentration levels no pollution threat is presented. However, gas phase reactions of mercury with ozone could cause a local ozone depletion and result in serious ecological hazards. Since the consequences of these reactions cannot presently be determined, a definitive study of the mercury-ozone reactions and their effect on the environment must be performed.

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I. SUMMARY

The possibilities of mercury pollution resulting from the failure of solar electric propulsion devices that use mercury propellant have been explored. The potential pollution threat was examined for (1) spacecraft loading; (2) spacecraft and launch vehicle mating and transportation; and (3) abort conditions.

Results of the study indicate that there is little danger of mercury pollution during pre-flight operations and initial SRM flight mode. Vaporization and spillage constitute the major pollution hazards during loading operations, but this problem is limited to the immediate vicinity of loading operations and can be overcome by employing the same handling procedures developed by the mercury refining industry. Spillage on the launch pad is easy to detect and remove by vacuum cleaning and by fixing the elemental mercury by Merc-X or sulphur.

A mercury spill on Cape Kennedy soil would be absorbed into the sandstone subsoil and chemically complexed and eliminated as a serious pollution hazard. Spillage into landlocked water is unlikely, since this situation would require that the payload be ejected backward from its normal flight path. Spillage into the ocean is a possibility, but the nature and magnitude of any resultant pollution would vary according to water depth, temperature, salinity, and pH.

Results also indicate that a launch pad fireball produced by the Titan III D booster would constitute such a great HCl pollution source (172,000 lb.) that the mercury propellant effects would be minor by comparison.

However, at between 15 and 45 km altitude, a fireball that involves the launch vehicle upper stages could have serious consequences. Combustion products from these stages are not likely to react with mercury, but the blast shock wave would disperse mercury vapor in the stratosphere.

The potential dangers from such a mercury cloud as it reacts with ozone in the stratosphere cannot be determined. The physical and chemical implications of releasing between 200 and 400 kg of mercury into the earth's atmosphere must be understood before solar electric propulsion devices can be launched through the upper atmosphere with any degree of confidence that an abort or accident will not serve to contribute mercury or toxic mercurials to our environment.

A research program aimed at achieving such an understanding is recommended.

II. INTRODUCTION

Solar Electric Propulsion (SEP) technology can be applied to the unmanned exploration of the solar system and is being considered for use in the Solar Electric Multimission Spacecraft (SEMMS). The importance of the multimission capability lies in increased flexibility, since solar electric propulsion allows missions not possible on a ballistic trajectory with existing launch vehicles, excluding Saturn V. This flexibility is further increased in that (1) spacecraft can be launched any year, (2) science payload can be increased, and (3) observation times can be increased for certain missions.

Possible missions requiring solar electric propulsion include multiple asteroid surveys, comet rendezvous, and Mercury, Jupiter, and Saturn orbiters (Ref. 1).

Due to the potential attractiveness of SEP devices, selection of the propellant becomes an important factor in determining performance characteristics. Of all the high atomic weight metals of interest, the one of greatest potential is the element mercury. Such factors as high atomic weight and non-corrosive characteristics make mercury very attractive as a propellant. However, the toxicity of mercury vapor and the relative ease by which highly toxic organic mercurials are formed requires that potential mercury pollution problems be surveyed and corrective actions defined where possible.

For currently planned missions the mercury propellant payload, in clusters of five or seven engines, amounts to between 200 and 400 kg mercury. This mercury under normal mission operations will be expended during thrust periods in interplanetary space and thus is not a pollution threat. However, potential mercury

pollution threats may exist under the following operations:

- (i) Spacecraft tankage loading and downloading.
- (ii) Spacecraft transport with loaded tanks.
- (iii) Spacecraft boost vehicle mate and demate.
- (iv) Spacecraft countdown and launch pad operations.
- (v) Post launch to interplanetary trajectory injection.

This report is a study of the effects and prevention of potential threats for the five operations previously cited. In each case the pollution threat has been analyzed in terms of source, hazard, sink, and abatement procedure, if any.

III. TECHNICAL DISCUSSION

In general, accidents or failures in any phase of the system operation from tankage loading to post-launch trajectory injection, will result in the release of mercury to the local environment basically through three different means: (1) small spillage (or vapors), (2) large spillage (up to 400 kg), and (3) a fireball. Naturally, the degree of the contamination or hazard resulting from any of the three means of release will depend on the amount of mercury released, but, additionally, the different possible types of problems created and thus the consequent methods for eliminating, reducing, or containing those problems will depend on the local environment into which the mercury is released. These areas of concern, covering all phases of the system operation are illustrated by the star chart in Figure 1. In the framework of this chart all of the potential mercury hazards that may occur in this system have been investigated. A synopsis of this study is presented in Table 1.

(i) Spacecraft Tankage Loading and Downloading

Since the maximum single quantity of mercury stored or shipped by the mercury industry in each individual flask is 76 pounds (34.5 kilograms) (Ref. 2), this is probably the largest amount that will be handled at one time during tankage loading operations. In these operations, the release of mercury into the local environment through small spillage and/or vaporization can present potential engineering problems to the launch vehicle and payload such as liquid metal embrittlement (LME) and corrosion (by amalgamation) of the vehicle construction materials and the metals in the electronic packages. Both LME and corrosion can be caused by either metallic mercury or mercury vapors (Ref. 3).

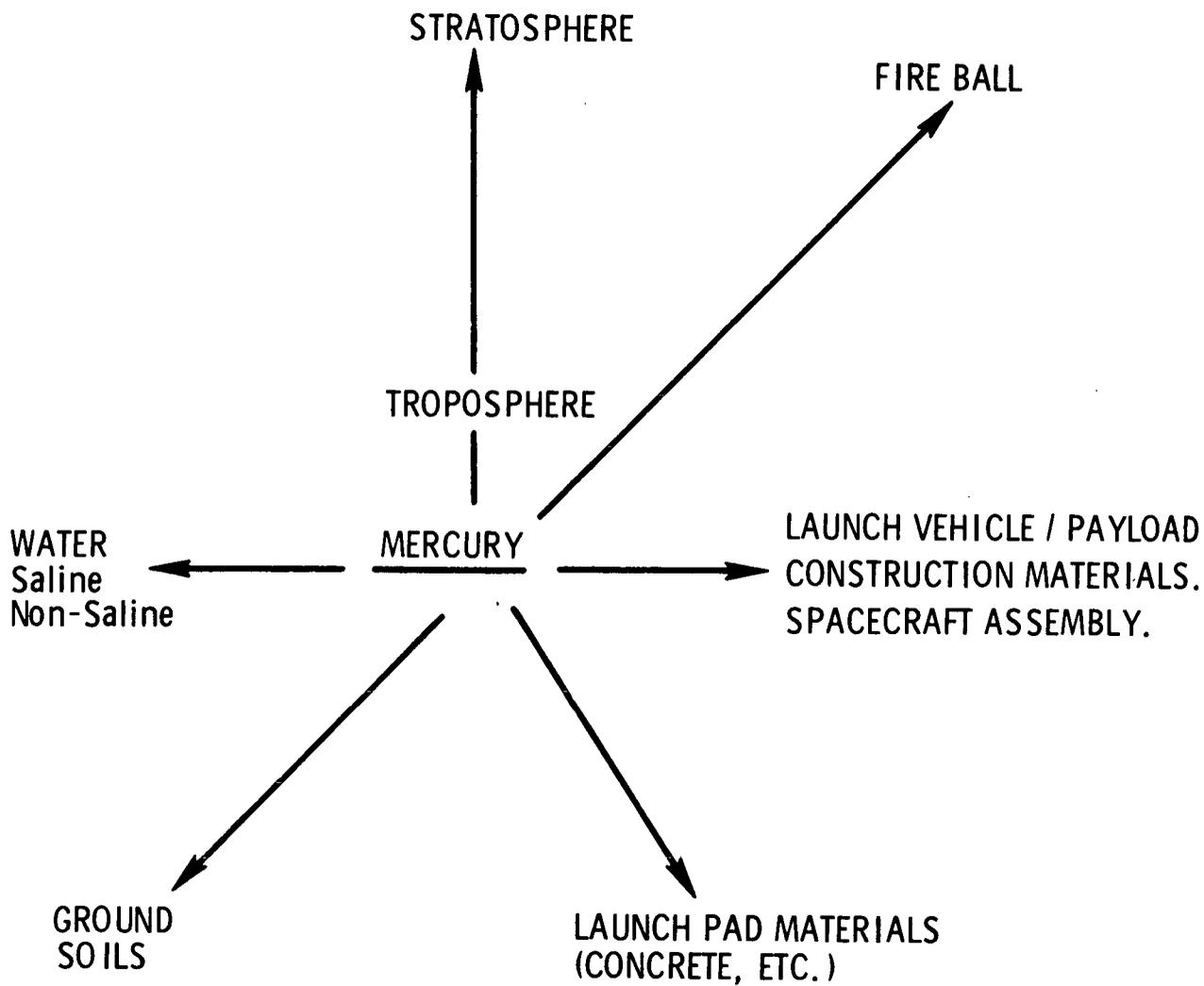


Fig. 1. Potential Mercury Pollution Areas.

TABLE 1

Operation and Hazards Related to Mercury Propellants.

Operation	Hg Release Method	Potential Hazard Area
Loading	Spillage, Vapors	LME, LV-SC Materials. Personnel.
Transport	Spillage	Soil, Water Pollution.
Mating	Spillage	Assembly Area Pollution. Soil, Water Pollution.
Countdown	Spillage, Fireball	Soil, Water and Air Pollution.
Post Launch	Fireball, Leakage	Atmospheric Pollution. Ozone Depletion.

Potential pollution hazards which may occur in the immediate vicinity of the loading operations are the exposure of personnel to high concentrations of mercury vapor or even direct skin contact with the metal. Metallic mercury and mercury compounds can be absorbed into the body by inhalation, ingestion, or contact with the skin (Ref. 4).

Mercury metal is a liquid at room temperature with a vapor pressure high enough to produce toxic concentrations of mercury vapor at room temperature if a considerable area of the metal surface is exposed to air. At room temperature, air which is saturated with metallic mercury vapor will contain about 20 milligrams of mercury per cubic meter (Ref. 5). This equilibrium saturation is much higher than the 0.1 milligrams per cubic meter limit recommended for daily, continuous exposure to metallic mercury or inorganic mercury compounds, but because air movements and air exchanges will prevent saturation equilibrium conditions need not be considered for small spills. However, the volatility of mercury dictates a need for minimizing spills and for keeping mercury covered (i. e. containers closed, store under water, etc.).

Since these potential pollution hazards and engineering problems associated with the handling and use of mercury have long been recognized, a large number of precautions have been recommended in the published literature, largely in industrial handbooks and safety manuals (Refs. 6, 7, 8, 9, and 10). The major of these precautions are:

- (1) Insure good ventilation, or preferably, work in a well ventilated hood.
- (2) Wear a gas mask, rubber gloves, and clean outer working clothes.

- (3) Do not eat, drink, or smoke in the working area.
- (4) Wash with hot water and soap and change clothes after leaving the work area.
- (5) Keep stored mercury in tightly closed polyethylene, wrought iron, or steel containers.
- (6) Store mercury containers in enamel or stainless steel trays or boxes and not on wood floors and shelves.
- (7) Transfer mercury over impervious tables or containers with the surfaces depressed and arranged to drain to a central point.
- (8) Provide a plastic, rubber, or cement cover on the floor and at the floor around walls to eliminate cracks.
- (9) Use a mercury vapor detector to check mercury vapor concentrations.
- (10) Prevent mercury spillage into sewer drains.

Corrective measures and procedures to be taken in the event of mercury spillage have also been recommended. Small quantities of mercury may be collected by a capillary tube attached to an aspirator bottle under vacuum, or by a so-called "mercury magnet", which is a spiral of copper wire treated with nitric acid and then amalgamated. Larger spills may require an industrial type vacuum cleaner especially designed to collect mercury without emitting it in the exhaust. Recovery of most spilled mercury is an easy task, but complete recovery is virtually impossible. Mercury droplets visible only under a microscope are trapped in crevices. Since complete removal cannot be made mechanically, chemical washes are suggested. Because mercury is a chalcophilic element (one that tends to concentrate in sulphides), sulphur dust has long

been used to fix mercury, but a water slurry of sulphur and calcium oxide or sulphur and caustic soda is more effective in changing the droplets into non-volatile sulphides (Ref. 4).

In tankage loading operations, therefore, if proper safety precautions are taken and if established industrial and laboratory procedures for handling mercury are used, the release of mercury through small spills and vaporization may be reduced to the point where there is neither a pollution hazard nor an engineering problem. Discussions with key individuals (Ref. 11, 12) in organizations that handle mercury in large quantities (several hundreds of pounds per day for many years (Ref. 13)) elicited such responses to a query on the dangers of handling mercury as: "Sure mercury is potentially dangerous, but so is electricity. You wouldn't sit in a bathtub full of water and put your fingers into a live electric socket, so neither would you take undue risks or use unsafe practices when handling mercury (Ref. 12)".

(ii) Spacecraft Transport With Loaded Tanks, and

(iii) Spacecraft Boost Vehicle Mate and Demate

In the transportation of the spacecraft with loaded tanks and also in its mating with the boost vehicle, potential mercury problems can occur through an accidentally caused dump or large spillage of the mercury propellant (up to 400 kg.) from the tanks onto the road surface, the assembly area floor, the ground soil, or into some adjacent body of water. Such a large spillage will be an obvious event, and hence immediate removal can be carried out efficiently by employing the handling procedures developed by the mercury industry discussed earlier.

Thus a mercury spill onto the transport road surface or the assembly area floor (i. e. , concrete materials) can be removed with the Mer Vac vacuum cleaner, a unit especially designed to collect mercury without the emission of mercury from the exhaust. Also, because mercury is a chalcophilic element (i. e. , one that tends to concentrate in sulphides), chemicals such as sulphur or Hg X are used to fix residual mercury by causing the mercury to form mercuric sulphide, a substance that is innocuous.

It has also been shown that freshly ground quartz and silicate minerals have surface layers with disrupted lattices that are very efficient in adsorbing heavy metal ions (Ref. 14). Since the subsoil at Cape Kennedy is sandstone (Ref. 15) whose average mineral composition contains 67% quartz and 12% feldspar (silicate minerals) (Ref. 16), mercury spilled onto the ground soil will be chemically complexed and retained in this sandstone subsoil. This complexing will prevent the leaching and/or diffusion of spilled mercury into the water table, which is relatively close to the surface in Florida.

A mercury spill into a landlocked body of water will settle to the bottom. The most important steps by which inorganic and other mercury-containing species are dispersed in natural environments are most complex. A typical diagrammatic representation of transformation pathways for mercury in nature is shown in Figure 2 (Ref. 17). Some of the generalizations to be drawn from this figure are:

- (1) mercury, in whatever form, is potentially exchangeable among air, land and water phases;
- (2) mercury, in whatever form and from whatever phase, is potentially capable of being taken up by aquatic animals in the form of methyl-mercury or dimethylmercury;
- (3) in aquatic systems, methylmercury can be formed directly from inorganic (Hg^{2+}) under anaerobic conditions; but
- (4) under permanently anaerobic conditions, mercury will tend to accumulate in bottom sediments either as HgS or Hg^0 , and little methylated mercurials will form;
- (5) methylmercury or dimethylmercury can be formed from either HgS or Hg^0 in the presence of oxygen or under oxidizing conditions;
- (6) alkaline conditions will tend to promote the release of mercury from aquatic ecosystems via dimethylmercury.

The chemical behavior of mercury in water thus is rather complicated. The extent to which submerged mercury will become a pollution threat is dependent upon its microbial transformation into the highly toxic methyl form and the highly transportable dimethyl form (Ref. 18). This transformation and the general

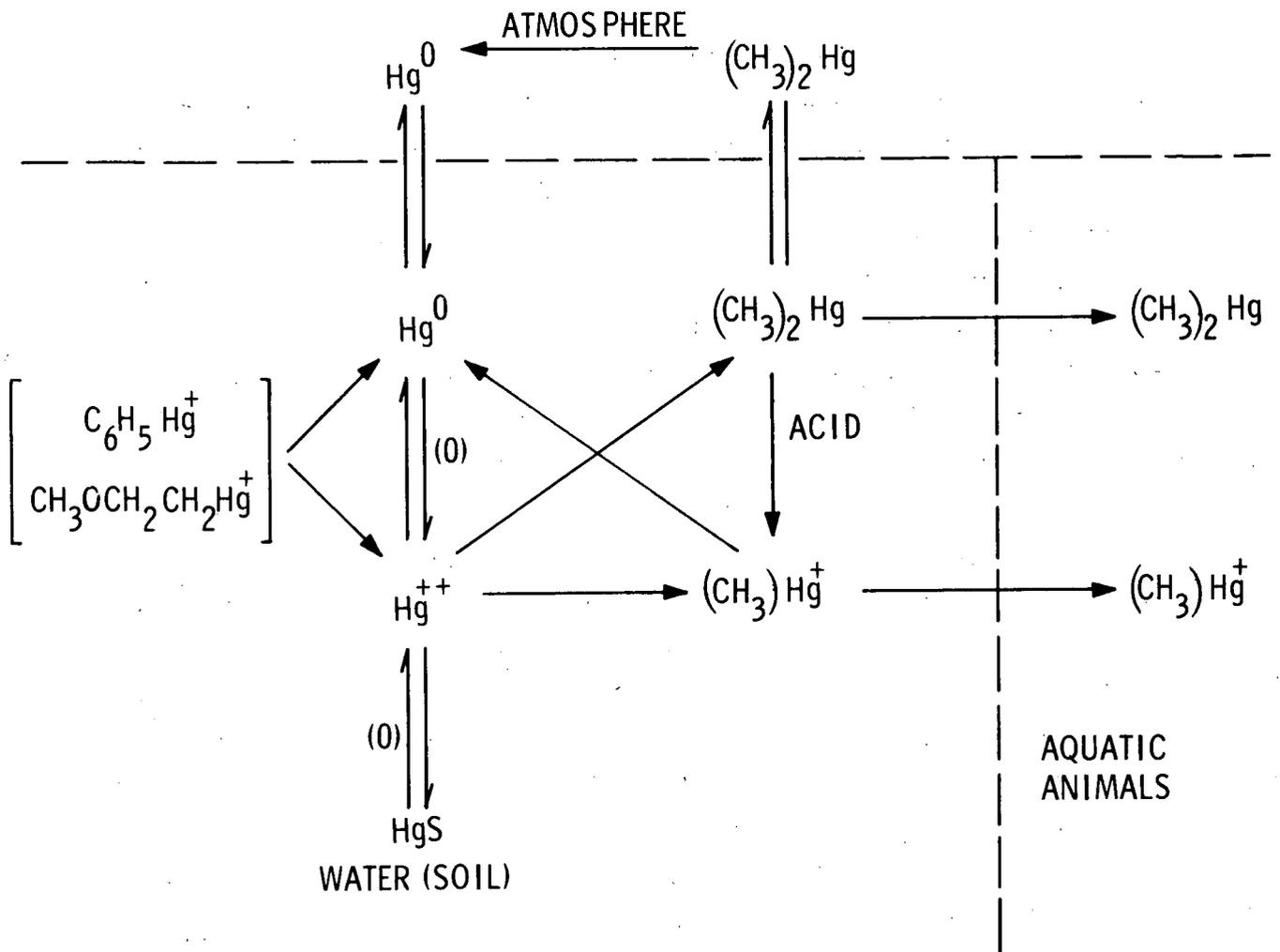


Fig. 2. Mercury Reactivity In the Environment.

chemical behavior of mercury in water depend on factors such as water temperature, pH of water and sediment, oxidizing or reducing conditions, and bacterial activity (Ref. 19).

Under normal conditions found in the fresh water bodies around Cape Kennedy, mercury, from a chemical viewpoint, could exist in one or more of its oxidation states. The initial dump would deposit mercury as Hg^0 , as from a spillage or leakage, but if mercury were involved in a fireball then mercury salts such as HgCl_2 would be deposited in the water body. The fate of these forms will depend to a great extent upon the reducing or oxidizing nature of the water. The intensity of oxidizing or reducing conditions in any chemical system is expressed as an electrical potential, in volts. The more oxidizing environments have positive potentials and the reducing environments negative potentials. By theoretical chemical equilibria calculations the potentials to be expected in aqueous solutions under various chemical conditions can be calculated. Typical equilibrium constants and energies of formation of certain mercury salts are shown in Tables 2 and 3. By inspection of these tables it is clear that mercury forms many solute species. Such data can be used to construct stability diagrams, Figures 3 and 4, which show the solid and liquid forms of mercury that will be stable in the conditions of pH and redox potential under which the water is stable.

At the conditions of pH and Eh appropriate to aerated or anaerobic water (pH 5 to 9 and Eh less than 0.5 volts) the species Hg^0 liquid and HgS are the principal ones likely to enter into equilibria affecting the solubility of mercury. The main features of the aqueous inorganic chemistry of mercury under equilibrium conditions are clearly indicated in Figures 3 and 4. Over much of the area of oxidizing conditions above pH 5 the predominant mercury species in solution is undissolved mercury, to a concentration of about 25 ppb.

TABLE 2

Equilibrium Constants and Standard Potentials at 25°C and 1 Atmosphere Pressure.

(l=liquids, g=gases, c=solids, ag=dissolved species)

Equilibrium	Constant (K)	E° (volts)	Source of Data
$\text{Hg}_2^{+2} + 2e = 2\text{Hg}^0 \text{ l}$ -----	-----	0.789	(Ref. 20)
$2\text{Hg}^{+2} + 2e = \text{Hg}_2^{+2}$ -----	-----	.921	"
$\text{Hg}^{+2} + 2e = \text{Hg}^0 \text{ l}$ -----	-----	.855	"
$\text{Hg}^0 \text{ l} + \text{Hg}^{+2} = \text{Hg}_2^{+2}$ -----	$10^{2.22}$	-----	"
$\text{Hg}^0 \text{ l} = \text{Hg aq}$ -----	$10^{-6.89}$	-----	(Ref. 21)
$\text{HgO c} + 2\text{H}^+ + 2e = \text{Hg}^0 \text{ l} + \text{H}_2\text{O}$ -----	-----	.925	"
$\text{Hg}_2\text{Cl}_2 \text{ c} = \text{Hg}_2^{+2} + 2\text{Cl}^-$ -----	$10^{-17.96}$	-----	"
$\text{HgCl}_2^0 = \text{Hg}^{+2} + 2\text{Cl}^-$ -----	$10^{-13.25}$	-----	(Ref. 22)
$\text{HgCl}_3^- = \text{Hg}^{+2} + 3\text{Cl}^-$ -----	$10^{-15.35}$	-----	"
$\text{HgCl}_4^{-2} + 2e = \text{Hg}^0 \text{ l} + 4\text{Cl}^-$ -----	-----	.386	(Ref. 20)
$\text{HgSO}_4^0 \text{ aq} = \text{Hg}^{+2} + \text{S}^{-2}$ -----	$10^{-1.42}$	-----	(Ref. 21)
$\text{HgS(cinnabar)} = \text{Hg}^{+2} + \text{S}^{-2}$ -----	$10^{-52.37}$	-----	(Ref. 22)
$\text{HgS(metacinnabar)} = \text{Hg}^{+2} + \text{S}^{-2}$ -----	$10^{-53.68}$	-----	"
$\text{HgS c} + \text{S}^{-2} = \text{HgS}_2^{-2}$ -----	4.57	-----	"
$\text{Hg (HS)}_2^0 = \text{Hg}^{+2} + 2\text{HS}^-$ -----	$10^{-37.73}$	-----	"
$\text{Hg(NH}_3)_4^{+2} = \text{Hg}^{+2} + 4\text{NH}_3 \text{ aq}$ -----	$10^{-19.28}$	-----	"
$\text{Hg(CH}_3\text{CO}_2)_2 \text{ c} + 2\text{H}^+ = \text{Hg}^{+2} + 2\text{CH}_3\text{COOH aq}$ -----	$10^{-3.11}$	-----	"
$\text{Hg(CH}_3)_2 \text{ l} + 2\text{H}^+ = \text{Hg}^{+2} + 2\text{CH}_4 \text{ aq}$ -----	$10^{7.80}$	-----	"
$\text{Hg(CH}_3)_2 \text{ l} + \text{H}_2\text{O} = \text{CH}_4 \text{ aq} + \text{CH}_3\text{OH aq} + \text{Hg l}$ -----	$10^{19.74}$	-----	"
$\text{CH}_3\text{Hg}^+ + \text{OH}^- = \text{CH}_3\text{HgOH aq}$ -----	$10^{9.50}$	-----	(Ref. 23)
$\text{C}_6\text{H}_5\text{Hg}^+ + \text{OH}^- = \text{C}_6\text{H}_5\text{HgOH aq}$ -----	$10^{1.0}$	-----	"
$\text{CH}_3\text{HgCl l} = \text{CH}_3\text{HgCl aq}$ -----	$10^{-1.70}$	-----	"
$\text{CH}_3\text{HgCl aq} = \text{CH}_3\text{Hg}^+ + \text{Cl}^-$ -----	$10^{-5.46}$	-----	"

TABLE 3

Standard Free Energies of Formation of Certain Mercury Species, in Kilocalories per Mole.

(Leaders indicate no common names. l=liquids, g=gases, c=solids, aq=dissolved species.
Data from Ref. 20 and Ref. 21)

Formula	Description	Free Energies (ΔG°)
Hg ⁰ l	Metallic mercury	0.0
Hg ⁰ g	Mercury vapor	16.3
Hg ⁰ aq	Dissolved mercury	9.4
Hg ₂ ⁺²	Mercurous ion	36.70
Hg ⁺²	Mercuric ion	39.30
Hg ₂ Cl ₂ c	Calomel	- 50.35
HgCl ₂ c	Mercuric chloride	- 42.7
HgO c	Red oxide	- 13.995
HgO c	Yellow oxide	- 13.964
HgOH ⁺		- 12.5
HgO OH ⁻		- 45.5
Hg(OH) ₂ aq		- 65.70
HgS c	Cinnabar	- 12.1
HgS c	Metacinnabar	- 11.4
Hg ₂ SO ₄ c		-149.589
HgSO ₄ ⁰ aq		-140.6
Hg ₂ CO ₃ c		-105.8
HgCl ₂ ⁰ aq		- 41.4
HgCl ₄ ⁻²		-107.7
Hg(CH ₃) ₂ l		33.5

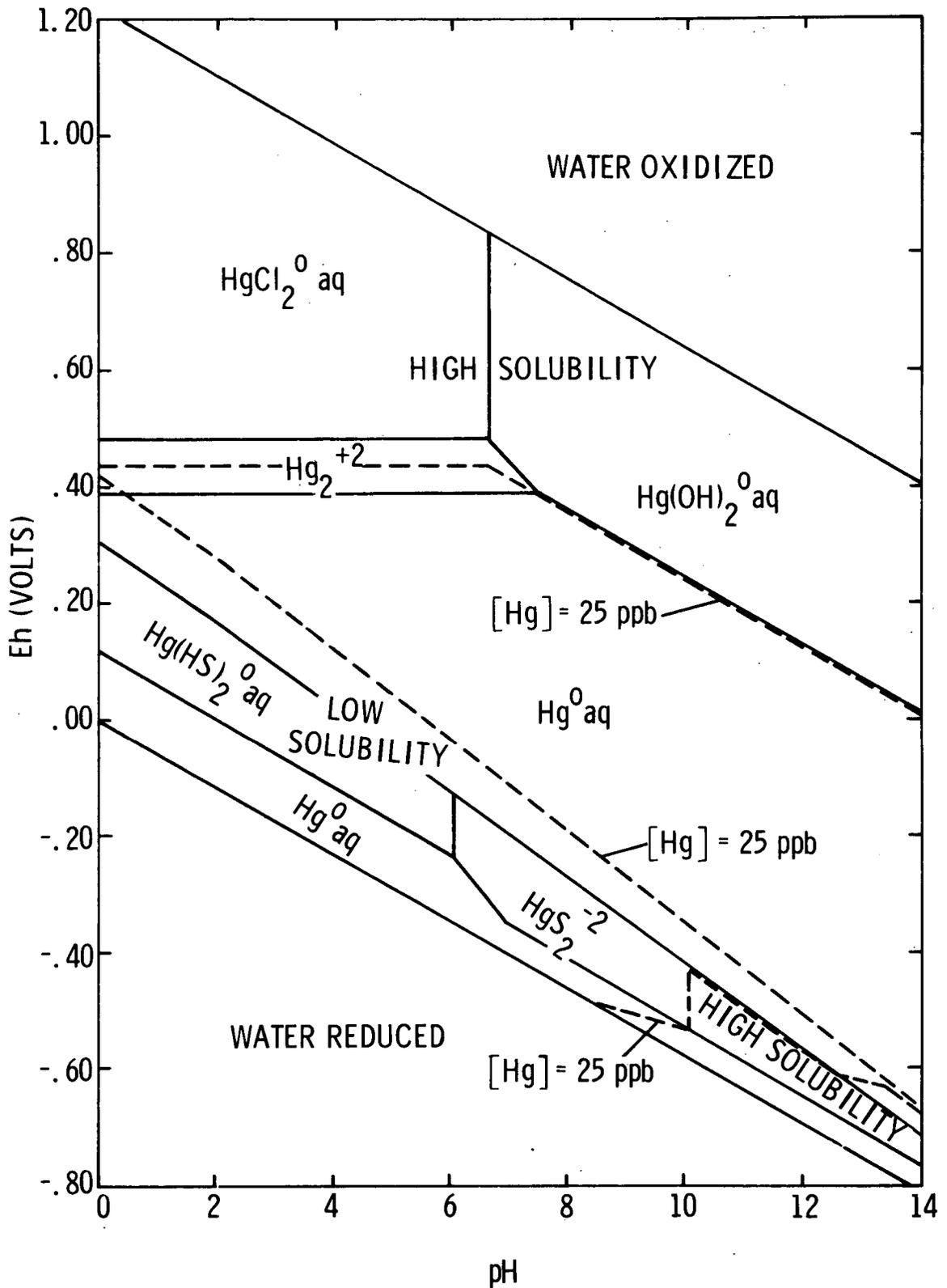


Fig. 3. Fields of Stability for Aqueous Mercury Species at 25°C and 1 Atmosphere Pressure. System Includes Water Containing 36 ppm Cl^- , Total Sulfur 96 ppm As Sulfate. Dashed Line Indicates Approximate Solubility of Mercury In This System.

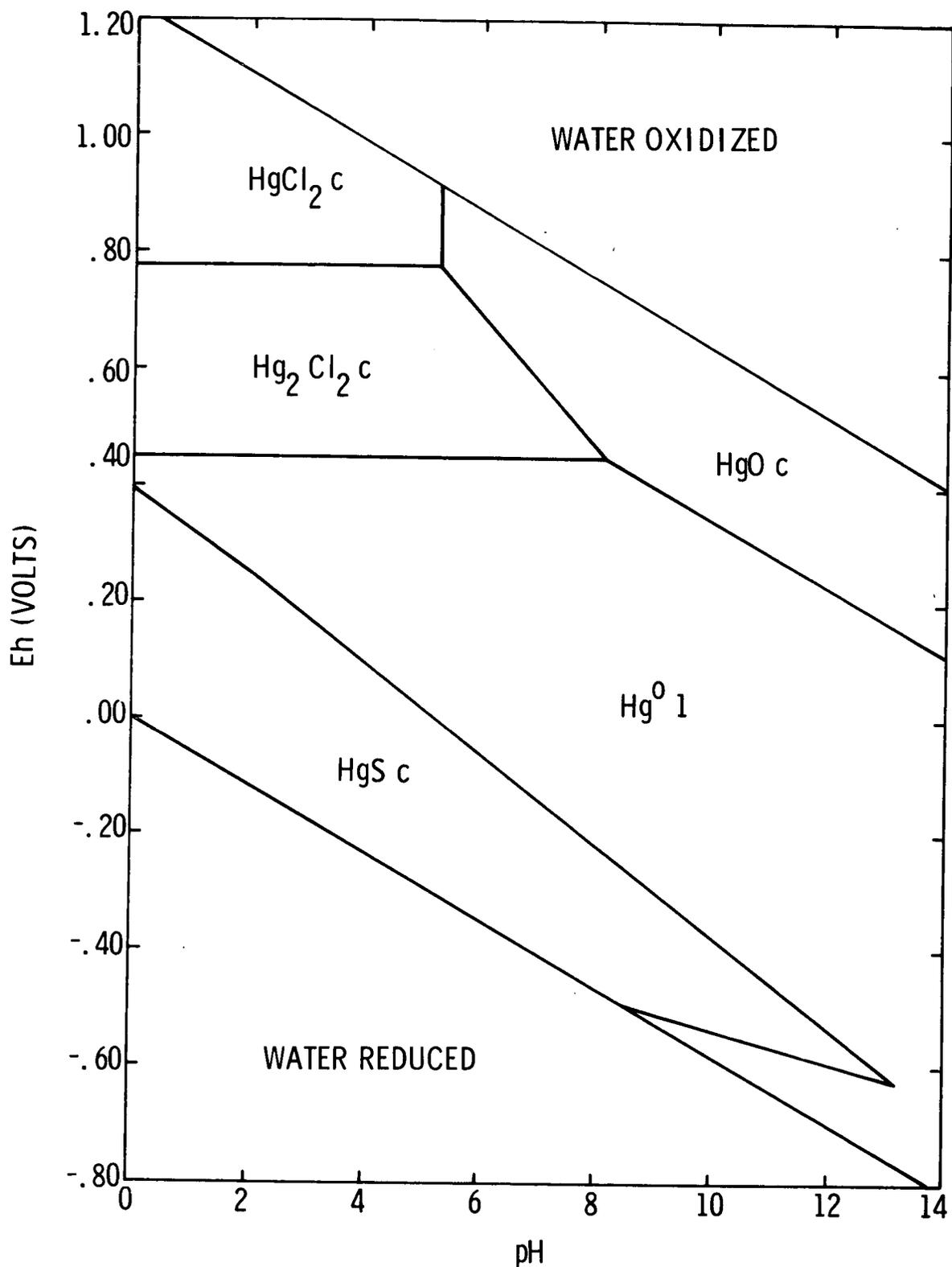


Fig. 4. Fields of Stability For Solid (c) and Liquid (l) Mercury Species At 25°C and 1 Atmosphere Pressure. System Includes Water Containing 36 ppm Cl⁻, Total Sulfur 96 ppm as SO₄²⁻.

This represents the likely upper limit of mercury in any lake or stream that is low in chloride.

Mildly reducing conditions, to be found in stream and lake sediments, can cause the mercury to be precipitated as the sulphide. In fields of HgS_2 near neutral pH the equilibrium solubility of mercury may be lower than 0.002 ppb.

In high chloride containing solutions, e. g. saline water, the solubility of mercury in oxygenated water may be greatly increased by the formation of the uncharged HgCl_2 complex, or anionic complexes such as HgCl_4^{2-} .

The main conclusion to be drawn from this discussion is that the aqueous chemistry of mercury is both complex and not fully resolved. Fortunately, however, techniques have been developed which control and eliminate the formation of organic mercurials from mercury deposited in the sediments of water bodies (Ref. 14 and 24). One such technique is the application of a layer of sand or gravel to a thickness of 6 cm over a contaminated area to eliminate the pollution threat (Ref. 24). This technique, an example of several existing, still is in the development stage and has not yet been shown to be perfected in field tests. However, it is expected that no unsurmountable difficulties will arise in the application of this technique and others like it.

The possible spillage into ocean waters involves chemistry similar to that discussed for land-locked bodies, although the abatement procedures will be determined by the location of the pollution threat. If the spillage is near shore waters, it could be buried as discussed earlier. Dumps farther from land do not appear to be likely since the launch vehicle at a downrange distance of 0.1 nautical mile already is at an altitude of about 7,000 feet, (Ref. 25),

where the main potential pollution threats are from fireball effects to be discussed in the next section.

Consequently, the potential pollution threat of mercury released in a large spillage during spacecraft and boost vehicle mating and transportation can be eliminated with existing corrective procedures as used in normal industrial and laboratory practices. The only uncertainty at this time is the procedure currently being developed for the elimination of pollution from water bodies. It is also readily apparent that this type of pollution threat is minimal with respect to spillage on the ground, since for mercury to be deposited in a water body requires some form of transportation to that body. Nevertheless, the subject of mercury getting into water bodies becomes more realistic during the launch pad operations and in considering possible fireball effects.

(iv) Spacecraft Countdown and Launch Pad Operations

During spacecraft countdown and launch pad operations, potential pollution problems can occur through a large spillage of mercury, as in spacecraft transportation and mating, and also through a launch pad abort resulting in a major fireball (including all of the propulsion systems of the launch vehicle) whose blast shock wave would disperse all of the mercury propellant over the launch pad area.

The pollution threat of a large mercury spill onto the launch pad construction materials (concrete, etc.) can be eliminated, as previously discussed in the spacecraft transportation and mating operation, by vacuum cleaning and by fixing the mercury with sulphur or HgX.

The proposed launch vehicle for the Solar Electric Multi mission Spacecraft (Ref. 1) is the Titan III D/ Centaur (Figure 5) whose propellant systems are listed in Table 4 (Ref. 26). Inspection of this propulsion system shows that the solid propellant is by far the major contributor to the fireball with the N_2O_4 , N_2H_4 , and UDMH systems being a secondary source of combustion species. At the present time, the best estimate of the chemical composition of a major fireball is based upon theoretical calculations of the combustion products for these propellant systems (Ref. 27). These species expressed as a percentage of the total initial propellant charge are given in Table 5. Inspection of this list of species produced during a fireball shows that the possible dissemination of 400 kg of mercury is a minor pollution threat compared to the potential threats arising from such species as HCl.

The reason for this is that 20.2% of the combustion products from the decomposition of the solid propellants of the Titan III D vehicle is hydrochloric acid (HCl), which means that about

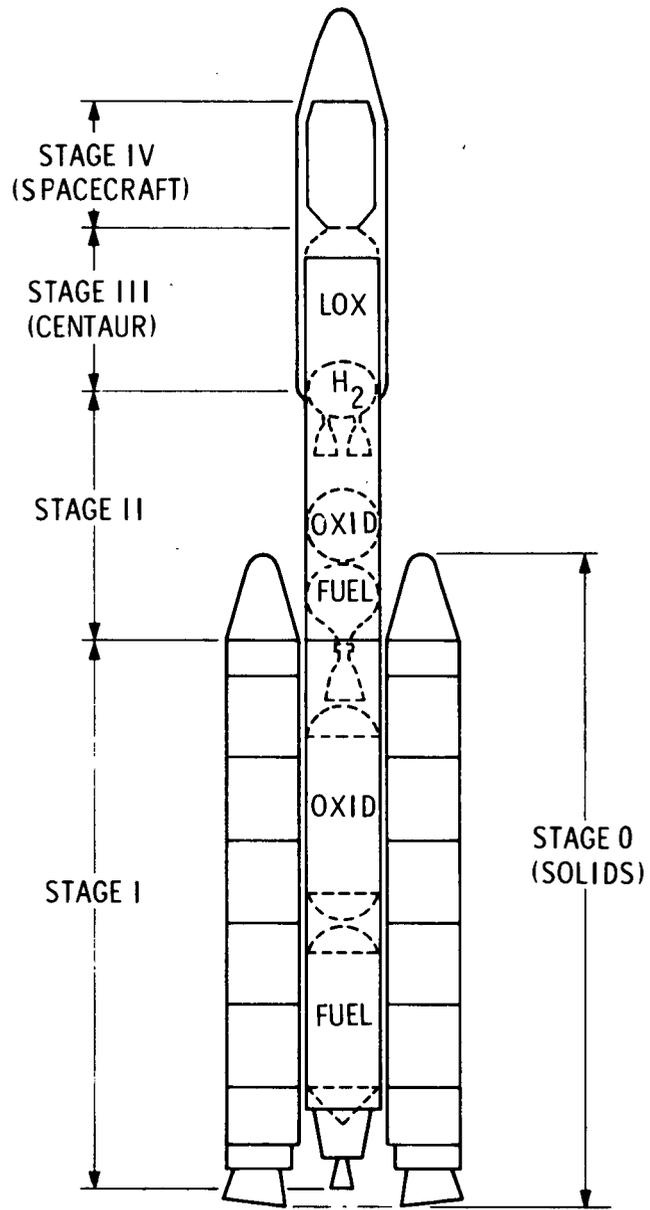


Fig. 5. Stage Relationship For Titan III D/ Centaur Vehicle.

TABLE 4

Titan III D/ Centaur Propellant Systems

System		Propellant Weight(lb)	Propellant Composition
Stage 0	Solids (2)	850,000	70% AP 16% Al 14% HC <.03% Ferrocene
Stage I		260,000	65% N ₂ O ₄ 17.5% N ₂ H ₄ 17.5% UDMH
Stage II		66,000	Same as Stage I
Stage III	Centaur	30,000	17% H ₂ 83% O ₂

TABLE 5

Major Combustion Species for TITAN Propulsion Systems

System	Species	%
SRM	Al_2O_3	29.6
	CO	23
	HCl	20.2
	H_2O	10.6
	N_2	10
	CO_2	3
	H_2	1.9
	Cl	0.7
N_2O_4 N_2H_2 UDMH	N_2	42
	H_2O	32.4
	CO	10.4
	CO_2	9.7
	OH	2.6
	NO	1.2

172,000 pounds of HCl will be released through a major fireball. Since about 90,000 pounds of water also is released and since the water and HCl will be in the vapor phase, a huge HCl cloud will be formed which is far more hazardous than the pollution threat posed by the 880 pounds (400 kg) of mercury released.

However, the fate of the released mercury should not be overlooked. There are basically two sinks for this released mercury, (1) as elemental metal which will be deposited on the ground or in water and spread over a large area at a low concentration level and (2) deposited as a mercury salt, probably HgCl_2 , again over a wide area and at a low concentration level. The effects and fate of this deposit were discussed in the preceding section of this report.

(v) Post-Launch to Interplanetary Trajectory Injection

In the post-launch phase of the system operation (i. e. , from lift off to interplanetary trajectory injection) mercury can be released into the environment from ruptured propellant tanks, resulting from structural failures in the launch vehicle and spacecraft, and also through a fireball. Consequent pollution problems will vary as a function of the launch vehicle trajectory since the structure, composition, and principal physical features of the atmosphere vary considerably with altitude. Examination of potential mercury pollution problems in this phase, therefore, requires that consideration be given simultaneously to the specific time (i. e. , altitude and range) and particular local environment (i. e. , atmospheric structure) of the mercury release.

For example, the flight azimuths considered by JPL for SEMMS launch vehicle trajectories are shown in Figure 6, which indicates that a mercury release about 260 nautical miles downrange from Cape Kennedy, particularly on the 114° azimuth, could pollute the northeastern islands in the Bahamas. However, when the elapsed time from liftoff and vehicle altitude are considered, Stages zero and I will have been jettisoned, and the vehicle will be at 400,000 feet. Mercury released at this altitude through either leakage or a fireball will remain in the upper atmosphere for several years (Ref. 28) and become diffuse through turbulence and high winds. Farther downrange along the azimuth, the vehicle rises to even higher altitudes.

The altitude-range-time data used in this study are based on the Viking '75 mission trajectory(Ref. 25) shown in Figure 7. Viking '75, Mars orbiter/lander mission, utilizes a flight system consisting of a Viking spacecraft and a Titan IIID/ Centaur launch vehicle. The Viking '75 mission and flight system are similar to those proposed for the SEMMS missions, which include asteroid

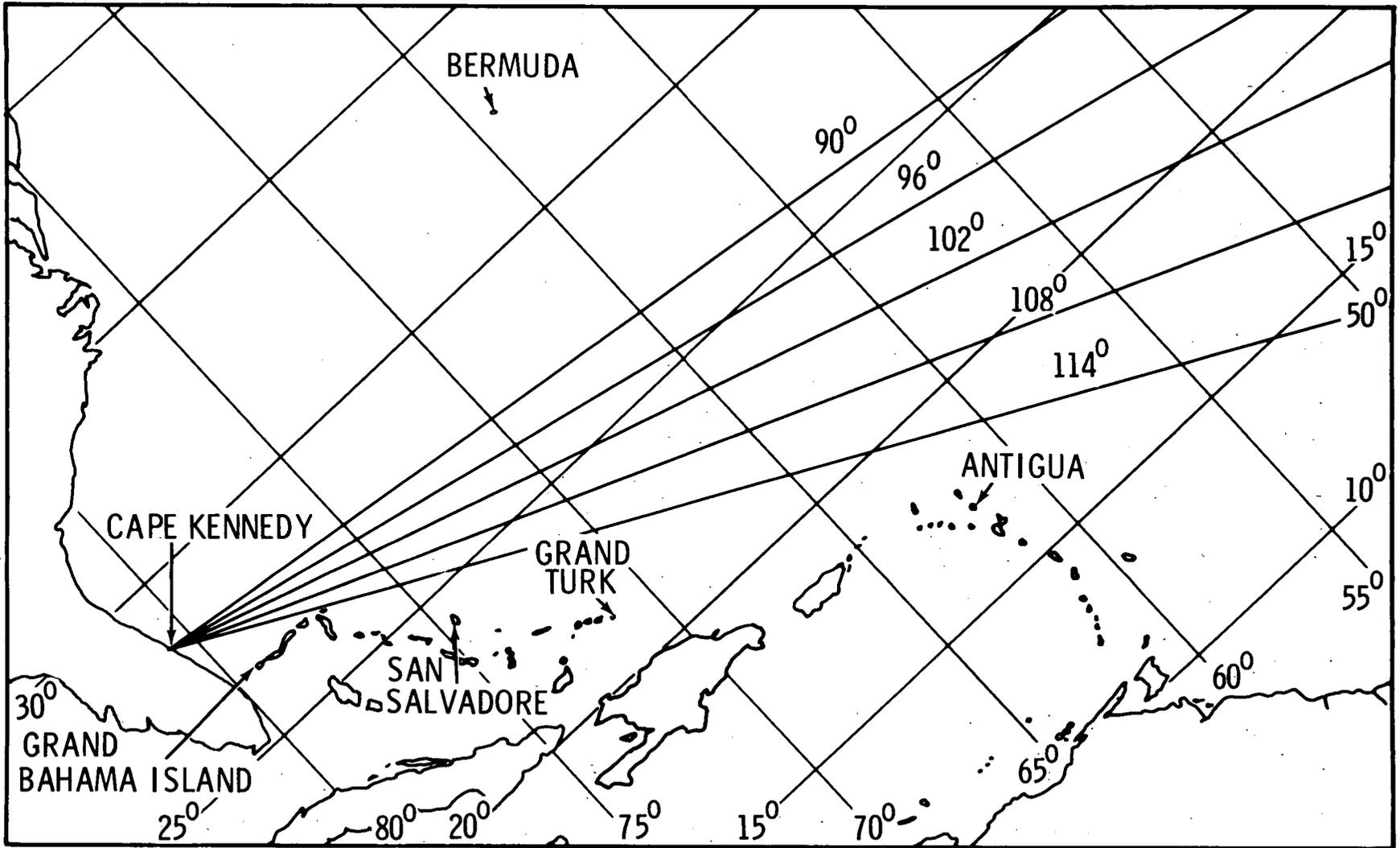


Fig. 6. Possible Flight Azimuths For SEMMS Missions.

and comet rendezvous, and Mercury, Jupiter and Saturn orbiters and which also are projected to use a Titan III D/ Centaur launch vehicle. The Viking '75 trajectory therefore can be considered representative of a SEMMS trajectory as well.

In such a trajectory, elapsed time from liftoff to parking orbit insertion at approximately 110 miles is about ten minutes. Solid rocket motor propellant is burned out after two minutes from liftoff and the liquid rocket propellants of Stages I and II are burned out after 4.3 and 7.8 minutes, respectively. The respective stage separation is effected at the time of each burnout.

The potential pollution problems or hazards occurring as a result of mercury released into the atmosphere along the vehicle trajectory are distinctly dependent upon the structure of the atmospheric region, or layer, into which the mercury is deposited. Atmosphere division into layers is based mainly upon the temperature structure. A plot of atmospheric temperature as a function of altitude is shown in Figure 8 (Ref. 29). The high temperature region around 50 kilometers is due to ozone absorption of solar radiation. The temperature rise above 100 km is attributed to direct absorption of solar energy by molecular oxygen (Ref. 30). The boundary between layers, in reality, is not distinct, because atmospheric temperature, pressure and composition vary with geographic location and also are influenced by diurnal and seasonal changes. The lowest 10 to 15 kilometers (6 to 9 miles) of the atmosphere, where the temperature decreases with height, is called the troposphere; above to about 50 kilometers is the stratosphere, containing the ozone layer (15 to 45 km). The region above the stratosphere where the temperature decreases with altitude up to about 85 kilometers is called the mesosphere, and above it where the temperature increases with altitude is the thermosphere.

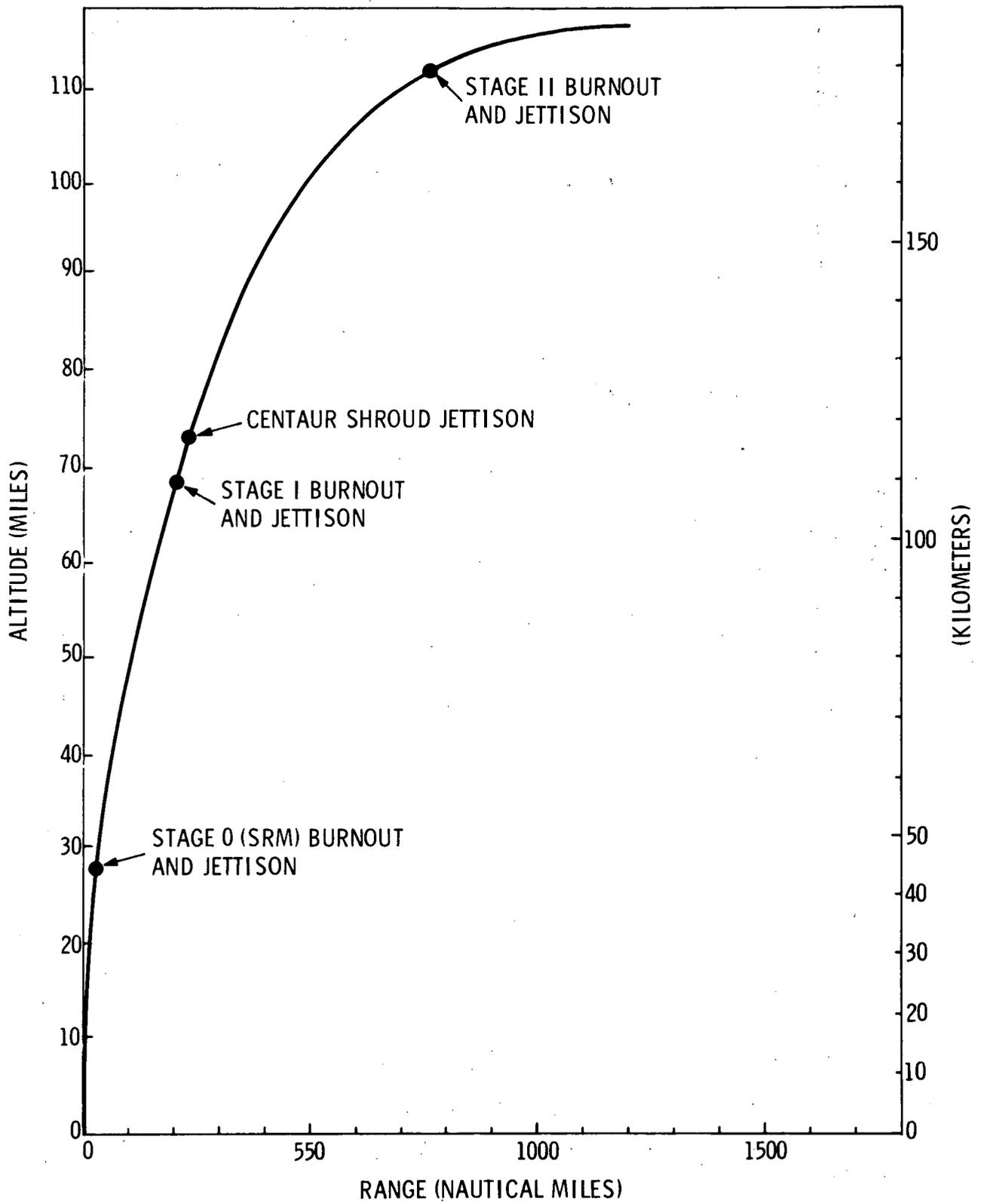


Fig. 7. Viking '75 Mission Trajectory.

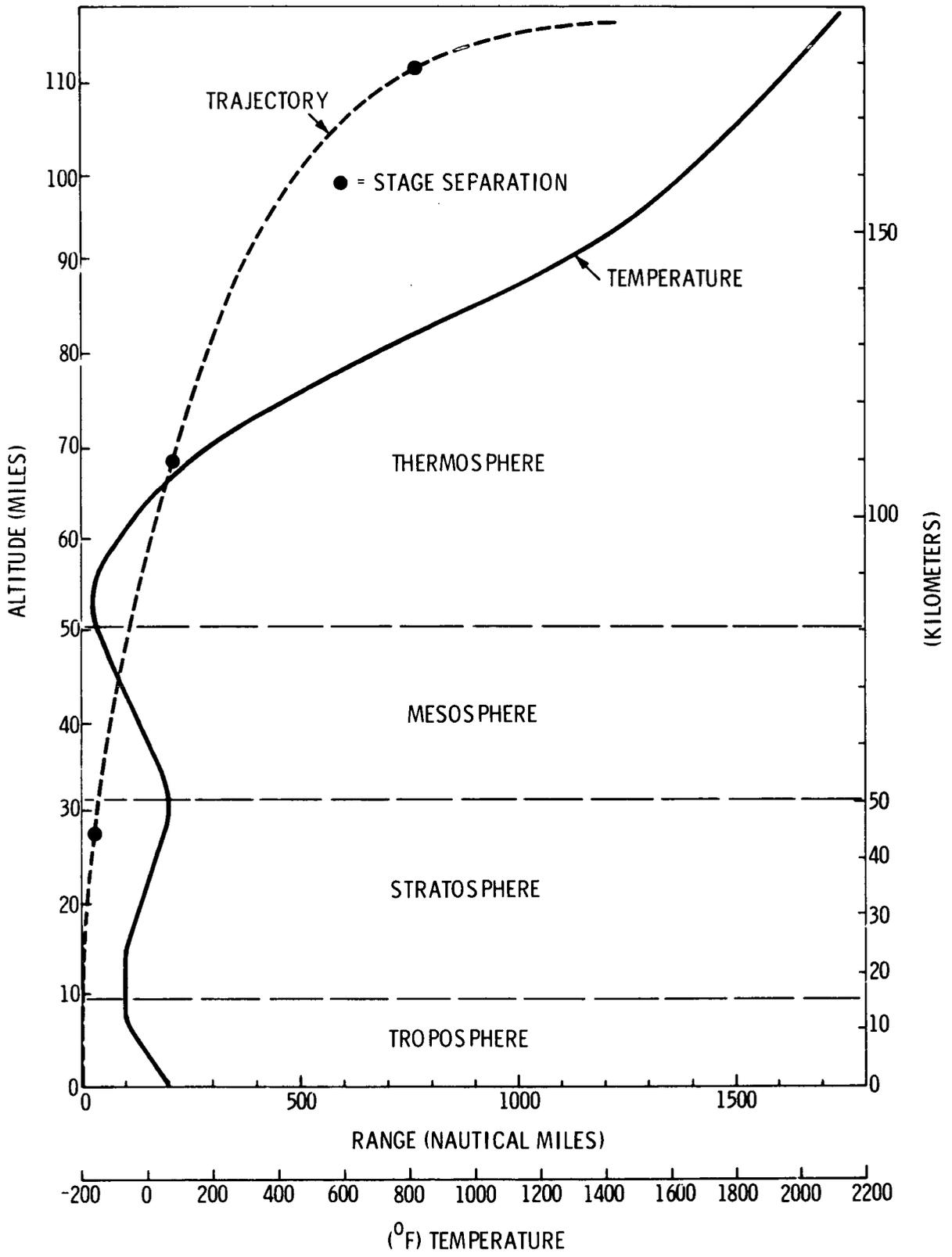


Fig. 8. Atmospheric Temperature Profile.

An important feature of the atmospheric temperature structure is that the inversions in the stratosphere and in the thermosphere impede vertical mixing between layers. For example, typical contaminants in the lower stratosphere have about 6-month residence times, and above 20 km they have residence times estimated at 1 to 5 years (Ref. 31). Mixing is thus much more rapid within a layer than between layers. Mercury released into the atmosphere above the troposphere (15 km) thus will not present a pollution threat. Instead, the effects of possible direct atmospheric chemical changes caused by the gas phase reactions of mercury with the constituents of the atmosphere must be examined.

The launch vehicle's flight through the troposphere and into the stratosphere lasts about a minute. By this time, 60% of the SRM propellant will be consumed, and the vehicle will be 3 nautical miles downrange. Mercury released through spillage or a fireball within this time will be washed out of the air by rain or by direct fallout. Since there is no land beneath the vehicle trajectory for 3 nautical miles downrange, the mercury will fall into the ocean. The fate of this mercury and its pollution abatement procedures were discussed earlier.

The possibility that up to 400 kg of elemental mercury released into the troposphere could have a profound chemical effect appears very remote. Under the conditions of temperature and solar flux in the troposphere, there are no known reactions of mercury with any of the major components of air which have appreciable reaction velocities. Although reactions of mercury with minor constituents such as H_2S , SO_2 , and NO_2 are conceivable, the bulk of the mercury is removed from the air by rainfall or "dry" fallout (Ref. 32).

Estimates of possible mercury pollution concentrations resulting from a tropospheric release can be made. Assuming, (i) 20°C, (ii) a vapor pressure of 1.2×10^{-3} Torr (Ref. 5), and (iii) a vertical distribution of mercury determined by the "barometer" formula (Ref. 33), 400 kg of mercury is sufficient to saturate the air with mercury in an area just under 0.01 square miles at a concentration of 1.6 ppm. This area would correspond to the maximum airborne mercury. If it is assumed that under the same circumstances the mercury is uniformly distributed axially in the Earth's atmosphere, and if it is further assumed that the concentration of mercury found in non-mineralized areas of the U.S. Southwest is typical of worldwide conditions (Refs. 34 and 35), then 400 kg will only increase the total atmospheric mercury by about 0.01%. Alternatively, it can be asked, "over what area will 400 kg double the natural mercury background?". This area is 2.5×10^4 square miles. These estimates show that atmospheric mercury, arising from a spacecraft failure, will be a problem over a relatively small fraction of the Earth's surface.

The launch vehicle will traverse the stratosphere in about a minute, but mercury released through leakage or a fireball within that time could have serious consequences. The combustion products from a fireball of the vehicle propellants (see Table 5) are not likely to react with mercury, but under the temperature and solar ultraviolet flux in the stratosphere, the mercury vapor dispersed by the fireball will be raised to an excited electronic state and become highly reactive (Ref. 36).

The stratosphere serves the extremely important function of protecting life on Earth. Vacuum and near ultra violet solar photon flux impinging on the stratosphere serve as a forcing function for the production of ozone (see Figure 9), where the production is equivalent to less than 1 cm^3 of gas at NTP per cm^2 .

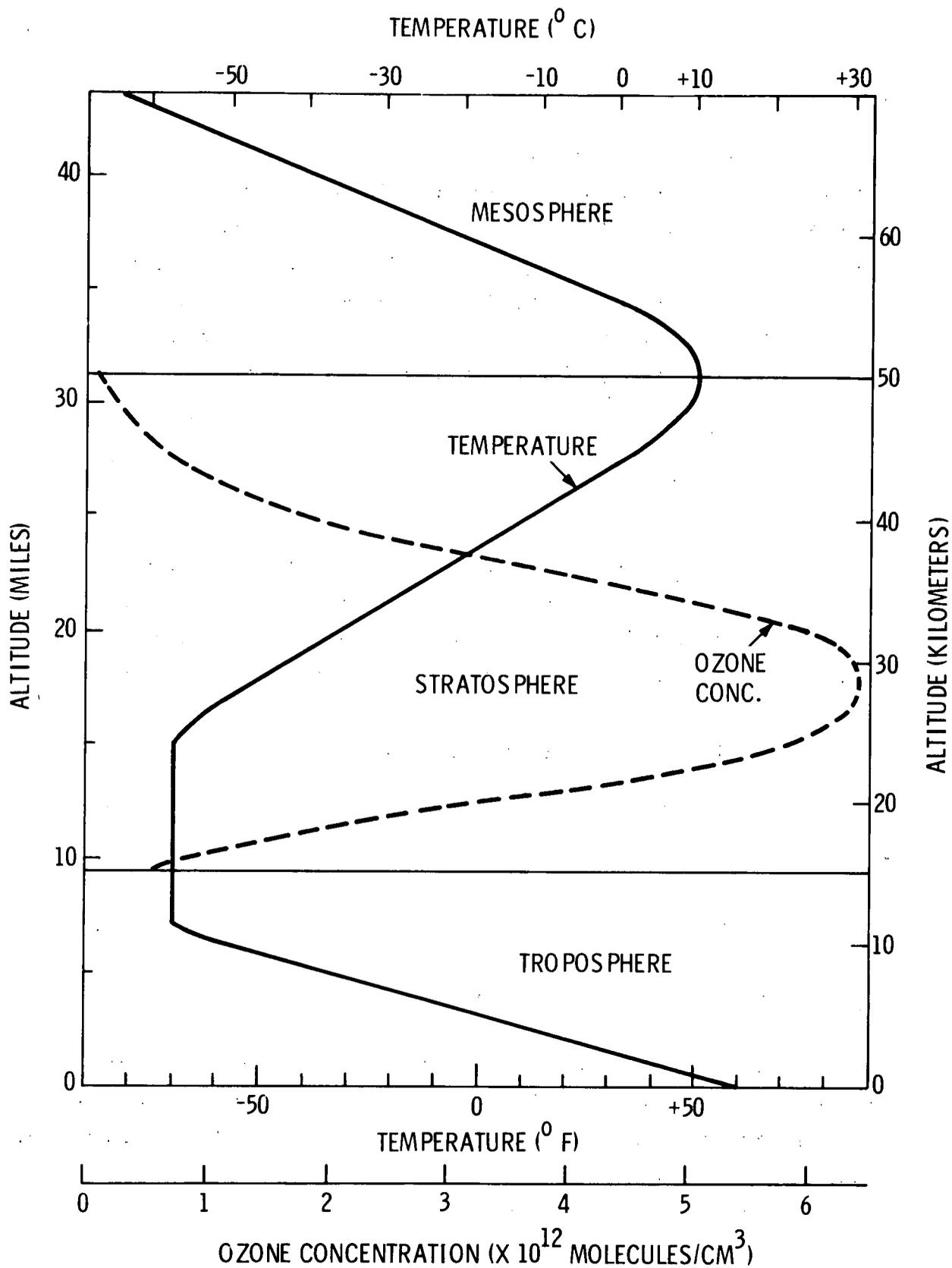
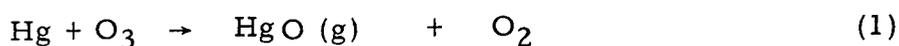
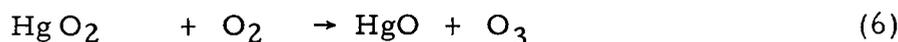
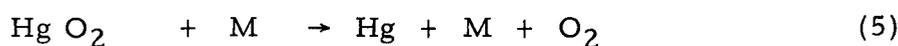
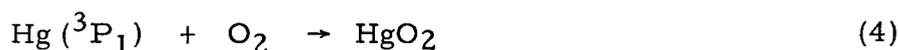
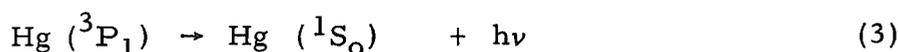
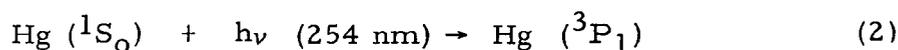


Fig. 9. Atmosphere - Temperature - Ozone Profile.

It is this small quantity of gas which is principally responsible for absorbing sunlight in the wavelength region 200-300 nm, which would be most harmful to life systems. The temporary removal of the ozone over a given region of the Earth would have serious ecological consequences (Ref. 37). Possible effects of mercury on the ozone concentration must be examined carefully since it is possible that ozone depletion by mercury could occur through the reaction:



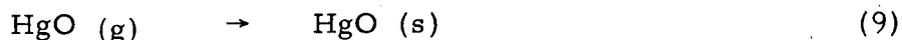
No satisfactory study of this reaction has been carried out. Evidence for the reaction comes from extensive studies of the mercury photosensitized formation of ozone, reviewed by Calvert and Pitts (Ref. 38). The mechanism of this process appears to be:



The observation that a single Hg atom can yield about 40 ozone molecules (Ref. 39) suggests that the HgO can undergo decomposition thermally or photochemically to regenerate Hg atoms. However, neither of the thermal reactions:



is feasible for the rapid regeneration of Hg atoms because of their endothermicity (Ref. 40). A reasonable suggestion is that reaction 8 occurs photochemically and that the chain-breaking process (if there is one, since the reaction can reach a steady state because of the attenuation of the 254-nm exciting radiation by ozone) could be



The principal past effort has been directed at determining the mechanism of the mercury photosensitized formation of ozone, and little has been reported on possible rate constants. The reported values of the quantum yields show a pressure dependence which has not been explored systematically. Nonetheless, the information available is sufficient to allow several qualitative conclusions to be made regarding the mercury release problem.

In particular, if the mercury is present above about 45 km, the O₃ concentration should be increased by the mercury photosensitized process. The extent of the increase will depend on the mercury concentration and the various rate constants, neither of which are known. This (temporary) increase at high altitudes is not likely to change markedly the total atmospheric ozone absorption path.

The 45-km figure was chosen because, at this height, about 50% of the 254-nm radiation is calculated to be absorbed by the ozone, based on the known absorption coefficient (Ref. 41) and the estimated ozone concentration profile (Figure 9) (Ref. 42). At lower altitudes, the ozone will absorb substantially more 254-nm radiation, so that reaction 2 is inhibited. In this lower region, the mercury will react quickly according to reaction 1. Depending on the rate of the mercury regeneration steps, a relatively small

concentration of mercury could deplete the ozone quickly. For this reason, the kinetics of the ozone-mercury reactions under stratospheric conditions of temperature and pressure should be determined.

It is clear that a mercury release in the lower stratosphere could lead to a local reduction in ozone which, in turn, could have undesirable ecological consequences. But, there are two reasons which make it impossible to estimate the potential seriousness of such a release at this time: (i) the unknown rate constants in the ozone-mercury reaction, and (ii) the undefined time-dependent spatial concentration profile that the released mercury would attain. The best estimate of the mercury concentration profile only can be approximate. This uncertainty makes it even more important to determine kinetic data on the ozone-mercury reaction scheme.

The fate of mercury released into the upper atmosphere (mesosphere and thermosphere) cannot be stated specifically, because the composition of this region varies constantly and because the high winds and turbulence will cause rapid dispersion and dilution of the mercury with little vertical transport. The relative amounts of the various atmospheric constituents in this region change considerably. Changes from molecular to atomic states following dissociations by solar radiation and changes from the various consequential chemical reactions are undefined. The composition also is affected by atmospheric motions (of air masses), mixing and diffusion.

High winds and turbulence in the upper atmosphere are well documented (Ref. 30) but not fully understood. Radical changes in zonal circulation from summer (prevailing easterlies) to winter (prevailing westerlies) occur in the mesosphere (50 to 80 km), but in the thermosphere between 85 and 110 km both summer and winter winds

are prevailing westerlies. Between 115 and 180 km summer winds are almost exclusively from the NE. In winter and at altitudes between 115 and 130 km, prevailing winds are from the NE ; between 130 and 180 km the winds are from the N or NW.

Because of the temperature increase with height in the upper atmosphere, vertical motions rarely exceed a few centimeters per second and often are much smaller. Contrasting this is the lateral wind velocity. Mesosphere mean velocities are about 60 m/sec at between 55 and 65 km altitude. At 105 ± 4 km, the mean velocity is 82 m/sec, but 6 km below and 7 km above there are two pronounced velocity minima with values smaller by about 30 m/sec. Above about 110 km, the velocity generally increases approximately linearly with a rate average of 1.8 m/sec per 10 km.

Therefore, since mercury deposited into the upper atmosphere, either through leakage or a fireball, would be dispersed rapidly and widely and remain in the upper atmosphere for years, there is no pollution threat from a release beyond the stratosphere.

IV. CONCLUSIONS

- (1) Mercury pollution resulting from small spills or vaporization during tankage loading operations can be prevented if proper safety precautions are taken and if established industrial and laboratory procedures for handling mercury are used.
- (2) A large mercury spill onto the transport road surface or the assembly area floor during transportation and mating will be obvious and can be eliminated by vacuum cleaning and by chemically fixing the mercury.
- (3) Mercury spilled onto the Cape Kennedy soil will be chemically complexed and retained by the sandstone subsoil and thus be prevented from entering the water table.
- (4) The application of a layer of sand or gravel several centimeters thick over a large spillage of mercury which has settled to the bottom of a body of water adjacent to the system operation will control and eliminate organic mercurial formation.
- (5) Pollution hazards of the HCl cloud formed after a launch pad fireball will far outweigh any pollution threat posed by mercury released through the fireball.
- (6) Mercury released into the earth's atmosphere through leakage or a fireball during the post-launch phase of the system operation will not present any pollution problems.
- (7) Gas phase reactions of mercury with ozone in the stratosphere could lead to a local reduction in ozone, which, in turn, could have undesirable ecological consequences.

- (8) At the present time, it is not possible to determine the potential seriousness of a mercury release in the ozone layer; rate constants in the ozone-mercury reaction are not known, and the time dependent spatial concentration profile of the released mercury has not been defined.

V. RECOMMENDATIONS

- (1) The safety precautions and procedures for handling mercury recommended in industrial and laboratory handbooks and safety manuals should be closely followed in all phases of the system operation.
- (2) Proper apparatus and chemicals for collecting and fixing large and small amounts of spilled mercury should be available during system operations, and ground crews should be trained in their use.
- (3) Abatement techniques such as the application of a layer of sand on submerged mercury should be developed further.
- (4) A study should be performed to determine the mechanism (s) and the rates of the individual reaction steps of the mercury catalyzed decomposition of ozone.
- (5) The results of the study recommended in (4) above should be analyzed to determine how the stratospheric ozone concentration will be modified, in terms of an ecological threat, by a major release of mercury.

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